Dedication

To my parents: Aziz Kazanc and Hatice Kazanc
Abstract

This work examined the gaseous (NO\textsubscript{x}, SO\textsubscript{2} and CO) and the particulate emissions (ash) from burning of pulverized coals and biomasses under either conventional combustion in air or oxy-fuel combustion conditions. Oxy-fuel combustion is a ‘clean-coal’ process that takes place in O\textsubscript{2}/CO\textsubscript{2} environments, which are achieved by removing nitrogen from the intake gases and recirculating large amounts of flue gases to the boiler. Removal of nitrogen from the combustion gases generates a high CO\textsubscript{2}-content, sequestration-ready gas at the boiler effluent. Flue gas recirculation moderates the high temperatures caused by the elevated oxygen partial pressure in the boiler. In this study, combustion of the fuels took place in a laboratory laminar-flow drop-tube furnace (DTF), electrically-heated to 1400 K, in environments containing various mole fractions of oxygen in either nitrogen or carbon-dioxide background gases.

The effects of replacing background N\textsubscript{2} gas with CO\textsubscript{2} (to simulate oxy-combustion conditions) on gaseous and particulate emissions were observed by monitoring them under both O\textsubscript{2}/N\textsubscript{2} and O\textsubscript{2}/CO\textsubscript{2} environments and results were presented in this study. In the case of four coals (a bituminous, a sub-bituminous, two lignites), bagasse and coal/bagasse blends studied, NO\textsubscript{x} emissions in O\textsubscript{2}/CO\textsubscript{2} environments were lower than those in O\textsubscript{2}/N\textsubscript{2} environments. SO\textsubscript{2} emissions from all fuels remained largely unaffected by the replacement of the N\textsubscript{2} diluent gas with CO\textsubscript{2}. Both submicron and super-micron particulate emission yields of three coals from different ranks (a bituminous, a sub-bituminous, a lignite) and biomasses (olive residue, corn residue, and torrefied pine sawdust) were typically lower in O\textsubscript{2}/CO\textsubscript{2} than in O\textsubscript{2}/N\textsubscript{2} environments. Replacement of the background N\textsubscript{2} gas with CO\textsubscript{2} did not have any effect on the particle size distribution of the particulate matter obtained from a 13-stage ash impactor and multi-modal ash
particle size distributions were observed for both coals and biomasses in all cases regardless of the gas environment. Chemical analysis of collected particulates was conducted by Scanning Electron Microscope - Energy Dispersive X-ray Spectroscopy (SEM-EDS) with emphasis to those of submicron size (PM$_1$). In either background gases, submicron (PM$_1$) ashes of the bituminous, the sub-bituminous and the lignite coals were mainly composed of silicon, aluminum, iron, magnesium, calcium, potassium, sodium and sulfur. Moreover, potassium was the major element in submicron particles for both corn and olive residue while calcium was the major element in the submicron particles of torrefied pine sawdust. Phosphorous and sulfur also existed in high amounts in the submicron particles of corn residue. In the case of coals, sulfur was the preeminent component of the PM$_{0.1-0.18}$ while silicon and aluminum were the preeminent components of the PM$_{0.56-1}$ regardless of the rank and background gases. The chemical compositions of the submicron-size particles from coals and biomasses in the PM$_{0.56-1}$ sub-category were not affected by the replacement of the background N$_2$ gas with CO$_2$. Similarly, this replacement did not affect the chemical compositions of the submicron-size particles from the olive residue and corn residue biomasses in the PM$_{0.1-0.18}$ sub-category. To the contrary, the composition of the PM$_{0.1-0.18}$ sub-category was affected by replacing N$_2$ with CO$_2$, and mass fractions of Si, Ca, and Al decreased whereas Na, K and S increased. Scanning Electron Microscopy (SEM) revealed that submicron particles were spherical, whereas super-micron particles were often of irregular shapes, fractured spheres, and spheres with small particles attached to their surface and regardless of the background gas.

NO$_x$ emissions from the various fuels burned in this study did not clearly reflect their nitrogen content (0.2-1.4%), except when large content differences were present. SO$_2$ emissions from all fuels typically increased with increasing sulfur content of the fuels (0.07-1.4%), and
decreased with increasing calcium content of the fuels (0.28-2.7%). Blending the sub-bituminous coal with bagasse reduced its SO$_2$ yields, whereas blending the bituminous coal with bagasse reduced both its SO$_2$ and NO$_x$ yields. Coal rank also did not have any effect on submicron particulate emissions. Submicron particulate yields (PM$_1$) were found to be comparable in the effluents of all three coals, ~2.0 mg/g$_{\text{fuel fed}}$, independently of their ash contents, whereas supermicron particulate yields were nearly analogous to the ash contents of the three coals. In the case of biomasses, olive residue resulted in by far the largest submicron ash yields with an average of 20.5 mg/g$_{\text{fuel fed}}$, while torrefied pine sawdust, with an average of 0.5 mg/g$_{\text{fuel fed}}$, had the lowest submicron yields. The yields of these two biomasses were analogous with the ash contents of the parent fuel. The submicron yields (average of 2.0 mg/g$_{\text{fuel fed}}$) of corn residue, however, were lower than expected when compared to the parent fuels ash content. This yield is comparable to those of the coals tested herein.

NO$_x$ emissions were found to increase with increasing oxygen mole fraction till ~50% O$_2$ was reached in both background gases; thereafter, they monotonically decreased with increasing oxygen concentration. Particulate emission yields typically increased with increasing oxygen mole fraction in the furnace for both coals and biomasses. Furthermore, in PM$_{0.1-0.18}$ sub-category, when the O$_2$ mole fraction increased in either N$_2$ or CO$_2$, the mass fractions of Si, Ca and Al increased at the expense mostly of Na, K and S, but also Fe in the case of the sub-bituminous coal.
Acknowledgement

I would like to express my sincere appreciation and gratitude to my advisor, Professor Yiannis A. Levendis, for his excellent guidance, caring, patience, and friendship. I would like to acknowledge my committee members, Professor Hameed Metghalchi and Dr. Thomai Panagiotou, for their time and valuable suggestions. Special thanks go out to Professor Reza Sheikhi, who was willing to participate in my defense committee at the last moment. I would also like to thank late Professor Adel Sarofim for invaluable advice.

I would like to commemorate and thank Professor Yaman Yener, one of my committee members who recently passed away, for his endless support. He played a great role in my acceptance to graduate school at Northeastern University and continued to support me throughout my academic life. Being far away from family, he was a father figure for me as well as for the Turkish community in Boston. He was a great scientist, teacher, and a real friend.

I would like to acknowledge financial support provided by National Science Foundation, under Award Number CBET-0755431.

I would like to thank the faculty and staff at the Department of Mechanical and Industrial Engineering at Northeastern University. Special thanks to Mr. William Fowle for his technical assistance in SEM analysis. Many thanks are given to Joyce Crain, Noah Japhet, and Jonathan Doughty for their help.

I would like to thank my lab mates Reza Khatami and Chuanwei Zhuo for their support and technical assistance; it would have been a lonely lab without them. I also acknowledge my
coworkers Paula Manoel-Crnkovic and Tiziano Maffei who provided technical assistance and data for the journal papers. Special thanks to Amanda Ruscio who patiently corrected my writings, assisted me with the experiments, and accompanied me during my miserable visits to lab during weekends.

I am deeply grateful to my advisor at Middle East Technical University, Prof. Ahmet Yozgatligil, who supported and encouraged me along the way with his illuminating suggestions and friendship.

I would like to thank my friends in Boston who helped me stay sane through these difficult years. Special thanks to Mualla Eraslan, Seda Gokyer, Secil Reel Sen, and Mehmet Sen for being there when needed and for their joyful friendship. Many thanks are given to the Collage Dance Ensemble for the amazing moments we shared and taking off the pressure during this challenging journey.

Most importantly, none of this would have been possible without the love and patience of my family. I give all my appreciation and love to my parents, Aziz Kazanc and Hatice Kazanc, to whom this dissertation is dedicated to, for their endless support and encouragement. I owe my deepest gratitude to my father for believing in me: he taught me how to stand strong on my own against life’s challenges, which I really appreciate particularly during this endeavor. I always felt the prayers of my mother when I struggle, and speaking with her on the phone was more than a meditation for me. I also would like to thank my beloved sisters: Zubeyde Kazanc Macit for being an amazing friend and giving life to a wonderful kid, Onur Kagan; Kubra Kazanc for being such an understanding sister; and Gizem Kazanc for her presence and joy. I have such an adoring and caring family and I am thankful for everything that they have done for me.
# Table of Contents

Abstract ......................................................................................................................................................... iv

Acknowledgement ............................................................................................................................................... vii

Table of Contents .......................................................................................................................................... ix

List of Figures .................................................................................................................................................... xiii

List of Tables .................................................................................................................................................... xvii

Introduction ........................................................................................................................................................... 1

1. Emissions of $\text{NO}_x$ and $\text{SO}_2$ from Coals of Various Ranks, Bagasse and Coal-Bagasse Blends Burning in $\text{O}_2/\text{N}_2$ and $\text{O}_2/\text{CO}_2$ Environments. ......................................................................................... 9

   1.1 Introduction .................................................................................................................................................. 10

   1.2 Literature Review ....................................................................................................................................... 13

      1.2.1 Emissions of Nitrogen Oxides ($\text{NO}_x$) .......................................................................................... 13

      1.2.2 Emissions of sulfur dioxide ($\text{SO}_2$) ............................................................................................. 18

   1.3 Experimental Setup and Procedure ........................................................................................................ 19

   1.4 Experimental Results and Observations ................................................................................................. 25

      1.4.1. Effect of Fuel Rank and Fuel Type on the $\text{NO}_x$ and $\text{SO}_2$ emissions ............................................. 27

      1.4.2. Effect of background gas on the $\text{NO}_x$ and $\text{SO}_2$ emissions ......................................................... 29

      1.4.3. Effect of oxygen mole fraction on the $\text{NO}_x$ and $\text{SO}_2$ emissions ................................................... 29

      1.4.4. Conversion of fuel-nitrogen and sulfur to $\text{NO}_x$ and $\text{SO}_2$ emissions .............................................. 30

      1.4.5. $\text{CO}$, $\text{CO}_2$ and $\text{O}_2$ in the effluent gases ......................................................................................... 32

   1.5. Discussion .................................................................................................................................................. 33

      1.5.1. Effect of Fuel Rank and Fuel Type on the $\text{NO}_x$ and $\text{SO}_2$ emissions ................................................. 33

      1.5.2. Effect of background gas on the $\text{NO}_x$ and $\text{SO}_2$ emissions .......................................................... 36

      1.5.3. Effect of oxygen mole fraction on the $\text{NO}_x$ and $\text{SO}_2$ emissions ..................................................... 37
## 3. Fuels, Experimental Apparatus and Procedure

- **3.3. Fuels, Experimental Apparatus and Procedure** ................................................. 98
- **3.4. Experimental Results** ...................................................................................... 102
  - **3.4.1. Submicron Ash (PM₁) Composition** ......................................................... 102
- **3.5. Discussion** .................................................................................................... 109
  - **3.5.1. Submicron Ash (PM₁) Composition** ......................................................... 109
  - **3.5.2. Comparison of experimental data with predictions from the vaporization model of Quann and Sarofim** .................................................. 115
- **3.6. Conclusions** ................................................................................................. 122
- **3.7. Appendix 1** .................................................................................................. 125
- **3.8. Appendix 2** .................................................................................................. 126
- **3.9. Appendix 3** .................................................................................................. 129
- **3.10. Appendix 4** ................................................................................................ 135
- **3.11. References** ................................................................................................. 137

## 4. Characterization of Particulate Matter Emitted from Combustion of Various Biomasses in O₂/N₂ and O₂/CO₂ Environments

- **4.1. Introduction** .................................................................................................. 144
- **4.2. Literature Review** ....................................................................................... 147
  - **4.2.1. Ash Yields and Particle Size Distributions** .............................................. 148
  - **4.2.2 Chemical Composition of Ash Particles** ................................................. 152
- **4.3. Experimental Setup** .................................................................................... 155
- **4.4. Analysis and Results** ................................................................................ 161
  - **4.4.1. Ash Yields** ............................................................................................ 161
  - **4.4.2. Particle Size Distributions** .................................................................... 165
  - **4.4.3. Chemical Composition of Ash Particles** .............................................. 166
- **4.5. Discussion** .................................................................................................. 171
4.5.1. Ash Yields ................................................................. 171
4.5.2. Particle Size Distributions .............................................. 178
4.6. Conclusions ................................................................. 184
4.7. References ................................................................. 187

5. Conclusions .................................................................. 191

5.1. The effect of replacing background N₂ gas with CO₂ on both gaseous and particulate emissions. ................................................................. 192

5.2. The effects of fuel ranks, types, and elemental composition on both gaseous and particulate emissions................................................................. 194

5.3. The effects of oxygen mole fraction on both gaseous and particulate emissions. . 195

6. Suggestions for Future Work .................................................. 199
List of Figures

Chapter 1

Figure 1: Sample of Raw sugar cane bagasse (a) as received (b) after preparation. 20

Figure 2: Schematic of the electrically-heated laminar-flow drop-tube furnace. 22

Figure 3: Gas temperature profile along the centerline of the drop-tube furnace for different gas compositions. 23

Figure 4: Average bulk equivalence ratios and mole fractions of NOx, SO2 and O2 in the combustion effluents of four pulverized coals. 26

Figure 5: Average bulk equivalence ratios and mass yields of NOx and SO2 emissions from burning two different pulverized coals, pulverized bagasse and mixtures thereof. 27

Figure 6: Fuel-sulfur and fuel-nitrogen conversion to SO2 and NO during combustion of the four pulverized coals, pulverized sugar-cane bagasse and two blends thereof. 31

Chapter 2

Figure 1: Cross section view of the experimental set-up consisting of electrically-heated laminar-flow drop-tube furnace coupled with the 13-stage Nano-Moudi ash particle impactor, and close up views of the impactor stages, dilution N2 probe and particle injector. 60

Figure 2: PM1, PM2.5, PM1.5, PM10, and PM18 ash emission yields from burning of bituminous (PSOC 1451), sub-bituminous (DECS 26), and lignite (PSOC 1443) coals under various O2/N2 and O2/CO2 atmospheres. 67
Figure 3: Physical appearance of the ash collected from combustion of lignite coal (PSOC 1443) under 60%O\textsubscript{2}-40%CO\textsubscript{2} and 30%O\textsubscript{2}-70%CO\textsubscript{2} environments.

Figure 4: Particle size distributions (PSDs) of ash from burning of a bituminous (PSOC 1451), a sub-bituminous (DECS 26), and a lignite (PSOC 1443) coal under various O\textsubscript{2}/N\textsubscript{2} and O\textsubscript{2}/CO\textsubscript{2} gas compositions.

Figure 5: SEM pictures that show morphologies of ash from burning of a bituminous (PSOC 1451), a sub-bituminous (DECS 26), and a lignite (PSOC 1443) under air and the oxy-fuel combustion condition of 40%O\textsubscript{2} – 60%CO\textsubscript{2}.

Figure 6: TEM pictures that show structural details of submicron ash particles emitted during combustion of a bituminous coal (PSOC1451) in a 40%O\textsubscript{2} - 60%CO\textsubscript{2} environment.

Figure 7: PM\textsubscript{1}, PM\textsubscript{1-5}, and PM\textsubscript{18} ash emission yields from combustion of bituminous (PSOC 1451), sub-bituminous (DECS 26) and lignite (PSOC 1443) coals in various O\textsubscript{2}/N\textsubscript{2} and O\textsubscript{2}/CO\textsubscript{2} atmospheres versus experimentally-deduced maximum char temperatures (averaged over many particles).

Figure 8: High-speed high-magnification back-lit cinematography of the initial stages of single particles of bituminous (PSOC 1451), sub-bituminous (DECS 26) and lignite (PSOC 1443) coals burning in air, at a DTF temperature of 1400 K.
Figure 9: High-speed, high-magnification cinematography of typical combustion events of lignite coal particles (PSOC 1443) burning with 40%O₂.

Chapter 3

Figure 1: Cross section view 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 water-cooled particle collection probe where a flow of dilution nitrogen was provided.

Figure 2: Ash collected on an aluminum substrate (left); examination samples (right) where prepared out of the substrate for SEM-EDS analysis.

Figure 3: Yields of the vaporized major elements (based on analysis of stage 9 (PM₀.₁₋₀.₁₈) with SEM-EDS) of submicron ash particles (PM₀.₃₂) emitted from combustion of a bituminous (PSOC 1451), a lignite (PSOC 1443), and a sub-bituminous (DECS 26) coal in air and in two plausible oxy-fuel atmospheres (30%O₂-70%CO₂ and 40%O₂-60%CO₂).

Figure 4: Comparison of the chemical compositions, given as mass%, of stage 9 (PM₀.₁₋₀.₁₈) and stage 6 (PM₀.₅₆₋₁) ash particles, based on SEM-EDS, emitted from combustion of a bituminous (PSOC 1451), a sub-bituminous (DECS 26), and a lignite (PSOC 1443) coal in air.

Figure 5: Comparison of the chemical compositions, given as mass%, of stage 9 (PM₀.₁₋₀.₁₈) ash particles, based on SEM-EDS, emitted from combustion of a bituminous (PSOC 1451), a sub-bituminous (DECS 26), and a lignite (PSOC 1443) coal in air and in 60%O₂-40%N₂ environments.
**Figure 6:** Comparison of the partial pressures of SiO ($P_{SiO}$) at the char surface; a) calculated from experimental data, b) derived from Quann and Sarofim’s model predictions, and c) computed from Quann and Sarofim’s model coupled to a detailed char combustion code. Values are represented with respect to maximum average char temperature.

**Figure 7:** Temporal evolution of the mole fractions of O$_2$, CO, CO$_2$, and H$_2$O at the surface of an 85 μm sub-bituminous coal char particle during burning in air. Quann and Sarofim’s CO value is superimposed to the pertinent graph with a black horizontal line.

**Chapter 4**

**Figure 1:** Typical oxy-fuel combustion plant configuration.

**Figure 2:** Cross section view 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 water cooled particle collection probe where a flow of dilution Nitrogen was provided.

**Figure 3:** PM$_{0.32}$, PM$_1$ (submicron), PM$_{2.5}$, PM$_{1-5}$ (fine fragment mode), PM$_{10}$, and PM$_{18}$ ash emission yields from burning of Olive Residue, Corn Residue, and Torrefied Pine Sawdust under various O$_2$/N$_2$ and O$_2$/CO$_2$ atmospheres.

**Figure 4:** Particle size distributions (PSDs) of ash emissions from burning of corn residue, olive residue, and torrefied pine sawdust under various O$_2$/N$_2$ and O$_2$/CO$_2$ environments.
List of Tables

Chapter 1

Table 1: Chemical Composition of the Coals and the Bagasse Biomass. 21
Table 2: Fuel-S accounting for two of the coals in this study. 35

Chapter 2

Table 1: Chemical Composition of the Coals. 59
Table 2: Nominal cut size of the stages in Nano Nano-Moudi ash impactor. 63
Table 3: Comparison between nominal cut size and average measured ash particle sizes on three stages of the impactor. 64
Table 4: Carbon weight percentages of the submicron ash collected on Stage 9 from bituminous (PSOC 1451), sub-bituminous (DECS 26) and lignite (PSOC 1443) coals burning in air and in 30% O2-70% CO2 or 40% O2-60% CO2. 68
Table 5: Average maximum deduced char combustion temperatures of the bituminous (PSOC 1451), sub-bituminous (DECS 26), and lignite (PSOC 1443) coals. 81
Table 6: Melting and vaporization temperatures of some common oxides as well as sub-oxides and metals (reduced oxides) found in their ashes. 81
Table 7: Proposed temperature relations of the FFM ash particle formation. 82

Chapter 3

Table 1: Chemical Composition of the Coals. 99
Table 2: Nominal cut size of the stages in Nano Nano-Moudi ash impactor. 102
Table 3: Elemental composition of the bituminous (PSOC 1451), the sub-bituminous (DECS 26), and the lignite (PSOC 1443) coals.

Table 4: Oxide fraction of the High Temperature Ash (HTA) from burning of the bituminous (PSOC 1451), the sub-bituminous (DECS 26), and the lignite (PSOC 1443) coals.

Table 5: Chemical composition (mass % of ash content) of submicron ash particles (stage 9, PM\textsubscript{0.1-0.18}) from burning of a lignite coal (PSOC 1443) in a 40%O\textsubscript{2} - 60%CO\textsubscript{2} atmosphere.

Table 6: Comparison of the chemical compositions, given as mass%, of stage 9 (PM\textsubscript{0.1-0.18}) and stage 6 (PM\textsubscript{0.56-1}) ash particles, based on SEM-EDS, emitted from combustion of a bituminous (PSOC 1451), a sub-bituminous (DECS 26), and a lignite (PSOC 1443) coal in air, 60%O\textsubscript{2}-40%N\textsubscript{2} and three simulated oxy-fuel atmospheres (30%O\textsubscript{2}-70%CO\textsubscript{2}, 40%O\textsubscript{2}-60%CO\textsubscript{2}, and 60%O\textsubscript{2}-40%CO\textsubscript{2}).

Table 7: Experimentally-observed char burnout times, as well as maximum and average deduced char combustion temperatures of the bituminous (PSOC 1451), sub-bituminous (DECS 26), and lignite (PSOC 1443) coals in various environments.

Table 8: Vaporization temperatures of some common oxides as well as sub-oxides and metals (reduced oxides) found in their ashes.

Table A1: Techniques used to analyze chemical composition of submicron ash particles in the literature.
Chapter 4

Table 1: Biomass Type and Chemical Composition. 155

Table 2: Photographs of the olive residue, torrefied pine sawdust, and corn residue. First row demonstrates the particles as received and second row indicates ground powders. 156

Table 3: Nominal cut size of the stages in the Nano-Moudi ash impactor. 160

Table 4: Ash chemical compositions, given as mass %, of olive residue (OR), Torrefied Pine Sawdust (TOPI), and the ashed corn residue. 167

Table 5: Chemical composition (mass % of ash content) of submicron ash particles (stage 9, PM$_{0.1-0.18}$) from burning of a lignite coal (PSOC 1443) in a 40%O$_2$ - 60%CO$_2$ atmosphere. 169

Table 6: Chemical compositions, given as mass%, of stage 6 (PM$_{0.56-1}$) particles emitted from combustion of an olive residue (OR), Torrefied Pine Sawdust (TOPI), and Corn Residue (CR) in air and simulated oxy-fuel atmospheres (30%O$_2$-70%CO$_2$, 40%O$_2$-60%CO$_2$). 170

Table 7: Average deduced temperatures for the chars of torrefied pine sawdust (TOPI), olive residue (OR), and corn residue (CR) burning in air and in different oxy-fuel atmospheres. 170

Table 8: Ash content of fuels obtained by proximate analysis, ashing experiments in horizontal furnace, and the impactor results. The results are provided in wt %. Ash contents obtained from ashing experiments and the impactor were obtained from burning of the biomasses in air. 173
Table 9: Calculated deposition indices for the three biomasses utilized in this study (Olive Residue, Torrefied Pine Sawdust, and Corn Residue), the Olive Residue studied by Masia et al.\textsuperscript{35}, and the three coals previously studied in this laboratory.

Table 10: Melting and vaporization temperatures of some common oxides as well as sub-oxides and metals (reduced oxides) found in their ashes.

Table 11: High-speed, high magnification cinematography images of single particles of biomass (Olive Residue and Torrefied Pine Sawdust) in air and 50\% O\textsubscript{2} – 50\% CO\textsubscript{2}.
Introduction

Electricity consumption, which grows faster than any other form of energy utilization, is increasing with the increasing global population (which increases by 80 million people per year\(^1\)). The world’s electricity consumption is predicted to increase by approximately 84% from 17,200 billion kWh to 31,700 billion kWh by 2035\(^1\). According to this, 1 billion people will be living without electricity in 2030 (IEA). For yet others, power will remain seriously unaffordable\(^2\). Coal is used to generate 29.6% of the primary energy in the world and is the major source of electricity, delivering 40% of the worldwide electricity demand. In the US and some other countries this figure stands or exceeds 45%\(^3\) (80% in Australia). Coal is expected to remain the most important source of electricity in the foreseeable future as it is more abundant and cheaper than other fossil fuels\(^1\). The usage of coal is projected to increase by over 40.3% from 2010 to 2035\(^4, 5\). Especially, Non- Organization of Economic Cooperation and Development (OECD) Asian countries, i.e., China and India, will account for 87% of this increase to meet their electricity demand due to fast growing economic activity and population\(^5\).

Coal has a high potential to pollute the environment from its production through consumption. Burning of the coal leads to CO\(_2\) emissions, which is confirmed to cause global warming, as it contains carbon in its structure. Since coal is used as a primary power generation source around the world, all countries contribute to the emission of greenhouse gases. China, USA, and India are the top three countries that emit greenhouse gases via coal combustion in their power plants\(^6\). Greenhouse gas emissions from coal-burning power plants accounted for about 33% of the US emissions and for 43% of the global emissions in 2009\(^7\).
Moreover combustion of coal results in sulfur dioxide (SO$_2$), nitrogen oxides (NO$_x$), and carbon monoxide (CO) gaseous emissions as well as particulate ash emissions (PM$_1$, PM$_{2.5}$, etc.), which are also hazardous air pollutants, threatening human health and the environment$^8, 9$. Electric utilities are responsible for 73% of the total US emissions of SO$_2$ as well as 22% of the total US NO$_x$ emissions$^{10}$. Nearly all of the utility-generated SO$_2$ emissions and most of the utility-generated NO$_x$ (NO, NO$_2$) emissions arise from coal-burning power-plants, as coal contains sulfur and nitrogen in its matrix. NO$_x$ and SO$_2$ in addition to particulates, PM$_1$ and PM$_{2.5}$, are regulated atmospheric pollutants$^{10}$.

Strategies are being devised to either reduce the greenhouse gas emissions and/or to achieve 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 implementation of technologies that facilitate pre- or post-combustion capture of CO$_2$. One of these technologies is oxy-fuel 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 sequestration-ready high-CO$_2$-concentration gas effluent which may be subsequently stored in underground reservoirs. To moderate combustion temperatures in the furnace, the input oxygen stream is mixed with recycled dry flue gases (containing mostly CO$_2$); hence, combustion of coal takes place in O$_2$/CO$_2$ atmospheres. Another strategy to reduce greenhouse emissions is utilizing biomass as an energy source. In regards to its carbon dioxide emissions, biomass is considered nearly neutral since the carbon dioxide emissions released from converting biomass to energy are equivalent to the amount of carbon dioxide absorbed by the plants during their growing cycles$^{11-13}$. The energy used in the growing, harvesting, and transportation processes results in CO$_2$ emissions that are
detractors. As a result, when fired with primary fossil fuels, such as coal, the use of biomass can reduce the net production of carbon dioxide\textsuperscript{12, 13}. In addition, when combined with oxy-fuel combustion and CCS, the co-firing of biomass and coal has been observed to result in negative net emissions of carbon dioxide\textsuperscript{12, 14}.

Emissions from future oxy-fuel fired boilers, will not be emitted to the atmosphere, they are to be sequestered in underground reservoirs. However in a typical oxy-combustion plant configuration, such plants will still require environmental cleanup equipment to remove ash and other pollutants. If pollutants are not removed they would be (a) partly recycled to the boiler through the flue gas recirculation stream and could be detrimental to its operation, and (b) partly channeled to the \( \text{CO}_2 \) compressor and may interfere with its operation. Again, since environmental cleanup equipment has low efficiency in capturing \( \text{PM}_1 \), it is of technical interest to study the nature of these pollutants from oxy-combustion of both coal and biomass.

The dissertation is organized in six chapters:

**Chapter 1** discusses gaseous emissions of \( \text{NO}_x \), \( \text{SO}_2 \), and \( \text{CO} \) from burning of pulverized coals of various ranks, bagasse, and coal-bagasse blends in \( \text{O}_2/\text{N}_2 \) and \( \text{O}_2/\text{CO}_2 \) environments. A drop tube furnace was used to burn fuel powders and the resulting gaseous emissions were observed with in line gas analyzers. \( \text{O}_2/\text{N}_2 \) and \( \text{O}_2/\text{CO}_2 \) environments with oxygen mole fractions of 20\%, 40\%, 60\%, 80\%, and 100\% were utilized to perceive the oxygen and background gas effect on gaseous emissions. In this chapter the effects of coal rank on gaseous emissions from combustion were studied by observing these emissions from burning of three different ranks; lignite, sub-bituminous, and, bituminous. Furthermore, to comprehend the effects of biomass on gaseous emissions, coal and biomass blends as well as neat biomass were burned.
Chapter 2 describes the physical properties of the ash particulate emissions from burning of three coal ranks (a lignite, a sub-bituminous, and a bituminous) under various O$_2$/N$_2$ and O$_2$/CO$_2$ environments. Ash particles from burning of various coals were collected after combustion occurred in laminar drop tube furnace (DTF) with a Nano-Moudi ash impactor. The particles that were collected on each stage of the 13-staged impactor were analyzed physically. Physical analysis was done by obtaining mass yields of ash particles from both submicron (PM$_1$) and super-micron modes, mass size distribution for the particles between 0-18 µm, and morphology of the particles with Scanning Electron Microscopy (SEM).

Chapter 3 depicts the chemical characterization of submicron particulate matter (PM$_1$) emitted from combustion of coals of various ranks in air and O$_2$/CO$_2$ environments. This chapter examines the chemical composition of the particulates since upon re-circulation to the boiler in typical oxy-fuel applications; it can impact their potential for fouling and slugging therein. This is especially true for submicron particles (PM$_1$), which cannot be captured by conventional ash removal devices (electrostatic precipitators and bag houses) inserted in the exhaust product train. In this chapter, collected submicron ash particles as described in Chapter 2 were analyzed using SEM-EDS and EMA techniques. Comparison of the experimentally-obtained chemical composition of submicron particles with calculations based on Quann and Sarofim’s submicron formation model was attained. Moreover, since Quann and Sarofim’s model assumes constant carbon monoxide and carbon dioxide concentrations on the particle surface, a numerical coal combustion model was also used to obtain real-time CO and CO$_2$ concentrations. Results were interpreted based on observations of the combustion behavior and on the deduced particle temperatures of the same three coals burned in this laboratory under similar conditions.
Chapter 4 describes the physical and chemical characterization of particulate matter emitted from combustion of three biomasses; olive residue, corn residue, and torrefied pine sawdust, in $O_2/N_2$ and $O_2/CO_2$ environments. Physical characterization was done by obtaining mass yields of ash particles from both submicron (PM$_1$) and super-micron modes, mass size distribution for the particles between 0-18 µm, and morphology of the particles with Scanning Electron Microscopy (SEM). Chemical characterization was done by getting chemical composition of the collected particles with SEM-EDS. The results were compared to the data obtained from previous work with coal represented in Chapter 2 and Chapter 3.

Chapter 5 includes the conclusions of this work. Conclusions are presented in three categories; the effect of 5.1) replacing background $N_2$ gas with $CO_2$, 5.2) ranks, types, and elemental composition, and 5.3) oxygen mole fraction on both gaseous and particulate emissions.

Chapter 6 includes the suggestions for future work.
References


2. National Coal Council (2012): Harnessing Coal’s carbon content to Advance Economy,  
   Environment and Energy security, June 22, 2012, Study Chair: Richard Bajura, National  
   Coal Council, Washington, DC.


   Jacoby, H. D.; Joskow, P. L.; Mcrae, G.; Lester, R.; Moniz, E. J.; Steinfeld, E.; Katzer, J.,  

5. USEIA-IEO (2011): Energy Information Administration - International Energy Outlook,  

   145; Information Disclosure and Climate: The Thinking Behind CARMA - Working  

   (accessed May 5th ).


CHAPTER 1


Feyza Kazanc\textsuperscript{1}, Reza Khatami\textsuperscript{1}, Paula Manoel-Crnkovic\textsuperscript{2} and Yiannis Levendis\textsuperscript{1}

\textsuperscript{1}Mechanical and Industrial Engineering, Northeastern University, Boston, MA 02115, USA
\textsuperscript{2}Mechanical Engineering, Escola De Engenharia De São Carlos, University of São Paulo, Brazil
1. Emissions of NO$_x$ and SO$_2$ from Coals of Various Ranks, Bagasse and Coal-Bagasse Blends Burning in O$_2$/N$_2$ and O$_2$/CO$_2$ Environments.

Abstract

Oxy-coal combustion is a viable technology, for new and existing coal-fired power plants, as it facilitates carbon capture and, thereby, can mitigate climate change. Pulverized coals of various ranks, biomass, and their blends were burned in order to assess the evolution of combustion effluent gases, such as NO$_x$, SO$_2$ and CO, under a variety of background gas compositions. The fuels were burned in an electrically-heated laboratory drop-tube furnace in O$_2$/N$_2$ and O$_2$/CO$_2$ environments with oxygen mole fractions of 20%, 40%, 60%, 80%, and 100%, at a furnace temperature of 1400 K. The fuel mass flow rate was kept constant in most cases, and combustion was fuel-lean. Results showed that in the case of for four coals studied, NO$_x$ emissions in O$_2$/CO$_2$ environments were lower than those in O$_2$/N$_2$ environments by amounts that ranged from 19-43% at the same oxygen concentration. In the case of bagasse and coal/bagasse blends, the corresponding NO$_x$ reductions ranged from 22-39%. NO$_x$ emissions were found to increase with increasing oxygen mole fraction till ~50% O$_2$ was reached; thereafter, they monotonically decreased with increasing oxygen concentration. NO$_x$ emissions from the various fuels burned did not clearly reflect their nitrogen content (0.2-1.4%), except when large content differences were present. SO$_2$ emissions from all fuels remained largely unaffected by the replacement of the N$_2$ diluent gas with CO$_2$; whereas they typically increased with increasing sulfur content of the fuels (0.07-1.4%), and decreased with increasing calcium content of the fuels (0.28-2.7%). Under the conditions of this work, 20-50% of the fuel-nitrogen was converted to NO$_X$. The amount of fuel sulfur converted to SO$_2$ varied wildly, depending on
the fuel and, in the case of the bituminous coal, also depending on the O₂ mole fraction. Blending the sub-bituminous coal with bagasse reduced its SO₂ yields, whereas blending the bituminous coal with bagasse reduced both its SO₂ and NOₓ yields. CO emissions were generally very low in all cases. The emission trends were interpreted based on separate combustion observations.

1.1 Introduction

Half of the electricity in the US (40% globally) is generated by electric utilities burning coal. Electric utilities are responsible for 73% of the total US emissions of SO₂ as well as 22% of the total US emissions NOₓ emissions.¹ Nearly all of the utility-generated SO₂ emissions and most of the utility-generated NOₓ (NO, NO₂) emissions arise from coal-burning power-plants, as coal contains sulfur and nitrogen in its matrix. NOₓ and SO₂ are regulated atmospheric pollutants.¹ Such power-plants are also among the largest point source emitters of the major greenhouse gas: carbon dioxide (CO₂). Thus, regulatory pressure is expected in the future to reduce and/or capture and sequester CO₂ emissions. Whereas, power generation from CO₂-neutral renewable fuels is being promoted, coal utilization is expected to continue in the future, as the reserves of coal are abundant.² Thus, methods for achieving “clean”-coal combustion are of technological interest.

Following coal, petroleum and natural gas, biomass is the next abundant carbon-based energy resource.³ Co-combustion of biomass and coal has generated widespread interest, because of the reduced emissions of gases such as CO₂, SO₂ and NOₓ compared to those emitted by the combustion of neat coal. Biomass alone may not be used as a fuel in existing coal-fired furnaces due to its low bulk density, high moisture content and low energy content.⁴⁵ However, its co-
firing with coal is advantageous, based on its higher volatile matter content and its lower pyrolysis temperature which can aid the ignition and combustion characteristics of the blend. Each percentage point of coal replaced by biomass results in about 60 Mt of CO\textsubscript{2} avoided per year globally. Co-utilization of biomass, also provides an economical and sustainable method for electric power generation. Moreover, using waste biomass as a fuel curtails its prolonged storage which can generate methane (CH\textsubscript{4}), a potent greenhouse gas. Therefore, based on recognized environmental and economic benefits of using biomass as a fuel, it has been projected that the biomass share in electricity production may increase from the current 1.3% to some 3%-5% by 2050.

For the reasons discussed above this study incorporated bagasse, which is a waste residue after sugar and/or ethanol have been produced from sugar cane. The largest producers of bagasse are India and Brazil. The sugar cane harvest in Brazil was 570 million tons in 2009. This process generated 190 million tons of bagasse residue, which supplied 3% of the Brazilian energy matrix that year. It is projected that by 2020 this figure will increase to 14%.

Given the documented increasing concentration of carbon dioxide in the atmosphere, and its likely relation to global warming, several technologies are being developed to facilitate carbon capture and storage (CCS) from fossil-fuel-fired power plants. Among them, oxy-fuel combustion is of technological interest, as it requires the least design and operational departures from currently practiced combustion techniques. The popularity of oxy-fuel combustion, initially proposed by Horn and Steinber and Abraham has increased dramatically in recent years. This technology is capable of providing a CO\textsubscript{2} volume fraction in the flue gas of 95% or higher, which is desirable for subsequent sequestration purposes.
In oxy-combustion, a fuel is burned in an O$_2$-CO$_2$ environment, as opposed to an O$_2$-N$_2$ environment in the case of conventional combustion in air. The differences between air and oxy-fuel combustion are mainly in the properties of CO$_2$ and N$_2$ diluent gases such as density, heat capacity, thermal and molecular diffusivities and gas emissivity. These properties influence the heat transfer, flammability limits, ignition behavior and the combustion kinetics of burning pulverized coal.$^{18,19}$ Oxygen is supplied to the furnace by an air separation unit, and a portion of the flue gas is recycled to moderate the boiler temperature. Upon condensation of H$_2$O, the resulting combustion effluent is mostly CO$_2$, which may be subsequently pressurized, piped to a suitable underground reservoir, in which it is stored. As an additional benefit of this technology, sizeable reductions of NO$_x$ emissions have been reported.$^{20-22}$

This work is part of a broader basic investigation to assess the fundamentals of combustion behavior and evolution of gaseous and condensed phase emissions from coal and biomass, burning in different O$_2$/N$_2$ and O$_2$/CO$_2$ environments. This particular research addresses the evolution of the gas phase emissions of NO$_x$, SO$_2$ and CO$_2$. While there is not a standard background gas composition for oxy-coal combustion, the most accepted compositions, based on research undertakings and pilot studies, consist of 25%-42% O$_2$ mixed with typically dried recycled gases which, in turn, are mostly composed of CO$_2$. In contrast conventional fired combustion uses air, which is composed of 21% O$_2$-79%N$_2$. In oxy-coal combustion, the nitrogen is replaced by recycled CO$_2$. The oxygen range that was chosen for this study includes the conventional air-fired boiler setting (21% O$_2$), as well as the typical oxy-fuel combustion oxygen range (25%-42% O$_2$). The study was expanded to include even higher oxygen mole fractions (40%-100%) not only because high oxygen mole fractions can decrease the size of boilers and reduce electricity demand for their flue-gas recirculation fans but, also, to obtain a
fundamental understanding on the generation of pollutants over the widest possible range of oxygen mole fractions (20-100%), above that found in air. Four coals of different ranks (bituminous, sub-bituminous and lignite) were burned. Moreover, sugarcane bagasse (a biomass residue from sugar or bioethanol production) was also burned under similar conditions, either as a neat fuel or blended with coal. In this study, the fuels were burned in an externally-heated drop-tube furnace in atmospheres of O₂/N₂/CO₂ gases. Flue gas recycling was simulated by the presence of CO₂. Therefore, since actual flue gas recycling was not implemented herein, combustion-generated NOₓ or SO₂ were not returned to the furnace. Thus, the impact of replacing N₂ with CO₂ was examined without (a) the interfering effects of NO “re-burning” on the final NOₓ emissions and (b) the effects of extended the residence time of SO₂ in the furnace and inhibited decomposition of any formed CaSO₄ in the ash because of enhanced SO₂ concentration in the furnace.³³

1.2 Literature Review

1.2.1 Emissions of Nitrogen Oxides (NOₓ)

NOₓ emissions from burning coal are mostly comprised of “`thermal-NOₓ`” and “`fuel-NOₓ`”. The former stems from oxidation of atmospheric-nitrogen in the flame, whereas the latter originates from oxidation of the fuel-nitrogen. Pershing and Wendt³⁴ reported that the “`fuel-NOₓ`” constitutes over 75% of the total NOₓ emissions; a finding in good agreement with the results of Courtemanche and Levendis,³⁵ who reported that fuel-NOₓ contributed 80% of the total NOₓ for experiments at various furnace temperatures and equivalence ratios. Fuel-nitrogen in coal is contained predominantly in pyrrolic-type groups (50-60%); pyridinic and quaternary forms have also been detected. Nitrogen contained in pyridinic groups has been reported to be
more stable than that in pyrrolic groups. In the combustion process, fuel-nitrogen evolves during both the devolatilization and the char oxidation phases; the distribution depending on the fuel type, the temperature and the residence time. In the case of bituminous coals the volatile matter nitrogen is released in tarry compounds, which at high temperatures decay mostly to hydrogen cyanide (HCN) and soot-nitrogen. In the case of low rank coals and biomass, light nitrogen species may be directly released from the solid matrix as HCN, ammonia (NH₃) and cyanuric acid (HNCO). A survey of the many possible reaction paths by which HCN is converted to NO and other products, through an amine radical pool, shows the complexity of the gas-phase chemistry. Flagan and Seinfeld summarized the overall chemistry scheme as follows: fuel-N in tars converts expediently to HCN, proceeding to NH₃ intermediates, which then either oxidize to NO by reactions with oxidants such as OH or reduce to N₂ by reactions with NO. The majority of char-bound nitrogen may leave the surface as NO, which is formed as char nitrogen is oxidized to NO. This is then partially reduced by reactions with CO or char as it traverses the particle pores; un-reacted NO escapes from the boundary layer and mixes into the bulk gas. The char nitrogen conversion is complicated, as formation of CN or NH is also possible.

Conversion of the mass of fuel-nitrogen to NOₓ in experimental systems varies from relatively low levels up to nearly 100%. Levy reported that the range of conversion of coal-bound nitrogen to NOₓ is wide (15-40%), and called this variability in fuel nitrogen conversion, and the lack of its clear understanding, a major unresolved issue in fuel NOₓ combustion control. This was echoed at a later time by Visona and Stanmore and then, again, by Glarborg et al., who remarked that in spite of progress over the last three decades, the basic mechanisms for fuel nitrogen conversion, are still being clarified, and unresolved issues may limit the potential for
effective NO\textsubscript{x} control. The aforementioned variability also underscores the opportunity for significant reductions in NO\textsubscript{x} emissions by appropriately controlling the combustion environment. This is especially of interest to combustion staging and, most recently, to oxy-combustion. Laboratory experiments in pulverized coal combustion have shown that the stoichiometry exerts a strong effect on NO\textsubscript{x} levels and on the distribution of fuel nitrogen among gaseous products. Pohl and Sarofim\textsuperscript{44} burned bituminous and lignite coals in air over a wide range of bulk equivalence ratios ($\phi = 0.1-5.5$), at a furnace temperature of 1500 K. They reported that the conversion of the fuel-nitrogen to NO decreased with increasing $\phi$, from 60% at $\phi=0.2$ to 10% at $\phi>1.5$. They mentioned that at high $\phi$s, nitrogen remained in the un-reacted chars. In agreement with the above, Courtemanche and Levendis\textsuperscript{35} reported that, over a range of bulk equivalence ratios ($\phi=0.5-1.5$) and over a range of furnace temperatures (1300-1600 K), the conversion of the nitrogen in a bituminous coal to NO\textsubscript{x} decreased with increasing $\phi$ from 40% at $\phi=0.5$ to below 10% at $\phi=1.5$. The effect of furnace gas temperature, in the aforementioned range, on NO\textsubscript{x} was found to be significant. However, Kremer and Schulz\textsuperscript{45} reported the NO\textsubscript{x} emissions from combustion of high volatile bituminous coal to be rather independent of furnace temperature, as also did Spinti and Pershing\textsuperscript{46} for combustion of bituminous coal char.

During pulverized coal combustion, fuel nitrogen is either released with the volatiles or remains within the char, roughly in proportion to the char yield.\textsuperscript{39} This is supported by Haussmann and Kruger,\textsuperscript{41} who found that char nitrogen represents the majority of the original fuel nitrogen, in the gas temperature range of 1200-1700 K. Upon devolatilization, De Soete,\textsuperscript{47} and Chen and Niksa\textsuperscript{48} reported that the fraction of char nitrogen converted into NO during char oxidation is roughly proportional to the degree of char burnout. No evidence was found by Nelson et al.\textsuperscript{36} that the total fuel nitrogen released depends on coal rank or coal nitrogen content,
although the fraction of the coal-nitrogen released with the volatiles increases with decreasing rank, i.e., increasing oxygen content in the fuel.\cite{49} Spinti and Pershing,\cite{46} detected some influences of the coal rank in the char combustion phase, and reported that when chars burned in nitrogen-free oxidant the char-N to NO\textsubscript{x} conversion was higher for lignites (50-60\%) than for bituminous coals (40-50\%). In addition to burning bituminous and lignite coals, Pohl and Sarofim\cite{44} also burned lignite coal chars over a wide range of bulk equivalence ratios (\(\phi=0.1-5.5\)), at a furnace temperature of 1500K. They reported that the conversion of the fuel nitrogen in the lignite coal chars to NO decreased with increasing \(\phi\), from 25\% at \(\phi=0.2\) to 4\% at \(\phi>1.5\). Thus, by comparison with the aforementioned coal combustion experiments, they concluded that 60-80\% of the NO\textsubscript{x} was contributed by the oxidation of nitrogen released with the volatiles, i.e., the remaining 20-40\% NO\textsubscript{x} was released during char combustion. Pershing and Wendt\cite{50} burned both bituminous and lignite coals and their chars at \(\phi=1.15\) and also concluded that less than half of the original coal nitrogen is converted to NO\textsubscript{x} during the char combustion phase. Levendis\cite{51} reported on the roles of volatile matter combustion and char combustion phases of the Pittsburgh #8 bituminous coal on NO\textsubscript{x} formation at fuel-lean conditions (\(\phi=0.4\)). This coal released 60 wt\% of its fuel nitrogen during devolatilization, 35 wt\% during char combustion, with the remainder (5 wt\%) staying with carbon in the ash. However, not all of the released `fuel-nitrogen' formed NO\textsubscript{x}. Roughly 42-47\% of the coal-nitrogen was converted to NO\textsubscript{x}, out of which approx. 15\% was converted during the volatile and 30\% during the char combustion phases. The above is in agreement with the findings of Pohl and Sarofim,\cite{44} who also reported \(\approx40\%\) for coal-nitrogen conversion to NO\textsubscript{x} for the same coal (Pittsburgh #8) burning under similar fuel-lean combustion conditions (\(\phi=0.5\)). Increasing the gas temperature, in the limited range of 1400-1600 K, mildly increased the total amount of fuel nitrogen converted to NO\textsubscript{x}.\cite{51}
The effects of parameters such as nitrogen content in coal, particle size, surface area of the chars, total pressure, $O_2$ partial pressure in the gas, NO partial pressure in the gas, etc., are briefly discussed in this paragraph. Spinti and Pershing\textsuperscript{46} reported that the apparent conversion of char-N to NO$_x$ decreased as the level of the initial NO$_x$ mole fraction in the surrounding gas increased. To the limit, in their study, the char-N to NO$_x$ conversion dropped to nearly 0% at a level of 900 ppm NO$_x$ in the flame. Chaikalangmuang et al.\textsuperscript{52} reported that in un-staged burners, the formation of NO$_x$ increased with a coal’s volatile matter content, but in staged burners the formation of NO$_x$ decreased with increasing volatile matter content. Seeker et al.\textsuperscript{53} reported that small particles produce more fuel-NO than large particles. Aho et al.\textsuperscript{54} reported that NO formation decreased sharply with reactor pressure, and mildly increased with reactor temperature and oxygen mole fraction; they also provided an empirical formula to estimate the NO mole fraction based on those parameters ($y_{NO} \% = -11.63 + 0.04557 \times T \, (^{\circ}C) - 2.33 \times p \, (bar) + 15.992 \times p_{O2} \, (bar)$). Visona and Stanmore\textsuperscript{43} reported that increasing the inlet oxygen mole fraction (in the range of $y_{O2}= 5$-25%) generated more NO. This was corroborated by Spinti and Pershing\textsuperscript{46} (in the range of $y_{O2}= 21$-28%) and by Hu et al.\textsuperscript{55} (in the range of $y_{O2}= 20$-50%). At higher oxygen mole fractions ($y_{O2} > 50\%$) NO$_x$ emission decreased, and in pure oxygen it even went back to the same level as that in air. Lazaro et al.\textsuperscript{56} reported that the lower the surface area of the char the higher the fraction of the char-nitrogen that is released as NO (the NO/N ratio).

Finally, there has been some research related to the evolution of NO$_x$ in CO$_2$-rich atmospheres, as is the case in oxy-fuel combustion.\textsuperscript{17,23-25,27,55,57-60} Comprehensive reviews on oxy-fuel combustion have been published in recent years,\textsuperscript{21,22,61} and have reported on emissions of NO$_X$. In pilot-scale demonstrations on pulverized oxy-coal combustion, reductions in NO$_x$ emissions of as much as 65% have been observed.\textsuperscript{20,22} These drastic NO$_x$ reductions may be
caused by factors, such as the absence of atmospheric nitrogen, changes in the combustion characteristics of coal, re-burning of the recycled exhaust gas, reactions with char, etc.\textsuperscript{37,42,62}

1.2.2 Emissions of sulfur dioxide (SO\textsubscript{2})

Sulfur exists in coal in inorganic forms, predominantly pyrite (FeS\textsubscript{2}), or in organic forms, such as thiophene, sulfides and thiols. The sulfur content of coals varies from less than one percent to over 12wt\%.\textsuperscript{63} In fuel-lean combustion, the majority of this sulfur is typically oxidized to form SO\textsubscript{2}.\textsuperscript{29} Courtemanche and Levendis\textsuperscript{35} examined the emissions from combustion of a pulverized bituminous coal over a range of bulk equivalence ratios (\(\phi=0.5-1.5\)) and furnace temperatures (1300-1600 K). They reported that the conversion of the sulfur in the coal to SO\textsubscript{2} decreased with increasing \(\phi\), from nearly 100% at \(\phi=0.5\) to as low as 40% at \(\phi=1.5\). Moreover, a decrease in conversion with increasing furnace gas temperature was noticed. By examining the sulfur content in the parent coal and its char derivatives upon pyrolysis,\textsuperscript{45,64,65} it was determined that the sulfur that remained in the char was proportional to its mass yield. A few coals, however, were reported to exhibit preferential enriching of the char with sulfur.\textsuperscript{65} Atal et al.\textsuperscript{66} and Levendis\textsuperscript{51} studied the sulfur release during volatile matter combustion and char combustion phases of the Pittsburgh #8 bituminous coal, under fuel-lean conditions. Nearly all the released sulfur (90-95%) was converted to SO\textsubscript{2}. Small amounts of sulfur remained in the collected ash of this low-calcium content coal. Approx. 57 wt% of the sulfur content of this coal was released as SO\textsubscript{2} during the combustion of volatiles, whereas 33% of the parent coal sulfur was released during the combustion of char. This is contrary to the observation of Wells et al.\textsuperscript{65} who found that the char was preferentially enriched in sulfur. The difference could possibly be due to the experimental temperatures, heating rates and oxidative conditions.
SO₂ emissions generally correlate with the sulfur content of the fuels. Thus, the addition of biomass has been shown to reduce SO₂ emissions, mainly due to its low sulfur content in most cases and due to biomass ash composition. SO₂ emissions have also been correlated with the organic and inorganic sulfur content of fuels; it has been reported that bituminous coals have inorganic sulfur with a loosely bound portion that can be released at a faster rate than the inorganic sulfur. Finally, SO₂ emissions have also been reported to inversely correlate with the calcium content of the fuels, as well as to that of other alkaline-earth metals (sodium, potassium and magnesium). High sulfur retention in the ash has been reported during combustion of sub-bituminous and lignite coals having calcium content in the ash sufficiently high to result in near-stoichiometric calcium and sulfur amounts. Spliethoff & Hein showed that the higher the alkaline-earth content in the ash, the more the sulfur retention therein. Raask proposed an empirical formula for predicting the sulfate retention, Sᵣ, in the ash: $Sᵣ = \left( \frac{0.7 \text{ Na}\% + 0.41 \text{ K}\% + 0.8 \text{ Ca}\% + 1.32 \text{ Mg}\%}{\text{ S}\%} \right) \times (1 - 0.09 (\text{ ash}\%)^{2/3})$.

### 1.3 Experimental Setup and Procedure

Coals from four different ranks were burned in this study, as listed in Table 1. Samples for the four coals were obtained from the Penn State Coal Bank, and were ground and sieved. A size cut of 53-90 µm was used herein. Two of the coals (the PSOC-1451 bituminous and the PSOC-1443 lignite) were extensively characterized in previous research. Sugar cane bagasse was collected directly from a mill located in Brazil – São Paulo State. The bagasse was washed, dried at 90°C for 24 hours, chopped in a household blender and sieved. Pictures of the raw bagasse before and after preparation are shown in Figure 1. Bagasse particles were needle-like in shape and proved difficult to fluidize and feed to the furnace through the capillary tubing used to feed
the furnace injector, see Fig. 2. An exception was the case of particle sizes <53 µm that were selected for the experiments. These bagasse particles were fed to the furnace at a flowrate slower than that used for the coals. Properties of bagasse are also listed in Table 1. Blends of 25 wt% of biomass with two of the coals (the PSOC-1451 bituminous and the DEC-26 sub-bituminous) were also prepared and burned.

Figure 1: Sample of Raw sugar cane bagasse (a) as received (b) after preparation
Table 1. Chemical Composition of the Coals and the Bagasse Biomass

<table>
<thead>
<tr>
<th>Rank and Fuel Source</th>
<th>PSOC-1451</th>
<th>DECS-11</th>
<th>PSOC-1443</th>
<th>DECS-26</th>
<th>Bagasse</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bituminous High Volatile A Pittsburgh #8 Pennsylvania</td>
<td>Lignite A Beulah, North Dakota</td>
<td>Lignite A Titus, Texas</td>
<td>Sub-Bituminous B River Basin Wyodak, Wyoming</td>
<td>Sugarcane Residue Brazil</td>
</tr>
<tr>
<td>Proximate Analysis as received, and (upon re-evaluating moisture)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moisture (%)</td>
<td>2.5</td>
<td>33.4 (13.2)</td>
<td>28.5 (18.6)</td>
<td>26.3 (13.1)</td>
<td>4.4</td>
</tr>
<tr>
<td>Volatile matter (%)</td>
<td>33.6</td>
<td>37.4 (48.6)</td>
<td>44.2 (50.3)</td>
<td>33.1 (39.0)</td>
<td>83.9</td>
</tr>
<tr>
<td>Fixed Carbon (%)</td>
<td>50.6</td>
<td>22.9 (29.8)</td>
<td>12.0 (13.7)</td>
<td>35.1 (41.4)</td>
<td>7.7</td>
</tr>
<tr>
<td>Ash (%)</td>
<td>13.3</td>
<td>6.4 (8.4)</td>
<td>15.3 (17.4)</td>
<td>5.6 (6.5)</td>
<td>4.0</td>
</tr>
<tr>
<td>Ultimate Analysis (on a dry basis)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon (%)</td>
<td>71.9</td>
<td>66.2</td>
<td>56.8</td>
<td>69.8</td>
<td>44.3</td>
</tr>
<tr>
<td>Hydrogen (%)</td>
<td>4.7</td>
<td>4.0</td>
<td>4.1</td>
<td>5.7</td>
<td>5.7</td>
</tr>
<tr>
<td>Oxygen (%) (by diff.)</td>
<td>6.9</td>
<td>18.6</td>
<td>15.8</td>
<td>15.6</td>
<td>45.5</td>
</tr>
<tr>
<td>Nitrogen (%)</td>
<td>1.4</td>
<td>0.9</td>
<td>1.1</td>
<td>0.9</td>
<td>0.2</td>
</tr>
<tr>
<td>Sulfur (total) (%)</td>
<td>1.4</td>
<td>0.7</td>
<td>0.7</td>
<td>0.4</td>
<td>0.07</td>
</tr>
<tr>
<td>Sulfur (pyritic) (%)</td>
<td>0.82</td>
<td>0.31</td>
<td>0.09</td>
<td>0.07</td>
<td>-</td>
</tr>
<tr>
<td>Sulfur (organic) (%)</td>
<td>0.53</td>
<td>0.39</td>
<td>0.64</td>
<td>0.35</td>
<td>-</td>
</tr>
<tr>
<td>Sodium (%)</td>
<td>0.06</td>
<td>0.66</td>
<td>0.04</td>
<td>0.09</td>
<td>-</td>
</tr>
<tr>
<td>Calcium (%)</td>
<td>0.28</td>
<td>1.8</td>
<td>1.4</td>
<td>1.1</td>
<td>2.7</td>
</tr>
<tr>
<td>Ash (%)</td>
<td>13.7</td>
<td>9.6</td>
<td>21.4</td>
<td>7.6</td>
<td>4.2</td>
</tr>
<tr>
<td>Heating Value Dry Fuel (MJ/kg)</td>
<td>31.5</td>
<td>25.7</td>
<td>23.0</td>
<td>28.2</td>
<td>16.3</td>
</tr>
</tbody>
</table>

For the four coals and their proximate and ultimate analysis data was obtained from the Penn State Coal Sample Bank; upon opening the sealed containers of the supplied coal samples, variations of moisture content with storage in the laboratory were observed for all, but the bituminous, coals. The measured moisture content values are listed (in parentheses) and the remaining proximate analysis values were re-calculated and are also shown (in parentheses). The specific bagasse sample was analyzed at the University of São Paulo laboratories, São Carlos Campus.

Combustion experiments were conducted in an electrically-heated, drop-tube laboratory furnace (manufactured by ATS) (4.8 kW max), shown in Fig. 2. 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). Fuel particles were entrained in a metered stream of oxidant gases, and entered a long capillary tubing (with
1.14 mm inner diameter) from 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 watercooled stainless steel furnace injector. Therefrom, the fuel particles entered the furnace.

Figure 2. Schematic of the electrically-heated laminar-flow drop-tube furnace

A background mixture of gases was introduced to the furnace in an annular space between the water-cooled sorbent injector and the inner walls of the alumina tube in the furnace. The gas mixture was preheated therein. The combined input flow rate of the particle fluidizing gas and the furnace gas was 4 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 1-2 s. Combustion occurred under laminar-flow conditions in the 20 cm hot zone of the furnace. Furnace wall temperatures ($T_w$)
were continuously monitored by type-S thermocouples embedded in the wall. Gas temperatures ($T_g$) inside the furnace were measured at various axial and radial positions by an aspirated shielded thermocouple (suction pyrometer $^{66,73}$). The gas temperature profile, at various compositions of O$_2$-N$_2$-CO$_2$ gases along the centerline of the furnace are shown in Fig. 3. The radiation zone of the furnace spans the 0-25 cm range shown in this figure. For most of the axial profile of the furnace the gas temperature was measured to be fairly constant and close to the furnace set-point of 1400 K.

![Centerline Gas Temperature Profile](image_url)

Figure 3. Gas temperature profile along the centerline of the drop-tube furnace for different gas compositions.

The gaseous effluent of the furnace passed through a glass-microfiber filter to remove the ash, then through an ice-bath condenser to remove moisture. Thereafter, the effluent was channeled to continuous-flow analyzers to measure emissions of SO$_2$ (Rosemount Analytical UV SO$_2$ analyzer), NO$_x$ (Thermo Electron Model 10 Chemiluminescent NO-NO$_2$-NO$_x$ analyzer), CO (Horiba VIA-510 analyzer), and CO$_2$ (Horiba VIA-510 analyzer). Furthermore, the oxygen in the effluent was monitored throughout the experiments (Horiba MPA-510 analyzer). The outputs
of the analyzers were recorded by a Data Translation card (PCI-6221) in a microcomputer, using Lab View software.

Tests were conducted in gas atmospheres of either O₂/N₂ mixtures or O₂/CO₂ mixtures. Five oxygen mole fractions were implemented (20%, 40%, 60%, 80%, and 100%). Gas flowrates were metered by Matheson rotameters and mixture strengths were confirmed by using the oxygen analyzer. The injection rate of the coal powders was in the neighborhood of 0.4 g/min, whereas for the bagasse the injection rate was reduced to 0.06 g/min, to avoid plugging of the powder feeding system. Conditions were selected to be fuel-lean (ϕ<1) in the baseline case, i.e., combustion in air. The bulk equivalence ratio was defined as \( \phi = \frac{m_{\text{dry fuel}}/m_{\text{oxygen}}^{\text{actual}}}{m_{\text{dry fuel}}/m_{\text{oxygen}}^{\text{stoichiometric}}} \), where the stoichiometric fuel-to-air ratios of the fuels were calculated from the ultimate analysis, shown in Table 1. The actual fuel-to-air ratios were calculated based on the monitored mass flow rates of the fuels and of the inlet gases. The amount of pulverized fuel fed during each experiment was calculated by measuring the weights of the powder contained in the vial at the beginning and at the end of each run. As both the gas and the fuel flow rates were kept constant in all cases, exceedingly fuel-lean combustion conditions were implemented at oxygen concentrations higher than those in air. A limited number of experiments were also conducted where the mass flow rate of the fuel increased with increasing oxygen mole fraction to keep the equivalence ratio constant at \( \phi=0.8 \). Emissions of NOₓ, SO₂, CO and CO₂ were recorded as mole fractions, expressed in ppm or percentages. Yields of pollutants were computed, based on the amount of fuel introduced to the furnace. Fuel-N to NOₓ conversion percentages were finally calculated based on measured NOₓ emissions during combustion in CO₂. As this environment is devoid of atmospheric nitrogen, the only source of NOₓ emission was thought to be fuel-bound nitrogen, the amounts of which have been listed in Table 1. Every experiment lasted for 7-10
minutes after steady-state and steady-flow conditions were reached. Since samples have different physical properties, the consumed masses were different for the neat fuels and their blends. Triplicate experiments were conducted.

### 1.4 Experimental Results and Observations

This section documents the effects of several parameters on the major gaseous emissions, such as (a) the fuel type (bituminous, sub-bituminous, two lignites and bagasse, as well as blends of bagasse with both bituminous and sub-bituminous coals), (b) the replacement of N₂ by CO₂, as the diluent gas, and (c) the variation of oxygen mole fraction in the furnace.

The calculated bulk equivalence ratios, together with integrated average emissions of NOₓ and SO₂ from combustion of the four coals of this work, are shown in Fig. 4. Bagasse and bagasse/coal blends were not included in this plot since their feeding rates were lower than those of coal and, thus, mole fractions of emitted pollutants therefrom cannot be directly compared. Instead, a comparison of the emission yields (mass of emissions/mass of fuel fed) of all fuels was made in Fig. 5, upon normalization with the amount of fuel introduced to and burned in the furnace. The total gas flow rates and the fuel mass flow rates were kept constant in the entire series of experiments for each fuel, thus the average bulk equivalence ratios, \( \phi \), varied as shown in the first rows of Figs. 4 and 5. It monotonically decreased with increasing oxygen mole fraction. The equivalence ratios, \( \phi_{\text{bulk}} \), of different coals were expected to be similar since they were all introduced at the same nominal feeding rates; however, as this calculation was based on the dry mass of the fuels, the low-moisture bituminous coal exhibited the highest \( \phi_{\text{bulk}} \) among all coals. The low values of \( \phi_{\text{bulk}} \) in the case of bagasse are due to the implemented reduced feeding
rates for this low density fuel. Moreover, equivalence ratios of blends fall between those of their neat fuels constituents as expected (see Fig. 5).

![Equivalence ratio, NOx, SO2, and O2 plots for two environments](image)

**Figure 4.** Average bulk equivalence ratios and mole fractions of NOx, SO2 and O2 in the combustion effluents of four pulverized coals. Combustion took place in various O2/N2 (left column) and O2/CO2 (right column) environments. Furnace temperature was kept at 1400 K.
Figure 5. Average bulk equivalence ratios, and mass yields of NO\textsubscript{x} and SO\textsubscript{2} emissions from burning two different pulverized coals, pulverized bagasse and mixtures thereof. Combustion took place in various O\textsubscript{2}/N\textsubscript{2} (left column) and O\textsubscript{2}/CO\textsubscript{2} (right column) environments. Furnace temperature was kept at 1400 K.

1.4.1. Effect of Fuel Rank and Fuel Type on the NO\textsubscript{x} and SO\textsubscript{2} emissions

1.4.1.1. NO\textsubscript{x}: The NO\textsubscript{x} emissions from the bituminous coal were not too different from those of the lignite coals, even if the lignites had lower fuel-nitrogen content (1.4% for the former vs. 0.9% and 1% for the latter two). The NO\textsubscript{x} emissions from the sub-bituminous coal (0.9%
nitrogen content) were distinctly lower than those of the other coals in most cases, as shown in Fig. 4 (mole fractions) and in Fig. 5 (yields). The lowest yields, by far, were those from burning bagasse, in accordance with its very low fuel-N content (0.2%), see Fig. 5. The NO\textsubscript{x} emission yields from the bituminous/bagasse blends, also shown in Fig. 5, fell between those of the neat fuel constituents, in both N\textsubscript{2} and CO\textsubscript{2} environments. More importantly, at most of these points (with the exception of 20% O\textsubscript{2}) they were lower than the weighted-average emission yields (0.25 NO\textsubscript{x}-bagasse + 0.75 NO\textsubscript{x}-coal) of the neat bagasse and neat bituminous coal. This may be considered as an indication of possible synergistic interactions. On the other hand, the NO\textsubscript{x} emission yields from the sub-bituminous/bagasse blends, also shown in Fig. 5, exhibited a rather complex trend with some points in between and others higher than the emission yields from both the neat fuel constituents of the blend, in either N\textsubscript{2} or CO\textsubscript{2} environments. It should be mentioned, that the absolute NO\textsubscript{x} emissions (ppm) from the sub-bituminous/bagasse blends (not shown here) were in-between those of from the two neat fuel constituents.

1.4.1.2. SO\textsubscript{2}: The sulfur content of the fuels had a more direct effect on SO\textsubscript{2} yields, see Fig. 4. Bituminous coal had the highest sulfur content of all four coal types (1.4%); therefore emission of SO\textsubscript{2} was by far the highest from this coal, followed by the Titus lignite (0.7%), the Beulah lignite (again, 0.7%) and the the sub-bituminous coal (0.4%). Based on the SO\textsubscript{2} yields, shown in Fig. 5, bagasse (0.07%) was a distant last. The SO\textsubscript{2} emission yields from both blends, shown in Fig. 5, fell in between those of their neat fuel constituents, in both N\textsubscript{2} and CO\textsubscript{2} environments. In most cases, they were significantly lower than the weighted-average emission yields of the neat constituent fuels (0.25 SO\textsubscript{2}-bagasse + 0.75 SO\textsubscript{2}-coal). For the bagasse-bituminous blend, SO\textsubscript{2} yields were lower by 52-77% than those from its neat coal constituent; whereas for the bagasse-sub-bituminous blend, SO\textsubscript{2} yields were lower by 74-94% than those from its neat coal in either N\textsubscript{2} or
CO₂ environments. This result showed that SO₂ emission is dependent on coal type. Once again, this may be considered as an indication of some form of synergistic behavior.

### 1.4.2. Effect of background gas on the NOₓ and SO₂ emissions

#### 1.4.2.1 NOₓ: NOₓ emissions from the different coals, compared at the same O₂ mole fraction, were lower in the CO₂ environments than in the N₂ environment. Average differences for the four coals were in the range of 19 to 43%, depending on the O₂ mole fraction. The corresponding range for bagasse and coal/bagasse blends was 22-39%.

As expected, at low oxygen mole fractions, the effect of the background gas on the NOₓ emissions from all fuels was more pronounced. For all coals, the NOₓ emissions at 20% O₂ in CO₂ were on the average 43% lower than those recorded at 20% O₂ in N₂. Such difference decreased to 19% at 80% O₂. For bagasse and coal/bagasse blends, the NOₓ emissions at 20% O₂ in CO₂ were on the average 34% lower than those recorded at 20% O₂ in N₂. Such difference decreased to 22% at 80% O₂.

#### 1.4.2.2 SO₂: SO₂ emissions from burning all fuels were largely unaffected by the substitution of CO₂ with N₂ see Figs. 4 and 5.

### 1.4.3. Effect of oxygen mole fraction on the NOₓ and SO₂ emissions

#### 1.4.3.1 NOₓ: The NOₓ emissions from coal increased with increasing oxygen partial pressure; they reached maxima in the broad neighborhood of 40-60% O₂, and they decreased thereafter, see Fig 4. This trend was consistently observed for all coals, in either N₂ or CO₂ environments, but was not observed for bagasse, see Fig. 5. Also, this trend is valid regardless of the equivalence ratio. This was confirmed with supplementary experiments where the equivalence
ratio was kept constant ($\phi_{\text{bulk}} = 0.8$), by increasing the fuel feeding rates at increasing oxygen mole fractions, in the range of 20-100%. In all cases, NO$x$ emissions at 20% oxygen mole fraction were comparable with those at 100% $O_2$, regardless of whether the $\phi_{\text{bulk}}$ or the fuel feeding rate was kept constant. Similar, although less pronounced, trends were observed in the case of the coal/bagasse blends.

1.4.3.2 $SO_2$: In the case of the bituminous coal and, to a lesser extent of its blend, the $SO_2$ emissions decreased with increasing oxygen mole fraction. In the case of the other fuels, a rather steady trend was followed with increasing oxygen mole fraction, see Figs. 4 and 5.

1.4.4. Conversion of fuel-nitrogen and sulfur to NO$x$ and SO$_2$ emissions

The calculated conversions of the fuel nitrogen and sulfur elements to NO$x$ and SO$_2$ emissions are shown in Fig. 6. Moreover, NOx emissions normalized with the fuel-N content are represented in this figure. For sulfur, this calculation was performed in the cases of both $N_2/O_2$ and $CO_2/O_2$, whereas for nitrogen this calculation was performed only in the case of $CO_2/O_2$ to exclude the contributions of the atmospheric nitrogen. The sulfur conversions are shown on the top row of Fig. 6. Based on these results, it appears that the bituminous coal realized the highest conversions of sulfur to $SO_2$ (40-100%), whereas the remaining fuels realized conversions lower than 50%. Sulfur conversions were largely independent of the background gas. For most fuels, they were not affected by the oxygen mole fraction either, with the notable exception of the bituminous coal, and to a lesser extent its blend, where decreasing trends with increasing oxygen mole fraction were observed.

The fuel-nitrogen conversions are shown on the second row of Fig. 6. Based on these results, it appears that all coals realized conversions of fuel-nitrogen to NO$x$ in the range of 20-
50%. This is in agreement with the aforementioned results of Pohl and Sarofim44 and Courtemanche and Levendis.35 Nitrogen conversions were affected by the oxygen mole fraction in a fashion similar to that seen in the NOx emission plot of Fig. 4; i.e., in most cases there has been an increase with increasing oxygen mole fraction, followed by a decrease. The third row of the Fig. 6 provides an indication of the thermal NOx contribution of the fuels in N2 environment. As the emissions are normalized with their fuel-nitrogen content, the difference between NOx emissions in different environments can be inferred from this plot.

![Graphs showing fuel-sulfur and fuel-nitrogen conversion to SO2 and NO during combustion of the four pulverized coals, pulverized sugar-cane bagasse and two blends thereof. Combustion took place in various O2/CO2 (left column) and O2/N2 (right column) environments.](image)

Figure 6. Fuel-sulfur and fuel-nitrogen conversion to SO2 and NO during combustion of the four pulverized coals, pulverized sugar-cane bagasse and two blends thereof. Combustion took place in various O2/CO2 (left column) and O2/N2 (right column) environments.
1.4.5. CO, CO\textsubscript{2} and O\textsubscript{2} in the effluent gases

A few words should be said about the CO\textsubscript{2}, CO and O\textsubscript{2} mole fractions in the effluent gases. CO\textsubscript{2} was monitored only in the presence of the N\textsubscript{2} diluent gas, since the CO\textsubscript{2} analyzer in this laboratory has a detection range limited to 0-20\%. Results showed a correlation between the carbon content of the neat fuels and their CO\textsubscript{2} emissions. The highest CO\textsubscript{2} emissions (15-18\%, depending on the O\textsubscript{2} mole fraction) were observed from the bituminous coal, which has the highest carbon content (71.9\%). The lowest CO\textsubscript{2} emissions were observed (0.6-1.4\%) from neat bagasse (after accounting for its different feeding rate), which are in line with its lower carbon content (44.3\%). The trends of CO\textsubscript{2} emissions of the four coals with increasing oxygen mole fraction showed an initially mild increase until 40\% O\textsubscript{2} and, thereafter, they remained nearly constant with further increases in O\textsubscript{2} mole fraction. This behavior was attributed to incomplete combustion of the fuels in air, as evidenced by some black carbon residue in the ashes. The explanation for this mild increase is that, in spite of the calculated fuel-lean equivalence ratios, the laminar flow nature of the drop-tube furnace impairs the mixing of coal and oxidizer gases. The highest slope of this increase was exhibited by the bituminous coal, which has the highest content of fixed carbon and the lowest content of oxygen in its structure; whilst the lowest slope was exhibited by bagasse which has the lowest amount of fixed carbon and the highest amount of oxygen in its structure, see Table 1.

CO emissions were not detected at oxygen concentrations higher than 40\% for all fuel types in either N\textsubscript{2} or CO\textsubscript{2} environments. At 20\% oxygen partial pressure, CO emissions were still low but detectable. Moreover, CO emissions in the CO\textsubscript{2} environment were higher than those in
the N\textsubscript{2} environment; perhaps by direct reactions of CO\textsubscript{2} with carbon in the char (gasification).\textsuperscript{74} CO emissions from bagasse were not-detected at any oxygen concentration.

The mole fractions of un-reacted oxygen in the combustion effluents are also shown in Fig. 4. The bituminous coal has the lowest oxygen content on a dry basis (6.9%); therefore, atmospheric oxygen consumption during combustion of this coal was expected (and seen) to be the highest, whereas that from the other three oxygen-richer coals was lower.

1.5. Discussion

1.5.1. Effect of Fuel Rank and Fuel Type on the NO\textsubscript{x} and SO\textsubscript{2} emissions

1.5.1.1 NO\textsubscript{x}: Results shown in Figs. 4 and 5 reveal that the effects of either coal rank or coal nitrogen content on NO\textsubscript{x} emissions were not discernible. Coals that have the same nitrogen contents have different NO\textsubscript{x} emissions, as in the case of the Beulah lignite and Wyodak sub-bituminous coals (both have 0.9% fuel-N). Perhaps they contain different proportions of coal moieties where nitrogen resides (i.e., pyroles vs. pyridines); however, Glarborg\textsuperscript{37} stated that for fuel-N oxidation the O/N ratio is more important than the nitrogen functionalities in the coals; and reported that as O/N increases, NO release also increases. This argument has also been supported by Hu et al.\textsuperscript{55} Herein, the Beulah lignite has an O/N ratio that is higher by \textasciitilde20\% than that of the Wyodak sub-bituminous coal. This is in-line with the fact that the average NO\textsubscript{x} emission of Beulah lignite is higher by \textasciitilde40\% than that of the Wyodak sub-bituminous coal. Furthermore, according to Spinti and Pershing\textsuperscript{46} the ash content is also an important factor in the emissions of NO\textsubscript{x}. Ash in the pore matrix prevents reduction reactions of NO\textsubscript{x}. Indeed, this is in line with the higher NO\textsubscript{x} emissions from the Beulah lignite than from the Wyodak sub-bituminous coal, since the ash content of the former coal is higher. Finally, the NOx emissions
from bagasse are the lowest than those from the other fuels tested herein since it has the lowest fuel-N content by far (0.2%).

Moreover, there are additional factors that contribute to the disparities, or similarities, in NO\textsubscript{x} emissions from the types of fuels burned herein. These factors include differences in the predominant NO\textsubscript{x} precursors and formation pathways (HCN, NH\textsubscript{3}, HNCO, tar and soot nitrogen, etc.), differences in the partition between volatile and char nitrogen, as well as in predominant mode of combustion i.e., volatile matter flame vs. heterogeneous char combustion. The fact that the characteristics of the fuels and their modes of combustion vary dramatically, as documented in Ref. Levendis et al.,\textsuperscript{75} makes the explanation of the NO\textsubscript{x} release even more complicated. Equally-complicated is the explanation of the role of bagasse in the combustion of the blends, as discussed by Dong et al.,\textsuperscript{3} Vuthaluru,\textsuperscript{76} Arias et al.\textsuperscript{77}

1.5.1.2. SO\textsubscript{2}: The sulfur emissions from the different fuel types of this work correlate with the overall sulfur content in the fuels, as mentioned in the Results section. What merits discussion, however, is the fact that both the fuel sulfur emissions (Fig. 4) and the conversion of the fuel sulfur to SO\textsubscript{2} (Fig. 6) were much higher in the case of the bituminous coal, and to a lesser extent its blend, than in the cases of all other fuels. One explanation offered for this behavior is the fact that the bituminous coal has the lowest (by far) Ca/S ratio, see Table 1. Hence, retaining of significant amounts of sulfur in the ash,\textsuperscript{69,78} as calcium sulfate (CaO+SO\textsubscript{2}+1/2O\textsubscript{2} → CaSO\textsubscript{4}), would not be an effective mechanism for this fuel that has sub-stoichiometric Ca/S ratio. To the contrary, this may be an effective mechanism for the other fuels of this study that have super-stoichiometric Ca/S ratios. In fact, the SO\textsubscript{2} emissions from all the fuels of this work (shown in Fig. 4) correlate well (both in ordering and in magnitude) with the S/Ca mass ratios of the fuels,
derived from the data of Table 1. Moreover, the empirical equation of Raask\textsuperscript{71} predicts that 9% of the sulfur may be retained in the ashes of the bituminous coal, 80% in the ashes of the Texas lignite, and that the entire fuel-S may be retained in the ashes of the remaining two coals. To experimentally investigate the above, the ashes of two of the coals were analyzed by Electron Microprobe Analysis (EMA), and results were tabulated in Table 2.

Table 2. Fuel-S accounting for two of the coals in this study

<table>
<thead>
<tr>
<th>Combustion condition</th>
<th>Pittsburgh Bituminous Coal (Ca/S = 0.2)</th>
<th>Beulah Lignite Coal (Ca/S = 2.73)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20% O\textsubscript{2}-80%CO\textsubscript{2}</td>
<td>40% O\textsubscript{2}-60%CO\textsubscript{2}</td>
</tr>
<tr>
<td>S% in ash</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>S% in SO\textsubscript{2}</td>
<td>96</td>
<td>70</td>
</tr>
<tr>
<td>S% unaccounted for</td>
<td>0</td>
<td>23</td>
</tr>
</tbody>
</table>

In agreement with the above arguments, the results indicate that the majority of the sulfur in the fuel appears as SO\textsubscript{2} in the case of the bituminous coal, whereas it is retained in the ash in the case of the lignite coal. Considerable amounts of sulfur remained unaccounted for in this limited analysis, and it is possible that sulfur was converted to SO\textsubscript{3} or was absorbed by furnace alumina components. The reader should be cautioned that the particular furnace gas temperature (which is slightly lower than 1400 K) and the gas residence time (2 s herein) are very important parameters\textsuperscript{79} and may have favored the calcination reaction and the thermodynamic stability of the sulfate product. Finally, the release of fuel sulfur to the gas phase may have been also influenced by the distributions of pyritic and organic sulfur in these coals, both listed in Table 1, as discussed by Zaugg, et al.\textsuperscript{69} However, no clear trend could be obtained with these parameters.
1.5.2. Effect of background gas on the NO\textsubscript{x} and SO\textsubscript{2} emissions

1.5.2.1. NO\textsubscript{x}: As mentioned before, total NO\textsubscript{x} emissions from the different coals, compared at the same O\textsubscript{2} mole fraction, were lower by 19-43% in CO\textsubscript{2} than in N\textsubscript{2}. Part of this difference may be attributed to the contributions of atmospheric nitrogen (“thermal”-NO\textsubscript{x}, formed by the Zeldovich mechanism\textsuperscript{80}). In fact, Courtemanche and Levendis\textsuperscript{35} reported that for the combustion of this specific bituminous coal in air, the atmospheric nitrogen contributes 20-25% of the total NO\textsubscript{x}. To derive that value, results of experiments conducted in air were compared to those conducted in an argon-oxygen gas of equal specific heats. By contrasting the 20% O\textsubscript{2} cases herein in either N\textsubscript{2} or CO\textsubscript{2}, the difference in total NO\textsubscript{x} emissions from the bituminous coal is much higher; it is nearly 50%, see Fig. 4. In these two cases, however, neither the volumetric specific heats of the gas are equal (they actually differ by \textasciitilde 59%), nor the combustion behaviors, as work in progress in this laboratory shows. Moreover, this discrepancy may be a consequence of ambient CO concentration during combustion. According to Liu et al.,\textsuperscript{27} initial CO formation is higher in CO\textsubscript{2} than in N\textsubscript{2} background gases at the same oxygen mole fraction. This was confirmed herein at the 20% O\textsubscript{2} case. As CO favors the reduction of NO\textsubscript{x},\textsuperscript{27,37} lower NO\textsubscript{x} yields were observed in CO\textsubscript{2} than in N\textsubscript{2} background gases.

It should be clarified here, that the aforementioned average NO\textsubscript{x} reduction range of 19-43% obtained when the N\textsubscript{2} background gas is replaced by CO\textsubscript{2} was obtained by comparing reductions at the same O\textsubscript{2} partial pressures. However, when a comparison is made between combustion in air and combustion at different O\textsubscript{2}/CO\textsubscript{2} combinations, NO\textsubscript{x} reductions (averaged among all four coals) were calculated to be in the range of 9-43%. However, as NO\textsubscript{x} reductions during re-burning of coal have been reported to be as high as 65%,\textsuperscript{20, 22} the difference may be
attributed to the mechanism of “reburning” of NO\textsubscript{x}, since actual flue gas recirculation (FGR) was present therein, i.e., a gas containing CO\textsubscript{2}, NO\textsubscript{x}, etc. To the contrary, herein FGR was simulated by introducing neat CO\textsubscript{2} to the furnace, i.e., without any NO\textsubscript{x} content. This merits further investigation.

1.5.2.2. SO\textsubscript{2}: As mentioned before, there were no discernible effects of the background gas on SO\textsubscript{2} emissions.

1.5.3. Effect of oxygen mole fraction on the NO\textsubscript{x} and SO\textsubscript{2} emissions

1.5.3.1 NO\textsubscript{x}: An important observation herein concerns the trend of NO\textsubscript{x} emissions with oxygen mole fraction, which exhibited a peak in the 40-60\% O\textsubscript{2} range. This behavior has also been reported by Hu et al.,\textsuperscript{55} who noticed peak NO\textsubscript{x} emissions around 50\% O\textsubscript{2}. It should be mentioned here that current work in this laboratory shows that the combustion behavior of the fuel particles varies as the oxygen mole fraction increases, and as the N\textsubscript{2} background gas is replaced by CO\textsubscript{2}. Hence, several compounded, and often competing, factors may be the cause of this peculiar trend, including the following four: (a) Changes in the amine radical pool chemical kinetics, as the volatile flames get hotter at increasing oxygen mole fractions. (b) Changes in the effectiveness of the oxygen transport and diffusion phenomena at the burning char surfaces, (c) NO\textsubscript{x} reduction reactions with carbon on char surfaces, (d) NO\textsubscript{x} reduction reactions with carbon monoxide in the pores of chars.

Glarborg\textsuperscript{37} stated that different nitrogen species may evolve from unlike coal/biomass types burning under diverse conditions, however, all these species feed to an amine radical pool (see Fig. 8 of Ref.\textsuperscript{37}). Subsequent reactions of NH and N depend only on the flame conditions (stoichiometry, temperature, total fixed nitrogen level, etc.). In the experiments herein, envelope
flame temperatures increased with increasing oxygen partial pressure, as documented in ongoing pyrometric studies (see also Bejarano and Levendis, 81 Fig. 5). This temperature rise is expected to have enhanced the generation of NO from the amine radical pool, as exemplified with modeling predictions described in Fig. 9 of Ref. [37]. Indeed, as shown in Fig. 4; NO \(_x\) increased as the oxygen mole fraction increased from 20\% to 40-50\%. The fact that this trend did not continue with further increases of O\(_2\) and, thus temperature, indicates that other factors dominated at higher oxygen mole fractions. High-resolution high-speed cinematographic observations showed that in the case of the bituminous coal, combustion in air took place in two distinct phases: volatile matter burning in detached flames, followed by heterogeneous char oxidation. 75 However as the oxygen concentration increased beyond 40-50\%, the flames retracted to the particle surfaces and, in many cases (particles), only one combustion phase was observed, i.e., volatiles and char burned simultaneously. This complete change in combustion mode may have imposed severe oxygen diffusion limitations to the char surface (over the entire particle burn-time), as the burning volatiles therein minimized the oxygen penetration in the pores, and thereby reduced the contributions of the char-N to the total fuel-NO formation. As mentioned in the Introduction, the char-N contributions are very important during combustion in air, perhaps more important than those of volatile nitrogen. 44, 51 Thus, the hypothesized minimization of the char-N contributions to the NO formation mechanism, at high O\(_2\) mole fractions, can have significant consequences to the total amounts of NO released.

Moreover, as the char temperature increases with increasing O\(_2\) mole fraction (see Fig. 4 of Ref. [81]) the atmospheric oxygen diffusion in the char pore network becomes progressively more restricted. Then as reported before 37, 55 at high temperatures the char+O\(_2\) reaction becomes diffusion limited. Further increases in temperature promote mainly the char+NO reaction and/or,
according to Thomas,\textsuperscript{62} the CO+NO reaction in the pores. These reactions reduce the emissions of NO\textsubscript{x}. The latter reaction is expected to be more dominant in the case of the high-oxygen content low-rank coals and of the biomass.

1.5.3.2. \textit{SO}_2: The increasing deficit in the sulfur balance with increasing oxygen partial pressure may be due to the reactions involved in the Lead Chamber process\textsuperscript{82} in which sulfuric acid production is controlled by the combination of the following reactions:

\begin{align*}
2 \text{NO} + \text{O}_2 &= 2 \text{NO}_2 \\
\text{SO}_2 + \text{NO}_2 &= \text{SO}_3 
\end{align*}

The amount of NO\textsubscript{2} increases with O\textsubscript{2} concentration which would lead to larger amounts of SO\textsubscript{3} which would dissolve in the ice-bath. A recent study has also shown that the sampling of combustion products containing SO\textsubscript{2} resulted in oxidation reactions involving SO\textsubscript{2} in solution.\textsuperscript{83} Although plausible further research is needed to show that these reactions are responsible for the deficiency in the sulfur balance in this study.

\textbf{1.6. Conclusions}

This study burned five pulverized solid fuels in a laboratory drop-tube furnace (a bituminous, a sub-bittuminous and two lignite coals, as well as sugar-cane bagasse and its blends with two of the coals). Combustion took place under fuel-lean conditions in various O\textsubscript{2}/N\textsubscript{2} and O\textsubscript{2}/CO\textsubscript{2} environments. Emissions of hazardous gases were monitored with on-line analyzers. Results showed that:

- NO\textsubscript{x} emissions in O\textsubscript{2}/CO\textsubscript{2} environments were lower by 19-43\% than those in O\textsubscript{2}/N\textsubscript{2} environments, at the same O\textsubscript{2} mole fractions (22-39\% for bagasse and blends). However,
when combustion in air was compared to combustion at different O\textsubscript{2}/CO\textsubscript{2} combinations, NO\textsubscript{x} reductions (averaged among all four coals) were calculated to be in the range of 9-43% (9-33% for bagasse and blends).

- NO\textsubscript{x} emissions increased with increasing oxygen mole fraction until \(~50\%\) O\textsubscript{2} was reached; thereafter, they monotonically decreased with increasing O\textsubscript{2}. At 100\% O\textsubscript{2}, NO\textsubscript{x} emissions became comparable to those in air. This trend was observed regardless whether the fuel mass flow rate or the equivalence ratio was kept constant.

- NO\textsubscript{x} emissions from the various fuels burned did not clearly reflect their nitrogen content (0.2-1.4%), except when large differences were present.

- Conversion of the fuel-nitrogen to NO\textsubscript{x} was in the range of 20-50\% in all cases.

- SO\textsubscript{2} emissions remained largely unaffected by the replacement of the N\textsubscript{2} diluent gas with CO\textsubscript{2}. Only in the case of the bituminous coal, the SO\textsubscript{2} emissions depended on the O\textsubscript{2} mole fraction.

- The SO\textsubscript{2} emissions were found to be dependent on the sulfur and calcium contents of the fuels.

- Conversion of the sulfur in the fuel to SO\textsubscript{2} spanned the entire possible range, from a few percent to 100\% in the cases examined herein.

- The CO emissions of the fuels were negligible in all cases, except in 20\% O\textsubscript{2}, where they were measurable; they were higher in the CO\textsubscript{2} environment than in the N\textsubscript{2} environment.
Acknowledgements
The authors acknowledge financial assistance from the NSF award CBET-0755431. One of the authors (P M-C) is thankful to CAPES Foundation of the Ministry of Education of Brazil for a scholarship to join Northeastern University for a period of six months. The authors would like to thank Prof. Adel F. Sarofim for commenting on this manuscript.

1.7. References
1. EPA-Environmental Protection Agency- Available at [http://www.epa.gov/air/urbanair](http://www.epa.gov/air/urbanair), accessed on 14 March 2011.


77. Arias B.; Pevida C.; Rubiera F.; and Pis J.J. *Fuel* **2008**, 87(12), 2753-2759.


CHAPTER 2


Feyza Kazanc and Yiannis A. Levendis

Mechanical and Industrial Engineering, Northeastern University, Boston, MA 02115, USA
2. Physical Properties of Particulate Matter Emitted from Combustion of Coals of Various Ranks in $O_2/N_2$ and $O_2/CO_2$ Environments.

Abstract

This work examined the particulate emissions from pulverized coals burning under either conventional or oxy-fuel combustion conditions. Oxy-fuel combustion is a process that takes place in $O_2/CO_2$ 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 containing various mole fractions of oxygen in either nitrogen or carbon-dioxide background gases. A bituminous, a sub-bituminous and a lignite coal were burned at a DTF temperature of 1400 K. Tri-modal ash particle size distributions were observed with peaks in the sub-micron region (around 0.2 µm), as well as in the super-micron region (around 5 µm and >10 µm). Both submicron and super-micron particulate emission yields of all three coals were typically lower in $O_2/CO_2$ than in $O_2/N_2$ environments. Emission yields typically increased with increasing oxygen concentration in the furnace, with an exception noted at moderate oxygen mole fractions (20-30%) in $CO_2$, where significant amounts of unburned carbon were detected. Submicron particulate yields were found to be comparable in the effluents of all three coals, independently of their ash contents, whereas super-micron particulate yields were nearly analogous to the ash contents of the three coals. Scanning Electron Microscopy (SEM) revealed that submicron particles were spherical, whereas super-micron particles were often of irregular shapes, fractured spheres, and spheres with small particles attached to their surface.
2.1. Introduction

Coal is currently used to generate 40% of the electricity in the world\textsuperscript{1}. Coal is expected to remain an important source of electricity in the foreseeable future and its global consumption is projected to increase\textsuperscript{2}. 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 2009\textsuperscript{3}). However, since CO\textsubscript{2} 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 CO\textsubscript{2}. 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-CO\textsubscript{2}-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 CO\textsubscript{2}); hence, combustion of the coal takes place in O\textsubscript{2}/CO\textsubscript{2} atmospheres.

Details of oxy-fuel combustion of coal have been given in recent reviews, by Buhre et al.\textsuperscript{4}, Croiset et al.\textsuperscript{5}, Toftegaard et al.\textsuperscript{6}, Wall\textsuperscript{7}, Chen et al.\textsuperscript{8}, and Zheng\textsuperscript{9}. 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\textsubscript{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.

Whereas the emissions of nitrogen and sulfur oxides from oxy-coal combustion have been studied extensively\textsuperscript{10-15} and have been well-documented, reports on particulate emissions are only recently emerging.

Whereas it is rather evident that in the case of conventional power plants the fate of the ash particles, upon their release in the atmosphere, constitute an air pollution issue (especially the most problematic health-hazardous submicron sized particles\textsuperscript{16}), it would be legitimate to question why one would be concerned with the emissions from oxy-fuel combustion. After all, the flue gases of oxy-fuel combustion plants are supposed to be treated and sequestered. This issue has been credibly addressed by Tan and Croiset\textsuperscript{17}. They argued that the design of the product recovery train of an oxy-combustion plant is still at an early stage, as it is not yet known how impurities in the flue gas stream will impact its performance. It might be necessary to remove all of the impurities for the product recovery train to perform optimally. This argument is also true for the flue gas recirculation (FGR) tray, as well as for the effects of re-circulated impurities in the boiler. Tan and Croiset\textsuperscript{17} also argued that it is very possible for an oxy-fuel power plant to emit the flue gas directly to the atmosphere during high peak hours by temporarily shutting down the product recovery train to increase power output to the grid, thus making it necessary to maintain low emission levels of various pollutants. Therefore, this study aims at contrasting the physical aspects (yields, size distribution and morphology) of 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, various $O_2/CO_2$ and $O_2/N_2$ environments were examined in the
broad range of 20%<O_2<60%. The chemical aspects (composition) of the collected particulates will be the subject of a future publication.

2.2. Literature Review

There is a fairly large amount of research reported in the literature on the particulate emissions of coal in air and in other O_2/N_2 environments, whereas a few recent reports have emerged on particulate emissions under oxy-combustion conditions (O_2/CO_2 environments).

2.2.1. Particulate emissions from combustion of coal in air or in other O_2/N_2 environments

Particulate matter from conventional pulverized coal combustion has been the subject of extensive research over the years; which especially focused on ash of submicron size (PM_1). Such fine particle emissions are nearly impossible to capture with conventional particulate control devices (electrostatic precipitators, barrier filter, baghouses, etc.)^{18, 19}, and because of their small sizes and toxic-metal-enriched compositions, they have been classified as health-hazardous. They also participate in atmospheric reactions and are agents of visibility reduction^{18, 20}. Previous work has been reported on partition of the emissions of submicron and super-micron ash particulates from the combustion of coals of various ranks^{4, 21-25}. Submicron ash yields (PM_1) were reported to range between 0.1 and 9.6% of the total ash yields (as derived by the ASTM method) when coals were burned in atmospheres containing 20% O_2, with the balance being either N_2 or He. This range was also represented as 1-7 mg/g_coal burned in a study by Quann and co-workers^{23}. It has been reported elsewhere that particulate emissions in the 1-5 µm range (which has often been referred to as fine fragment mode) account for 10% -20% of the total ash yields, and that their formation is unaffected by the combustion conditions^{26, 27}. 
There has been agreement on the effects of oxygen mole fraction on both the submicron and super-micron ash yield. Increasing the oxygen mole fraction from 20% to 50% increased the yield of PM\textsubscript{1} ashes by factors ranging from 2-5\textsuperscript{22, 28}. Similarly, increasing the oxygen mole fraction from 21% to 50% increased the yields of PM\textsubscript{2.5} and PM\textsubscript{10} by factors of 2 and 3 respectively\textsuperscript{28}. These increases have been attributed to the increase of the combustion temperature\textsuperscript{22, 28} at higher oxygen mole fractions.

Through the combustion of various types of coals, the effect of coal rank on submicron ash yield was also investigated\textsuperscript{21-23, 29}; however, there has been some disagreement in the literature. McElroy et al.\textsuperscript{21} stated that coal rank has a very low impact on the submicron fraction of the generated ash, whereas Quann et al.\textsuperscript{23} reported higher submicron ash yields from burning lower rank coals, excluding Texas lignite. Quann et al.\textsuperscript{23} concluded that the mineral content of a coal and its distribution throughout the matrix were more important factors than ranking in the partition of the submicron ash yield. This phenomenon was also supported by Buhre et al.\textsuperscript{4} who burned only bituminous coals and observed that submicron emission yields were analogous to their sulphur contents.

Modality is an important parameter in assessing the particle formation mechanism. A mode is referred to as a peak in the particle size distribution, represented on a lognormal scale. It represents a group of particles that were formed by similar formation mechanisms. According to previous studies, ash particles distribute bi-modally in air-firing conditions\textsuperscript{21, 22, 24} with a coarse mode between 1-20 µm and a submicron mode between 0.07 to 0.15 µm\textsuperscript{21, 30-32}. The submicron mode has been attributed to vaporization of minerals followed by condensation and particle growth\textsuperscript{33-36}. Recent studies suggested that ash particles are actually distributed multi-modally\textsuperscript{30, 31}.
These studies reported three distinct particle modes, with an ultrafine mode corresponding to particles lower than 0.3 µm, a fine fragment mode (FFM) with particles between 0.5-5 µm, and a coarse mode with particles larger than 5 µm.

The morphology of the particles from burning of coal in various O_2/N_2 environments has also been investigated. It has been reported that the submicron and coarse particles are typically spherical in shape and have smooth surfaces however; FFM particles show complex morphology with higher surface-to-volume ratios than the coarse particles. Fix et al. categorized the FFM particles with respect to their morphologies namely; coarse (or bulk), multi-sphere, split-open, fragments, agglomerates, etc.

### 2.2.2. Particulate emissions from combustion of coal in O_2/CO_2 environments

Ash particulate emission yields from combustion of coal in O_2/CO_2 environments have not been well established yet. There are only a few studies published in the literature on ash formation in oxy-fuel combustion, while a new study is currently underway. Suriyawong et al. burned a sub-bituminous coal in air as well as in O_2/CO_2 environments, with O_2 mole fractions varying between 20-50%. They reported that when N_2 was replaced with CO_2 (with the O_2 mole fraction set to 20%) the collected mass of submicron ash decreased by 43% while the number concentration decreased by 40%. Correspondingly, the geometric mean size of the submicron particles decreased, by approximately 28%. Furthermore, they also reported that when the oxygen mole fraction in the O_2/CO_2 mixture increased from 20% to 50%, both the geometric mean particulate size and the number concentration of the submicron mode (PM_1) increased by a factor of 1.9 and 2.4, respectively due to faster mineral vaporization rates resulting from higher coal particle temperatures.
Sheng et al.\textsuperscript{49} burned a low-rank coal in air (simulated by 20\% O\textsubscript{2} in N\textsubscript{2}) and in O\textsubscript{2}/CO\textsubscript{2} environments, with O\textsubscript{2} mole fractions varying from 20-40\%. They reported that when N\textsubscript{2} was replaced with CO\textsubscript{2} (with the O\textsubscript{2} mole fraction set at 20\%), the submicron (PM\textsubscript{1}) ash yield decreased by 32\% and the PM\textsubscript{2.5} yield decreased by 24\%. However, when the O\textsubscript{2} mole fraction was increased to 40\% in CO\textsubscript{2} background gas, the PM\textsubscript{1} ash yield increased by a factor of 1.64 compared to the air case, whereas the corresponding increase in the PM\textsubscript{2.5} yield was by a factor of 3.4. Moreover, they observed that increasing the oxygen mole fraction from 20\% to 40\% within O\textsubscript{2}/CO\textsubscript{2} environments resulted in an increase of both PM\textsubscript{1} and PM\textsubscript{2.5} yields by factors of 2.5 and 4.5, respectively. In a follow-up study, Sheng et al.\textsuperscript{48} burned three different coals in the same 20-40\%O\textsubscript{2}/CO\textsubscript{2} environments as in their previous work as well in 20-40\%O\textsubscript{2}/N\textsubscript{2} to observe the effect of the background gas. They reported that increasing O\textsubscript{2} from 20\% to 40\% in N\textsubscript{2} did not affect the geometric particle mean size, whereas a commensurate increase of O\textsubscript{2} in CO\textsubscript{2} increased it by a factor of 2.9. Tri-modal PSDs were observed under all conditions, however, the geometric mean size of the submicron particles decreased, by approximately 50\% by replacing the background N\textsubscript{2} with CO\textsubscript{2} at the same 20\% O\textsubscript{2} mole fraction\textsuperscript{48,49}. To the contrary, Yu et al.\textsuperscript{51} reported that combustion of two bituminous coals and one sub-bituminous coal in either air or in oxy-firing conditions (27\% O\textsubscript{2}-73\%CO\textsubscript{2} and 32\%O\textsubscript{2}-68\%CO\textsubscript{2}) resulted in no significant differences in the PSDs for particles below 10 \textmu m; however, the PSDs varied with the coal type.

In addition to the aforementioned experimental studies, Krishnamoorthy and Veranth\textsuperscript{46} constructed a computational model to assess the average P\textsubscript{CO}/P\textsubscript{CO\textsubscript{2}} ratio inside single char particles during pulverized coal combustion. They predicted that, with all other parameters kept equal, increasing the CO\textsubscript{2} in the bulk gas reduces the vaporization of major ash components.
Sheng et al.\textsuperscript{49} conducted SEM analysis of the morphology of the particles with diameters in the neighborhoods of 0.1 and 4 µm, which are representative of the submicron mode and the fine fragment mode, respectively. They reported that most of the submicron ash particles from combustion of coals in air were of spherical shape, whereas a small amount of aggregate-like particles were present in the effluents of 20%O\textsubscript{2}/CO\textsubscript{2} combustion, indicating a lower combustion temperature in the latter case. However, when the oxygen mole fraction was increased from 20% to 40% in CO\textsubscript{2}, the submicron particles were observed to be spherical. The particles of the fine fragment mode were spherical, near-spherical, and irregularly-shaped in the effluents of both air and 20%O\textsubscript{2}/CO\textsubscript{2} combustion. The latter mode of combustion generated a larger number of irregularly-shaped particles. The authors argued that irregularly-shaped particles were formed by char fragmentation during combustion.\textsuperscript{49}

The findings of the aforementioned studies\textsuperscript{48-50} may be summarized as follows. At 20% O\textsubscript{2}, upon replacing the background N\textsubscript{2} with CO\textsubscript{2}, the submicron ash yield was found to decrease by 40%, and the geometric mean size of the submicron particles to decrease by 40%. Increasing the O\textsubscript{2} to 40% in CO\textsubscript{2}, increased the submicron yield by a factor of 2.5 and the geometric mean size of the submicron particles by a similar factor. Comparing the 40%O\textsubscript{2} in CO\textsubscript{2} case with the 20%O\textsubscript{2} in N\textsubscript{2} case (approx. air) it was reported that the submicron ash yield increased by 64%. However, Yu et al.\textsuperscript{51} did not observe any significant changes in PM\textsubscript{10} size distributions by switching the combustion environment from air to oxy-firing.

Since the effects of oxy-fuel combustion on particulate emission yields have not been completely documented, additional investigations on the emissions of both submicron and super-micron ash particles are warranted. In this study, three coals from different ranks were burned
under various O$_2$/CO$_2$ and O$_2$/N$_2$ environments and resulting particulate mass emission yields, mass PSDs, and detailed SEM and TEM analysis for the morphology of both submicron and super-micron particles are presented. Inferences to relevant observations on the combustion behavior of the same three coals in this laboratory have been made.

### 2.3 Experimental Set-up

Coals from three different ranks, bituminous (PSOC-1451), sub-bituminous (DECS-26), and lignite (PSOC-1443), were burned in this study. Their chemical compositions and properties are listed in Table 1. Samples for the three coals were obtained from the Penn State Coal Bank, and were ground and sieved. The size cut of 53-90 µm was used herein.

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.
### Table 1. Chemical Composition of the Coals

<table>
<thead>
<tr>
<th></th>
<th>PSOC-1451</th>
<th>DECS-26</th>
<th>PSOC-1443</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rank and Fuel Source</td>
<td>Bituminous High Volatile A Pittsburgh #8 Pennsylvania</td>
<td>Sub-Bituminous B River Basin Wyodak, Wyoming</td>
<td>Lignite A Titus, Texas</td>
</tr>
<tr>
<td>Proximate Analysis</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>as received, and (upon re-evaluating moisture)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moisture (%)</td>
<td>2.5</td>
<td>26.3 (13.1)</td>
<td>28.5 (18.6)</td>
</tr>
<tr>
<td>Volatile matter (%)</td>
<td>33.6</td>
<td>33.1 (39.0)</td>
<td>44.2 (50.3)</td>
</tr>
<tr>
<td>Fixed Carbon (%)</td>
<td>50.6</td>
<td>35.1 (41.4)</td>
<td>12.0 (13.7)</td>
</tr>
<tr>
<td>Ash (%)</td>
<td>13.3</td>
<td>5.6 (6.5)</td>
<td>15.3 (17.4)</td>
</tr>
<tr>
<td>Ultimate Analysis</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(on a dry basis)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon (%)</td>
<td>71.9</td>
<td>69.8</td>
<td>56.8</td>
</tr>
<tr>
<td>Hydrogen (%)</td>
<td>4.7</td>
<td>5.7</td>
<td>4.1</td>
</tr>
<tr>
<td>Oxygen (%) (by diff.)</td>
<td>6.9</td>
<td>15.6</td>
<td>15.8</td>
</tr>
<tr>
<td>Nitrogen (%)</td>
<td>1.4</td>
<td>0.9</td>
<td>1.1</td>
</tr>
<tr>
<td>Sulfur (total) (%)</td>
<td>1.4</td>
<td>0.4</td>
<td>0.7</td>
</tr>
<tr>
<td>Sulfur (pyritic) (%)</td>
<td>0.82</td>
<td>0.07</td>
<td>0.09</td>
</tr>
<tr>
<td>Sulfur (organic) (%)</td>
<td>0.53</td>
<td>0.35</td>
<td>0.64</td>
</tr>
<tr>
<td>Sodium (%)</td>
<td>0.06</td>
<td>0.09</td>
<td>0.04</td>
</tr>
<tr>
<td>Calcium (%)</td>
<td>0.28</td>
<td>1.1</td>
<td>1.4</td>
</tr>
<tr>
<td>Ash (%)</td>
<td>13.7</td>
<td>7.6</td>
<td>21.4</td>
</tr>
<tr>
<td>Heating Value Dry Fuel (MJ/kg)</td>
<td>31.5</td>
<td>28.2</td>
<td>23.0</td>
</tr>
</tbody>
</table>

For the three coals and their proximate and ultimate analysis data was obtained from the Penn State Coal Sample Bank; upon opening the sealed containers of the supplied coal samples, variations of moisture content with storage in the laboratory were observed for all, but the bituminous, coals. The measured moisture content values are listed (in parentheses) and the remaining proximate analysis values were re-calculated and are also shown (in parentheses).
Figure 1. Cross section view of the experimental set-up consisting of electrically-heated laminar-flow drop-tube furnace coupled with the 13-stage Nano-Moudi ash particle impactor, and close up views of the impactor stages, dilution N$_2$ probe and particle injector.

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. At this particle feeding rate the particle number density in the furnace is so low, at <20 particles/cm³, that each particle is surrounded by sufficient oxygen to burn independently of the others in the cloud. Another indicator of this effect is that \( \frac{[dm/dt]_{\text{gas}}}{[dm/dt]_{\text{coal}}} > 100 \), which reaffirms combustion in dilute clouds. The corresponding bulk fuel/oxygen equivalence ratios were calculated to be in the range of 0.01-0.09, depending on the oxygen mole fraction. Combustion of the coals 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. Sampling of the exhaust gases was conducted in the manner of Quann and Sarofim and Neville et al. as well as Buhre et al. and Gao and Wu. 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. The probe consisted of three coaxial layers. The outer two layers channeled cooling water along the entire length of the probe for maximum cooling effect. The inner layer consisted of porous stainless steel tubing (sintered metal). Within the probe nitrogen gas was transpired inwards through the porous wall to prevent the surface deposition of particles, see Fig. 1. This arrangement allowed the furnace effluent to be thermally quenched, chemically inerted, and diluted in order to minimize further gas-phase and condensed-phase reactions. This inert gas was also used as make-up flow, which is needed for proper operation of the Nano-Moudi cascade impactor. A
pressure gage port was inserted to the cooling probe to monitor the inlet pressure of the impactor. The inlet pressure was kept as close to 0 atm gage in all experiments, as recommended by the manufacturer of the impactor (*Applied Physics*). To maintain this pressure, approx. 3.7 lpm of make-up inert nitrogen flow was supplied, resulting in a gas dilution factor of 1.9. This value is in line with those used by Quann and Sarofim\(^3\) (3) and Gao and Wu\(^5\) (1.5) as well as those recommended by Boman et al.\(^5\) (3-4). Further dilution, e.g., by using a separate chamber (tunnel) and then channeling a slipstream thereof to the impactor, was not used since it has its own issues. The design parameters and operating conditions of such devices (such as dilution ratio, temperature and residence time) affect the total particle size distributions and the total particle number concentrations, as studies by Lipsky et al.\(^5\) and Gao and Wu\(^5\) have shown. Although the effects of sampling methods (specifically of the dilution ratio) on particulate matter (PM) properties have been studied there is significant discrepancy in the conclusions drawn; as a result, there is no standard method for PM sampling\(^5\). Moreover, further dilution while desirable for proper simulation of atmospheric release of combustion-generated particulates may perhaps be of less interest in practical applications of oxy-combustion work where it is expected that ash particles will be channeled from the boiler to the product recovery and the flue gas recirculation ducts of a power plant, as mentioned in the Introduction Section.

Particles were collected upon impaction plates, loaded with aluminum substrates, as they traveled through the impactor stages. The particles collected on the impactor stages can be categorized as follows: a) PM\(_{1}\) or submicron (stages 6-13), b) PM\(_{1.5}\) (stages 3-5), c) PM\(_{2.5}\) (stages 4-13), d) PM\(_{10}\) (stages 2-13), and e) PM\(_{18}\) (stages 1-13). The nominal particle size cuts collected on the stages of the impactor herein, see Table 2, were verified by conducting SEM observations. Sample results are tabulated in Table 3, and photographic displays are shown in Fig. 5. These
sample results substantiate the accuracy of the impactor measurements. The summation of the particles collected on all 13 stages in addition to the impactor inlet stage represent the total ash formed during combustion. The ash particles formed small heaps, as they accumulated upon the substrates as shown in Figure 3 (presented later in this paper). 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 inlet stage, which contained particles larger than 18 µm, was not taken into account for both the size distribution and the mass emission yields. Afterwards, each substrate was stored in a petri-slide plastic container for further analysis. Samples were prepared out of the stored aluminum substrates to observe the morphology of the particles with a Scanning Electron Microscope (SEM). During the preparation process, samples were carbon-coated to prevent charging.

Table 2. Nominal cut size of the stages in Nano Nano-Moudi ash impactor. Cut-off sizes were supplied by the instrument manufacturer (AP) based on the density of ammonium sulfate particles, whose density is 1.77 g/cm³. The density of ash particles varies and is not necessarily equal to this value.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Inlet</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>Filter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal Cut Size (nm)</td>
<td>18,000</td>
<td>10,000</td>
<td>5,600</td>
<td>3,200</td>
<td>1,800</td>
<td>1,000</td>
<td>560</td>
<td>320</td>
<td>180</td>
<td>100</td>
<td>56</td>
<td>32</td>
<td>18</td>
<td>10</td>
<td>0</td>
</tr>
</tbody>
</table>

Tests were conducted with oxidant gases consisting of either O₂/N₂ or O₂/CO₂ mixtures. Four oxygen mole fractions were implemented (20%, 30%, 40%, and 60%). The 30% and 40% oxygen mole fractions in CO₂ background gas were chosen to represent a plausible range of oxy-coal combustion conditions. 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 Sarofim. The amount of pulverized fuel fed during each
experiment was calculated by measuring the weights of the powder contained in the vial at the beginning and at the end of each run. 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.

Table 3. Comparison between nominal cut size and average measured ash particle sizes on three stages of the impactor. The measurements were performed on SEM images using Adobe Photoshop CS5 software.

<table>
<thead>
<tr>
<th>Impactor stage</th>
<th>Nominal particle cut size (nm)</th>
<th>Average particle size (based on SEM images) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Bituminous coal</td>
</tr>
<tr>
<td>5</td>
<td>1000-1800</td>
<td>978</td>
</tr>
<tr>
<td>9</td>
<td>100-180</td>
<td>91</td>
</tr>
<tr>
<td>11</td>
<td>32-56</td>
<td>44</td>
</tr>
</tbody>
</table>

2.4. Results

2.4.1. Ash yield partition into different modes

Emission yields of ashes from combustion of three coal ranks (bituminous, sub-bituminous, and lignite) in oxygen mole fractions up to 60% in N$_2$ and CO$_2$ background gases are shown in Fig. 2. The yields were categorized in five different groups; PM$_1$ (submicron), PM$_{2.5}$, PM$_{1.5}$ (fine fragment mode), PM$_{10}$, and PM$_{18}$ in order to investigate the effects of background gases (N$_2$ or CO$_2$) as well as of oxygen mole fractions on particulate generation.

The first row shows that the submicron ash yields (stages 6-13) were consistently lower under oxy-combustion (O$_2$/CO$_2$) conditions. An exception to this trend were the ash yields in the 30% O$_2$ - 70% CO$_2$ environments, marked by hollow red symbols in Figure 2, where substantial amounts of unburned carbon were evident (see Figure 3). In comparison to air, this condition
induced lengthy ignition delay times, suppressed the formation of volatile envelope flames and resulted in lower char temperatures\(^6\!), under the conditions of these laminar flow DTF experiments. It should be noted here that if particulate yields are corrected for their carbon contents, which were obtained using SEM-EDS analysis for Stage 9 particles and are displayed in Table 4, then the PM\(_1\) yields at 30% O\(_2\) - 70% CO\(_2\) would be lower than those in air. Stage 9 (56-100 nm) was selected to represent the submicron ash particles for the carbon content analysis tabulated in Table 4, as ash accumulations therein were plentiful. Stage 6 (560-1000 nm) ash accumulations, which were even more plentiful, were also chemically analyzed with SEM/EDS and the results were in line with those of Stage 9. The average submicron yield in N\(_2\) environments (over all O\(_2\) partial pressures) was nearly 4 mg/g\(_{\text{coal}}\) for all three coals and this value dropped to nearly 2.4 mg/g\(_{\text{coal}}\) in CO\(_2\) environments. Moreover, in both environments, ash yields generally increased with increasing oxygen mole fraction, again with the exception of 30% O\(_2\) - 70% CO\(_2\) case. Increasing the oxygen mole fraction in either N\(_2\) or CO\(_2\) increased the submicron ash yield by a factor of 2, based on the average submicron ash yields of all three coals. The bituminous coal exhibited the least amount of increase with increasing O\(_2\), whereas the lignite coal exhibited the most. There was no clear evidence that submicron ash yields were related to the coal rank; combustion of all coals generated PM\(_1\) yields in a comparable range.

The third row of Fig. 2 depicts PM\(_{1-5}\), i.e., fine fragment mode ash (stages 3-5) which constitute a significant amount of the total ash\(^4\,5\). The fine fragment and well as the PM\(_{10}\) and the PM\(_{18}\) ash yields showed similar trends; with the yield of PM\(_{1-5}\) being approximately half of the PM\(_{18}\) ash yield (see Figure 2). As with the submicron ash yields, the yields of both PM\(_{1-5}\) and PM\(_{18}\) were lower in CO\(_2\) environments in the cases of the bituminous coal (by 25%) and lignite coal (by 43%). The subbituminous coal ashes, however, showed rather comparable profiles in
both environments. Increasing the oxygen mole fraction in either environment, increased the PM$_{1.5}$, the PM$_{10}$ and the PM$_{18}$ yields for the lignite coal ashes, represented by increasing trends in Figure 2. However, the PM$_{1.5}$, PM$_{10}$ and PM$_{18}$ yields of the bituminous and sub-bituminous coal ashes were not affected much by increasing oxygen mole fractions.

As expected, the PM$_{18}$ yields from the different ranked coals were analogous to their respective ash contents, shown in Table 1. The average PM$_{18}$ ash yields from combustion of the three coals in O$_2$/N$_2$ atmospheres were 20, 10, and 27 (mg/g$_{coal}$) for bituminous, sub-bituminous, and lignite respectively, which is in line with the ash content (wt%) of the coals; 13.3, 6.5, and 17.4.
Figure 2. PM$_1$, PM$_{2.5}$, PM$_{1-5}$, PM$_{10}$, and PM$_{18}$ ash emission yields from burning of bituminous (PSOC 1451), sub-bituminous (DECS 26), and lignite (PSOC 1443) coals under various O$_2$/N$_2$ and O$_2$/CO$_2$ atmospheres.
Combustion condition | 60%O₂-40%CO₂ | 30%O₂-70%CO₂
---|---|---
Physical appearance of the small piles of ash particles collected on **Stage 5** of the impactor (PM$_{1-1.8}$) | | |

Figure 3. Physical appearance of the ash collected from combustion of lignite coal (PSOC 1443) under 60% O₂-40% CO₂ and 30% O₂-70% CO₂ environments.

Table 4. Carbon weight percentages of the submicron ash collected on Stage 9 from bituminous (PSOC 1451), sub-bituminous (DECS 26) and lignite (PSOC 1443) coals burning in air and in 30% O₂-70% CO₂ or 40% O₂-60% CO₂.

<table>
<thead>
<tr>
<th>Combustion in:</th>
<th>Coal →</th>
<th>Bituminous</th>
<th>Sub-bituminous</th>
<th>Lignite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>Carbon weight % in PM$_{0.1-0.18}$ ash (Stage 9)</td>
<td>5.6</td>
<td>4.8</td>
<td>9.8</td>
</tr>
<tr>
<td></td>
<td>PM$_{1}$ ash yields, uncorrected ( mg/g coal)</td>
<td>2.5</td>
<td>2.3</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>PM$_{1}$ ash yields, corrected for C % of Stage 9 (mg/g coal)</td>
<td>2.3</td>
<td>2.0</td>
<td>2.2</td>
</tr>
<tr>
<td>30%O₂-70%CO₂</td>
<td>Carbon weight % in PM$_{0.1-0.18}$ ash (Stage 9)</td>
<td>20.7</td>
<td>12.1</td>
<td>21.2</td>
</tr>
<tr>
<td></td>
<td>PM$_{1}$ ash yields, uncorrected ( mg/g coal)</td>
<td>2.8</td>
<td>2.3</td>
<td>2.8</td>
</tr>
<tr>
<td></td>
<td>PM$_{1}$ ash yields, corrected for C % of Stage 9 (mg/g coal)</td>
<td>2.2</td>
<td>2.0</td>
<td>2.2</td>
</tr>
<tr>
<td>40%O₂-60%CO₂</td>
<td>Carbon weight % in PM$_{0.1-0.18}$ ash (Stage 9)</td>
<td>7.6</td>
<td>6.8</td>
<td>6.6</td>
</tr>
<tr>
<td></td>
<td>PM$_{1}$ ash yields, uncorrected ( mg/g coal)</td>
<td>1.9</td>
<td>1.9</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>PM$_{1}$ ash yields, corrected for C % of Stage 9 (mg/g coal)</td>
<td>1.8</td>
<td>1.8</td>
<td>1.8</td>
</tr>
</tbody>
</table>
2.4.2. Particle size distributions

The particle size distributions (PSDs) of ashes from the combustion of the bituminous, sub-bituminous, and lignite coals are shown in Figure 4. The overall magnitude of the PSD curves reflected the ash content of the coals; lignite typically having the highest values and sub-bituminous having the lowest. The PM$_{18}$ size distributions may be recognized as multi-modal for all three coals (see the left column of Figure 4), under all combustion conditions. The bituminous and lignite coals exhibited a submicron mode, centered around 0.2 µm, and two fine fragment modes, centered around 1 µm and 5 µm. The sub-bituminous coal exhibited a submicron mode, centered around 0.2 µm, and a fine fragment mode, centered around 3 µm. In addition, the supermicron mode appeared to have occurred above 18 µm which, however, cannot be seen in the graph, as the inlet impactor stage (>18 µm) is not included. An expanded view of the submicron portion of the total ash size distribution can be seen on the right column of Figure 4. Increasing the O$_2$ mole fraction to 60% in N$_2$ shifted the geometric mean size of the lignite ash particles consistently to the left, i.e., to lower values, in both the submicron and the fine fragment modes. In addition to the 60% O$_2$-40% N$_2$ environment, the 40% O$_2$-60% N$_2$ and the 60% O$_2$-40% CO$_2$ environments also lead to similar shifts in the fine fragment mode for the ashes of the lignite coal. However, there was no clear trend of the effect of the O$_2$ mole fraction on the PSDs of the ashes of the bituminous and the sub-bituminous coals. Moreover, for all coals no clear trend on PSD was observed when the N$_2$ background gas was replaced by CO$_2$. 
Figure 4. Particle size distributions (PSDs) of ash from burning of a bituminous (PSOC 1451), a sub-bituminous (DECS 26), and a lignite (PSOC 1443) coal under various O$_2$/N$_2$ and O$_2$/CO$_2$ gas compositions.
2.4.3. Morphology of the collected ash particles

SEM images of the coal ashes generated in air and in the 40% O2 - 60% CO2 environment, representing a possible practical setting for oxy-coal combustion, are provided in Figure 5 to illustrate the effects of coal rank and ambient gases on the morphology of the various ash particle modes. Particles from stages 9, 10 and 11 were examined to illustrate the morphology of the PM1 mode, and particles from stage 5 were examined to illustrate the morphology of the PM1.5 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 different coals 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\textsuperscript{33-36}. This mechanism formed spherical particles with smooth surfaces, which can be observed in the first two rows of Figure 5. However, PM1.5 particles show evidence of different morphologies for the different coals. These particles were formed mostly via fracturing and shedding, in addition to the aforementioned vaporization-condensation mechanism; therefore some spherical particles as well as some irregularly-shaped particles can be observed in this mode (see Figure 5). Cenospheric PM1.5 particles were also observed in the ashes of the coals, particularly those of lignite.
Figure 5. SEM pictures that show morphologies of ash from burning of a bituminous (PSOC 1451), a sub-bituminous (DECS 26), and a lignite (PSOC 1443) under air and the oxy-fuel combustion condition of 40% O<sub>2</sub> – 60% CO<sub>2</sub>.
TEM images of the submicron ashes of bituminous coal in the oxy-fuel combustion condition of 40% O₂-60% CO₂ are represented in Figure 6. These images show evidence of a thin layer of coating around the particles and a dark region in the center. Moreover, a matrix is evident in the image (a) in which a particle was embedded. This matrix is made up of carbonaceous matter. Image (c) shows crystalline phases which may include mullite (containing Si and Al), lime (composed of Ca), and various metal sulfates, according to Ref. 63.

Figure 6. TEM pictures that show structural details of submicron ash particles emitted during combustion of a bituminous coal (PSOC1451) in a 40% O₂ - 60% CO₂ environment.

2.5. Discussion

2.5.1. Ash yield partition into different modes

The collected submicron ashes of the coals divided by their corresponding ash contents fell within the range reported in the literature (0.1%-9.6%)4, 21-25. The same types of coals were in fact also burned by Quann et al.23 in air and the submicron ashes were reported as 1.5%, 5.6%, and 0.54% of ASTM ashes for the bituminous (PSOC1451), sub-bituminous (DECS26), and
lignite (PSOC1443) coals, respectively. In this work, the corresponding values were calculated to be 1.9%, 2.3%, and 1.7% from the data in Figure 2, and did not necessarily correlate with coal rank, as also concluded by Quann et al.23 and McElroy et al.21. The differences between the yield values of this work and those of the early study of Quann et al.23 may be attributed to the dissimilar furnace temperature (1750 K versus 1400 K herein) as well as some elemental content differences of the mined coal seams over the years 21,23.

Figure 7. PM1, PM1-5, and PM18 ash emission yields from combustion of bituminous (PSOC1451), sub-bituminous (DECS 26) and lignite (PSOC 1443) coals in various O2/N2 and O2/CO2 atmospheres versus experimentally-deduced maximum char temperatures (averaged over many particles)57. All yields are expressed as mg/g of coal introduced to the drop tube furnace.
Increasing the oxygen mole fraction in both background gases, increased the submicron ash emission yield due to the increase in combustion temperatures\textsuperscript{61, 64}. This was quantified in this work, based on separate measurements of the temperature-time histories of single particles of the coals conducted in this laboratory using thee-color pyrometry and high-speed cinematography\textsuperscript{61, 64, 65}. As stated by Neville et al.\textsuperscript{53}, temperatures determined from single particle experiments may be assumed to also apply to the temperature of the particles in these dilute cloud experiments where the coal particle number density was low and each particle should have burned in effective isolation from others. The effects of maximum char particle temperatures (averaged over many particles) on the submicron ash emission yields are shown in Figure 7. Therein, the consequence of increasing char temperature on increasing submicron ash emission yields is evident in both environments (N\textsubscript{2} and CO\textsubscript{2}). A notable exception to this trend has been the ash of the 30\%O\textsubscript{2}- 70\%CO\textsubscript{2} environment, which was found to have an elevated unburned carbon as documented in Table 4 and depicted in Figure 3, therefore, this condition was not included in these plots.

The submicron ash yields (PM\textsubscript{1}) were higher in N\textsubscript{2} environments than in CO\textsubscript{2} environments at the same oxygen mole fraction; this can be explained qualitatively by the reduction mechanism that was proposed by Quann and Sarofim\textsuperscript{35}. According to this mechanism, refractory metal oxides (e.g., SiO\textsubscript{2}) are reduced by CO, generated from the char oxidation, to more volatile metal sub-oxides (e.g., SiO) and CO\textsubscript{2}. However, at the presence of high partial pressures of CO\textsubscript{2} 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\textsuperscript{22,24,28}. As particle temperatures in O\textsubscript{2}/CO\textsubscript{2} atmospheres have been found to be lower than those in O\textsubscript{2}/N\textsubscript{2} atmospheres\textsuperscript{61,64}, submicron ash formation is less likely in CO\textsubscript{2} environments. Lending support to this argument, McElroy et al.\textsuperscript{21} 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 emissions\textsuperscript{21}. Similarly, a recent study in this laboratory\textsuperscript{12} found that the NO emissions from the combustion of the three coals of this study in the same drop-tube furnace increased with increasing oxygen concentrations, where particle temperatures were shown to be higher\textsuperscript{61,64}.

The yields of ultra-fine particles (PM\textsubscript{0.1}) from burning of lignite and sub-bituminous coals in air were 0.210 mg/g\textsubscript{coal-burned} and 0.074 mg/g\textsubscript{coal-burned}, respectively. These yields were higher than the corresponding PM\textsubscript{0.1} yields of these two coals burning in a 30%O\textsubscript{2}-70%CO\textsubscript{2} atmosphere by 3 times and 1.5 times, respectively. This is in line with the findings of Carbone et al.\textsuperscript{66} who also reported higher particle volume yields when substituting N\textsubscript{2} with CO\textsubscript{2}. However, the PM\textsubscript{0.1} yield from burning of the bituminous was nearly constant at 0.3 mg/g\textsubscript{coal-burned} in both air and 30%O\textsubscript{2}-70%CO\textsubscript{2} atmospheres.

The mass of PM\textsubscript{1.5} particles (FFM) constituted approximately 50% of the mass of PM\textsubscript{18} ash particles under all combustion conditions, as shown in Figure 2. This is consistent with the findings of Helble and Sarofim\textsuperscript{26} who reported that PM\textsubscript{1.5} particles constituted 20% of the total ash particles. Kang et al.\textsuperscript{37} stated that increased coal fragmentation increased the PM\textsubscript{1.5} particle yields, which may partially explain the high yields of such particles in the ashes of the lignite
coal. Low rank coals are known to be friable. In fact, a study on the combustion characteristics of the coals herein with high-speed, high-resolution cinematography documented that the fragmentation degree of the lignite coal (PSOC 1443) was higher than that of the sub-bituminous coal which, in turn, was much higher than that of bituminous coal (PSOC 1451), which hardly fragmented. Examples of the fragmentation characteristics of the coals in the DTF herein is shown in Figure 8. Lignite experienced the highest degree of bulk fragmentation and it generated the highest PM$_{1.5}$ yields in most N$_2$ and CO$_2$ environments, as shown in Figure 2. Moreover, the increasing trend of the PM$_{1.5}$ yields of this coal with respect to the oxygen mole fraction may be explained by the observation that combustion of the individual fragments of these rather friable particles occurred in one mode, where volatile matter and char outer layers appeared to burn simultaneously in attached envelope flames. This mode of combustion is expedient and, at high oxygen mole fractions, the particle fragments burn faster, leaving little time for mineral inclusions to coalesce and, consequently, to form larger ash particles.

![Combustion in air](image)

**Figure 8.** High-speed high-magnification back-lit cinematography of the initial stages of single particles of bituminous (PSOC 1451), sub-bituminous (DECS 26) and lignite (PSOC 1443) coals burning in air, at a DTF temperature of 1400 K. The vastly different degrees of fragmentation are evident. The diameter of the wire shown in the far left is 100 µm. More information is given in Refs. 61, 65, 67.
Replacing N\textsubscript{2} with CO\textsubscript{2} as the background gas, at the same O\textsubscript{2} mole fraction, decreased the degree of bulk fragmentation of the lignite coal\textsuperscript{61}, as shown in Figure 9. In turn, lower PM\textsubscript{1.5} yields in CO\textsubscript{2} background gases (see Figure 2) may be partially explained by the lower degree of framentation.

![Lignite](image)

**Figure 9.** High-speed, high-magnification cinematography of typical combustion events of lignite coal particles (PSOC 1443) burning with 40\%O\textsubscript{2}. Fragmentation is more intense in N\textsubscript{2} (left) than in CO\textsubscript{2} (right) background gases. The DTF temperature was 1400 K.

PM\textsubscript{1.5} and PM\textsubscript{10} emission yields from bituminous and sub-bituminous coals were not substantially affected by increasing O\textsubscript{2} mole fractions as much as their respective submicron ash emission yields were. Contrary to lignite, combustion of the bituminous coal, under the conditions of this study (20-60\%O\textsubscript{2}) occurred in two phases with little, if any, visible bulk fragmentation\textsuperscript{61, 65}. Volatile matter and chars burned sequentially. Volatile matter burned in detached envelope flames\textsuperscript{61, 65}. Chars swelled and formed cenospheric structures\textsuperscript{65}. The burnout times of the bituminous chars were lengthier than those of the lignite fragments. As a result, higher temperatures at higher oxygen mole fractions may have induced competing and, possibly, mutually-cancelling effects at the final stages of char combustion: ash coalescence and increased perimeter fragmentation of the cenospheric chars.
2.5.2. Particle size distributions

Contrary to what was observed in some previous studies\textsuperscript{47, 48, 50}, the PSDs of the three coals herein were not clearly affected by the replacement of N\textsubscript{2} with CO\textsubscript{2}, as shown in Figure 4. This is in agreement with the findings of Yu et al.\textsuperscript{51} who reported no difference in PSDs for particles below 10 µm when air was switched to oxy-firing conditions. However, the increase in the oxygen mole fraction affected the PSDs of the lignite coal. At higher oxygen mole fractions, the geometric mean size shifted to smaller sizes for both PM\textsubscript{1} (submicron) and PM\textsubscript{1-5} (FFM) particles.

Two distinct peaks in FFM of the bituminous and lignite coals may be attributed to their cenospheric and brittle structures, respectively. According to Linak et al.\textsuperscript{38}, one of the mechanisms that form FFM particles is material shedding due to expansion of gases within the coal particles which result in fracture of cenospheric chars. Moreover Helble and Sarofim\textsuperscript{26} proposed that FFM particles formed by perimeter fragmentation (also called peripheral fragmentation) of the char during combustion, which increases with increasing macro-porosity. These may be the reasons for the formation of the smaller peak in FFM (around 1 µm) from burning of the bituminous coal which, upon devolatilization, forms chars of cenospheric structure\textsuperscript{61}. In the case of the lignite coal, the smaller peak in FFM (around 1 µm) may be explained by the brittle and friable structure of the parent coal that leads to high bulk fragmentation degrees\textsuperscript{61}. According to Helble and Sarofim\textsuperscript{26} fragmentation is the dominant mechanism of the formation of the ash particles in the 1-5 µm FFM range. The differing fragmentation degrees of the lignite, sub-bituminous and the bituminous coals are illustrated in Figure 8 for combustion in air.
2.5.3. Morphology of the collected ash particles

According to Mamane et al.⁶⁸, 95% of the PM₁ particles are smooth-surfaced spheres, which is in qualitative agreement with the findings herein. Suriyawong et al.⁵⁰ stated that the background gas (N₂ or CO₂) did not change the submicron particle formation mechanism as similar spherically-shaped particles were observed in both environments; additionally, no discernible coal rank effect was observed on these particles. It should be mentioned here that the time scales of luminous coal char particle combustion were in the range of 20-100 ms, based on pyrometric and cinematographic studies conducted in this laboratory⁶¹. Most of the ash forming reactions are likely to have occurred in that time frame where particle temperatures are high (>1800K), see Table 5. Thereafter the ash particles, particularly the submicron ones were carried through the DTF by the gas flow and may have reacted further slowly at the cooler gas temperature of the post-combustion zone (<1400K). Their overall residence times in the hot zone of the furnace were in the order of 1 s.

In this study, approximately 50% of the PM₅ (FFM) particles were found to be spherical with some shape-related irregularities, possibly stemming from the fragmentation mechanism. This is in agreement with Seames et al.³⁹ who observed that approximately 30-40% of such particles were spherical. These spherical particles form when the melting temperatures of the predominant ash constituents are lower than those of char combustion. The ash constituents (mineral inclusions) melt during the char burnout time and then coalesce to form spheres, as shown in Figure 5. In the case of the lignite coal, fractured hollow ash particles were observed in both air and in 40%O₂- 60%CO₂ environments. Cenospheric ash particles may have formed when combustion temperatures exceeded the vaporization temperatures of some mineral
constituents. If minerals located in the inner parts of a particle vaporized and expanded against softening/melting minerals located at the periphery of a particle then ash cenospheres could have formed. Table 5 lists experimentally-determined maximum char combustion temperatures (averaged over many particles), and Table 6 lists vaporization and melting temperatures of some common oxides and sub-oxides found in coal ashes.

Table 5. Average maximum deduced char combustion temperatures of the bituminous (PSOC 1451), sub-bituminous (DECS 26), and lignite (PSOC 1443) coals.

<table>
<thead>
<tr>
<th></th>
<th>$T_{\text{char combustion}}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bituminous in air</td>
<td>1825</td>
</tr>
<tr>
<td>Bituminous in 40% O₂-60%CO₂</td>
<td>2090</td>
</tr>
<tr>
<td>Sub-bituminous in air</td>
<td>2131</td>
</tr>
<tr>
<td>Sub-bituminous in 40%O₂-60%CO₂</td>
<td>2084</td>
</tr>
<tr>
<td>Lignite in air</td>
<td>2069</td>
</tr>
<tr>
<td>Lignite in 40%O₂-60%CO₂</td>
<td>2033</td>
</tr>
</tbody>
</table>

Table 6. Melting and vaporization temperatures of some common oxides as well as sub-oxides and metals (reduced oxides) found in their ashes (from Ref. and other web-based sources).

<table>
<thead>
<tr>
<th></th>
<th>CaO</th>
<th>Ca</th>
<th>Al₂O₃</th>
<th>AlO</th>
<th>SiO₂</th>
<th>SiO</th>
<th>Fe₂O₃</th>
<th>FeO</th>
<th>MgO</th>
<th>Mg</th>
<th>Na₂O</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{\text{melting}}$ (K)</td>
<td>2873</td>
<td>1112</td>
<td>2327</td>
<td>-</td>
<td>2000</td>
<td>2048</td>
<td>1838</td>
<td>-</td>
<td>3073</td>
<td>923</td>
<td>1359</td>
<td>371</td>
</tr>
<tr>
<td>$T_{\text{vaporization}}$ (K)</td>
<td>4123</td>
<td>1757</td>
<td>3253</td>
<td>-</td>
<td>2500</td>
<td>2153</td>
<td>-</td>
<td>-</td>
<td>3873</td>
<td>1380</td>
<td>1405</td>
<td>1156</td>
</tr>
</tbody>
</table>

As the vaporization temperatures of the reduced suboxides or metal vapors (Ca, AlO, SiO, Mg, Na, etc.) of the refractory oxides (CaO, Al₂O₃, SiO₂, MgO, Na₂O, etc.) are comparable or lower than the deduced combustion temperature of the lignite chars, under both air and oxy-combustion conditions, the particle with the hollow, spherical morphology depicted in Figure 5.
may be composed of these elements. On the other hand, the cenospheric structure of the bituminous coal chars often results in cenospheric ash particles, as shown in Figs 5 and 6. Irregular particles were also observed under all conditions, as shown in Figure 5. It is possible that such particles formed when the melting temperature of included minerals exceeded the char combustion temperatures. In that case they would not go through melting process; rather they could be a product of fragmentation mechanisms, as discussed by Seames et al.\textsuperscript{39}. Proposed temperature relations of the FFM ash particle formation are summarized in Table 5:

### Table 7. Proposed temperature relations of the FFM ash particle formation.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Particle Shape</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T_{\text{melting}} &gt; T_{\text{combustion}})</td>
<td>irregular particles</td>
</tr>
<tr>
<td>(T_{\text{vaporization}} &gt; T_{\text{combustion}} &gt; T_{\text{melting}})</td>
<td>solid shapes</td>
</tr>
<tr>
<td>(T_{\text{combustion}} &gt; T_{\text{vaporization}})</td>
<td>hollow spheres</td>
</tr>
</tbody>
</table>

### 2.6. Conclusions

In this study, three pulverized solid fuels were burned in a laboratory drop-tube furnace (a bituminous, a sub-bituminous and a lignite coal). Combustion took place in various \(O_2/N_2\) and \(O_2/CO_2\) environments. Particulate emissions were collected on 13 stages of a \textit{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. Moreover, images from ash particles were captured with a SEM. Results showed that:

- Submicron emission yields in \(O_2/CO_2\) environments were lower than those in \(O_2/N_2\) environments, at the same \(O_2\) mole fractions.
• Coal rank did not have any significant impact on the submicron ash emission yields in air.

• Increasing the oxygen mole fraction increased the submicron emission yields; this increase was more significant in N₂ environments than in CO₂ environments for all coal types tested. Moreover, the submicron ash yields of lower rank coals (lignite and sub-bituminous) were more affected by the oxygen mole fraction than those of the bituminous coal (PSOC 1451).

• PM₁₅ (FFM) particle yields in O₂/CO₂ environments were lower than those in O₂/N₂ environments, at the same O₂ mole fractions.

• The degree of fragmentation that the coals experienced during combustion increased their respective PM₁₅ yields (lignite>sub-bituminous>>bituminous).

• Multi-modal ash particle size distributions were observed in all cases.

• Spherical particles were mostly observed in the submicron ash mode whereas a mix of irregularly-shaped particles and spherical particles were observed in the PM₁₅ (FFM) in both air and simulated oxy-combustion (40%O₂- 60%CO₂) conditions.

Acknowledgements

The authors acknowledge financial assistance from the NSF award CBET-0755431. Technical assistance by Mr. Reza Khatami is also acknowledged.
2.7. References

1. International Energy Agency.  


16. EPA-Environmental Protection Agency

   [http://www.epa.gov/ttn/naaqs/standards/pm/s_pm_index.html](http://www.epa.gov/ttn/naaqs/standards/pm/s_pm_index.html) (accessed 5th April).


43. Fix, G.; Seames, W. S.; Mann, M. D.; Benson, S. A.; Miller, D. J., Fuel Processing Technology 2011, 92, 793-800.


59. Khare, S. P.; Wall, T. F.; Gupta, R. P.; Elliot, L. K.; Buhre, B. J. P. In Retrofitting of air-
fired pf plant to oxy-fuel: combustibility and heat transfer impacts, Proceedings of the
30th international technical conference on coal utilization and fuel system, Clearwater,
FL, USA, April 21–25; Clearwater, FL, USA, 2005; pp 651-662.

in oxyfuel combustion, Impacts of fuel quality on power production, Snowbird UT,
October 29–November 3; Snowbird UT, 2006.

61. Khatami, R.; Stivers, C.; Joshi, K.; Levendis, Y. A.; Sarofim, A. F., Combustion and
Flame 2012, 159, 1253-1271.


63. Giere, R.; Blackford, M.; Smith, K., Environmental Science & Technology 2006, 40,
6235-6240.


65. Levendis, Y. A.; Joshi, K.; Khatami, R.; Sarofim, A. F., Combustion and Flame 2011,
158 (3), 452-465.

66. The Coal Resource, A Comprehensive Overview of Coal; World Coal Institute:


69. Rowe, R. C.; Sheskey, P. J.; Quinn, M. E., Handbook of Pharmaceutical Excipients. 6 th
CHAPTER 3

Energy & Fuels, 2013, accepted for publication.

Feyza Kazanc and Yiannis A. Levendis*
Mechanical and Industrial Engineering, Northeastern University, Boston, MA 02115, USA

and

Tiziano Maffei
Dipartimento CMIC “G. Natta”, Politecnico di Milano, 20133, Milano, Italy

90
3. Chemical Composition of Submicron Particulate Matter (PM$_1$) Emitted from Combustion of Coals of Various Ranks in Air and O$_2$/CO$_2$ Environments.

Abstract

A laboratory-scale investigation has been conducted on the physical and chemical characteristics of particulate matter emissions (ashes) from pulverized coals burning in air or in simulated oxy-fuel environments. Oxy-fuel combustion is a process that takes place in O$_2$/CO$_2$ gases, using an air separation unit (ASU) to supply the oxygen and a flue-gas recirculation (FGR) stream to supply the carbon dioxide to the boiler. In order to investigate the effects of the background gas on the particulate matter generated by the combustion of coals of different ranks, a bituminous, a sub-bituminous and a lignite coal were burned in an electrically-heated laminar-flow drop-tube furnace (DTF) in both O$_2$/N$_2$ and O$_2$/CO$_2$ environments (21%<O$_2$<60%). A recent publication by the authors reports the physical characteristics of the particulate matter; hence, this work focuses on the chemical composition, specifically targeting the difficult-to-capture submicron size (PM$_1$) ashes. Particulate matter was collected by a low-pressure multi-stage cascade impactor and was analyzed for the chemical composition by Scanning Electron Microscopy - Energy Dispersive X-ray Spectroscopy (SEM-EDS). Selected samples were also examined by Electron Microprobe Analysis (EMA). Results showed that submicron (PM$_1$) ashes of the bituminous, the sub-bituminous and the lignite coals contained mostly Si, Al, Fe, Mg, Ca, K, Na and S. Prominent components of large submicron particle (PM$_{0.56-1}$) compositions were Si and Al (Ca in sub-bituminous), whereas small submicron particles (PM$_{0.1-0.18}$) were markedly enriched in S. The mass yields of elemental species found in the submicron-size particles from all three coals were lower when combustion occurred in CO$_2$, instead of N$_2$ background gases.
The chemical composition of the PM\textsubscript{0.56-1} sub-category was not affected by the background gas. To the contrary, the composition of the PM\textsubscript{0.1-0.18} sub-category was affected by replacing N\textsubscript{2} with CO\textsubscript{2}, and mass fractions of Si, Ca, and Al decreased whereas Na, K and S increased. Furthermore, in PM\textsubscript{0.1-0.18}, when the O\textsubscript{2} mole fraction increased in either N\textsubscript{2} or CO\textsubscript{2}, the mass fractions of Si, Ca and Al increased at the expense mostly of Na, K and S, but also Fe in the case of the sub-bituminous coal. Experimentally-derived partial pressures of the volatile sub-oxide SiO (P\textsubscript{SiO}) at the char surface were compared with the predictions of an ash vaporization model without and with coupling with a particle combustion model; they were found to be in the range of the model predictions.

### 3.1. Introduction

Global carbon dioxide (CO\textsubscript{2}) emissions keep rising; in fact, in 2010 total global CO\textsubscript{2} emissions had increased by 30% since 2000 and amounted to 33 billion tones\textsuperscript{2}. Consumptions of coal and natural gas fuels for power generation were responsible for about 40% and 20% of this amount respectively. As CO\textsubscript{2} in the atmosphere is the likely leading cause of global climate change, it is desirable to decrease its emissions by improving power-plant efficiencies and by implementing carbon capturing and sequestration (CCS) processes. A power generation technology that can facilitate CCS is oxy-coal combustion, where pulverized coal is burned with oxygen, mixed with wet or dry re-circulated flue gases, instead of air. Thereby, a high-CO\textsubscript{2}-concentration gas effluent is generated, ready for CCS. Reviews of oxy-fuel combustion of coal have been compiled in recent years by Buhre et al.\textsuperscript{3}, Croiset et al.\textsuperscript{4}, Toftegaard et al.\textsuperscript{5}, Wall\textsuperscript{6}, Chen et al.\textsuperscript{7}, and Zheng\textsuperscript{8}. 
Whereas the gaseous emissions from oxy-coal combustion have been well-researched and sufficiently-documented\textsuperscript{2-8}, reports on particulate emissions have been very limited\textsuperscript{9-12}. However, in oxy-coal power plants, a fraction of the (particulate-laden) boiler flue gases will be re-circulated into the boiler (to moderate flame temperatures) and the rest will be compressed for CCS. Therefore, information on the amounts, the size distributions, and the compositions of the ash particulate matter is needed for hardware design, choice of materials and selection of operating conditions. Moreover, it is likely for an oxy-fuel power plant to emit flue gases directly to the atmosphere during high peak hours by temporarily shutting down the product recovery train to increase power output to the grid, thus making it necessary to maintain low emission levels of various pollutants\textsuperscript{13}. Previous work in this laboratory\textsuperscript{9} and elsewhere\textsuperscript{10-12} have examined the yields of particulate matter from oxy-combustion of coal and their size distributions, and have compared them with those from conventional combustion in air. The submicron ashes are particularly worrisome, as they account for a significant fraction of the emitted ashes (in the order of 20\% the mass of the PM\textsubscript{18} collected particulates in this study) and, yet, environmental cleanup equipment (such as electrostatic precipitators and baghouses) have very low capture efficiencies for such small particles\textsuperscript{14}. Therefore, it is encouraging to note that all pertinent investigations\textsuperscript{9-12} found that the submicron (as well as the super-micron) particulate matter emission yields are typically lower in O\textsubscript{2}/CO\textsubscript{2} than in O\textsubscript{2}/N\textsubscript{2} environments.

This work examined the chemical composition of the submicron particulate matter, since upon re-circulation to the boiler it can impact corrosion, fouling and slugging therein. Coals of three different ranks were burned in selected O\textsubscript{2}/N\textsubscript{2} (including air) as well as in O\textsubscript{2}/CO\textsubscript{2} environments. Specifically, it examined the chemical composition of ash particles in two separate submicron categories and compared the measurements of major mineral components of
the coals (e.g. Si) with predictions of the ash-vaporization model proposed by Quann and Sarofim\textsuperscript{15}. Moreover, since Quann and Sarofim’s\textsuperscript{15} model only allows for constant carbon monoxide and carbon dioxide concentrations on the particle surface throughout combustion, a numerical coal combustion model\textsuperscript{16} was also integrated to provide real-time CO and CO\textsubscript{2} concentrations. Experimental and computational results were interpreted based on combustion behavior observations and on measured single particle temperatures of the three coals burned in this laboratory under these conditions\textsuperscript{17}. By choosing conditions in O\textsubscript{2}/CO\textsubscript{2} that matched the char particle temperature in air, the effect of the background gas on PM\textsubscript{1} emissions could be decoupled from that of temperature.

\textbf{3.2. Literature Review}

\textbf{3.2.1. Chemical composition of the submicron ashes in air and in O\textsubscript{2}/CO\textsubscript{2} environments}

A variety of techniques have been utilized in the literature to obtain the chemical composition of the submicron ash particles from burning coal, as listed in Appendix 1, Table A1. These techniques were mostly dependent on the substrate type used to collect the ash particles and on the type of the elements which were investigated.

Submicron ash particle yields from conventional pulverized coal combustion in air have been the subject of extensive research over the years because of their health-hazardous, toxic-metal-enriched compositions\textsuperscript{2,10,15,18-21}. Previous works on composition of submicron ash particles from air combustion determined that submicron ash particles are mainly composed of Silicon (Si), Aluminum (Al), Iron (Fe), Calcium (Ca), Sulfur (S), and Sodium (Na)\textsuperscript{2,10,15,18,19}. Si, S, and Na have been mostly detected in smaller submicron particles (d<0.3 µm)\textsuperscript{2,18,20,21}, meanwhile in larger submicron particles (0.3 µm < d <1 µm) the elements Al, Ca, Fe, and Si have
been generally observed\textsuperscript{2, 18, 20, 21}. Yu et al.\textsuperscript{21, 22} and Teramae and Takarada\textsuperscript{20} correlated mass fraction size distributions of common elements found in the ash to tri-modal particle size distributions. According to the total mass fraction size distributions of Si, Al, and S presented in those works\textsuperscript{20-22}, three ash particle modes were detected. Tri-modal particle size distribution represents three distinct particle formation modes, with an ultrafine mode corresponding to particles lower than 0.3 µm (PM\textsubscript{0.3}), a fine fragment mode (FFM) with particles between 0.5-5 µm (PM\textsubscript{0.5-5}), and a coarse mode with particles larger than 5 µm (>PM\textsubscript{5})\textsuperscript{21, 23-25}. In particles below 0.3 µm (PM\textsubscript{0.3}) the fractions of Si, Al, and S were found to be constant with particle diameter. In particles between 0.3 and 1 µm (PM\textsubscript{0.3-1}), Si and Al fractions followed an increasing trend with particle diameter, whereas S fractions were observed to decrease with particle diameter.

According to Quann et al.\textsuperscript{19}, major elements detected in submicron ash particles are generally present in the coal as discrete mineral phases: for example, Si as quartz (SiO\textsubscript{2}), Al as kaolin [Al\textsubscript{2}Si\textsubscript{2}O\textsubscript{5}(OH)\textsubscript{4}], Ca as calcite (CaCO\textsubscript{3}) or dolomite [MgCa(CO\textsubscript{3})\textsubscript{2}], and Fe as pyrite (FeS\textsubscript{2}). These minerals can be found as inclusions in the char organic matrix or detached from the carbonaceous matter of coal. In low rank coals, such as sub-bituminous and lignites, the alkaline earth metals (Mg, Ca) and alkali metals (Na, K) were reported to be in ion-exchanged form as cations of carboxylic and phenolic groups in the organic matter\textsuperscript{26}. However, Texas lignite has been noted to be an exception, having little ion-exchangeable alkalines or alkalis\textsuperscript{19}. Therefore, Quann et al.\textsuperscript{19} concluded that ranking was not an important parameter in ash volatilization; rather the mineral composition and distribution of the individual coal were the main determinants. Buhre et al.\textsuperscript{27} supported this argument by reporting a variety of mineral compositions in the ashes of five bituminous coals with different elemental compositions. They
also reported that the S content of the coals correlates well with the respective submicron ash yields, which was supported by the experimental data from Quann et al.\textsuperscript{19}.

There has been an agreement on the effects of combustion temperature on both the submicron ash yield and its composition. It has been reported that increasing temperature increased both the submicron emission yield and the content of the refractory oxides in the submicron ash particles\textsuperscript{15, 28}.

Coal size also has an effect on vaporization of the mineral oxides in the submicron ash particles. According to Figure 5 in Quann and Sarofim’s paper\textsuperscript{15}, decreasing the initial coal particle size increases the vaporization of metal oxides in the char matrix.

Chemical compositions of the submicron ash particles from combustion of coal in O\textsubscript{2}/CO\textsubscript{2} environments have not yet been well established. There are only a few studies published in the literature on the chemical composition of PM\textsubscript{1} in oxy-fuel combustion\textsuperscript{10, 11, 29, 30}. Suriyawong et al.\textsuperscript{10} analyzed submicron ash particles smaller than 0.5 μm (PM\textsubscript{0.5}) for their chemical composition from burning of a sub-bituminous coal in air as well as in 20% O\textsubscript{2}-80% CO\textsubscript{2} environment. They reported lower Si yields (280 μg/g\textsubscript{coal-burned}) compared to those of Fe (380 μg/g\textsubscript{coal-burned}) and Ca (700 μg/g\textsubscript{coal-burned}), even if the Si content of the parent coal was higher than the contents of Fe and Ca. They also reported that the yields of the vaporized elements were lower in 20%O\textsubscript{2}-80%CO\textsubscript{2} combustion, as compared to the respective yields in conventional combustion in air for most of the major elements found in submicron particles, particularly Si, Al, Fe, and Ca, however this difference was not pronounced for K and S. Sheng et al.\textsuperscript{11} analyzed the composition of submicron ash particles from burning of coals in either N\textsubscript{2} or CO\textsubscript{2} background gases with O\textsubscript{2} varying from 20-40%. They reported that submicron particles
formed in 20% O₂-80% CO₂ combustion had lower Si, Fe, and Ca contents as compared to those formed in air combustion, but had higher Na, K, and S contents. Moreover, when O₂ increased from 20% to 40% in the CO₂ background gas, the contents of Si, Fe, Ca and Al were much higher than those formed in conventional combustion in air. This was explained by the inferred higher particle temperature in the 40%O₂/60%CO₂ case. Jia and Lighty³⁰ obtained elemental mass fraction size distribution for their ash particles with diameters smaller than 7.3 µm from burning of two bituminous and a sub-bituminous coals in a either N₂ or CO₂ background gases with O₂ mole fractions of 21% and 31.5%. They reported that ultrafine particles (d<0.1 µm) formed in CO₂ background gases had lower Si and Fe yields as compared to those formed in N₂ background gases when the O₂ mole fractions were matched. Moreover, when O₂ increased from 21% to 31.5% in either N₂ or CO₂ background gas, the yields of Si and Fe were increased while the yields of S decreased in ultrafine particles therein.

3.2.2. Modeling of submicron ash formation.

Formation of submicron particulate matter (PM₁) from conventional pulverized coal combustion in air has been the subject of research over the past years ³¹-³³. The submicron ash particles have been attributed to vaporization of minerals embedded in the coal matrix, followed by condensation and particle growth ¹⁵, ³⁴-³⁶. Quann and Sarofim¹⁵ proposed a vaporization model for the formation of these submicron ash particles. According to their mechanism, refractory metal oxides (e.g., SiO₂, MgO, CaO) are reduced in the pores of coal char particles by CO generated from the oxidation of char, to form more volatile metal sub-oxides or metals (e.g., SiO, Mg, Ca) and CO₂. Subsequently, these sub-oxide or metal vapors diffuse outwards to the char surface and, upon nucleation and condensation, form submicron ash particles. This model is
highly temperature dependent, as vaporization is directly related to particle temperature\textsuperscript{27, 31, 37}. The reduction reactions in this mechanism (eg. SiO\textsubscript{2}+CO=SiO+CO\textsubscript{2}) were assumed to be in chemical equilibrium.

Senior et al.\textsuperscript{37} calculated submicron ash emission yields from burning of a bituminous coal in air, based on the model of Quann and Sarofim\textsuperscript{15}. They calculated the PM\textsubscript{1} yield to be in the order of 1 mg\textsubscript{ash}/g\textsubscript{coal-burned}, which is in line with experimental results reported in literature\textsuperscript{31}.

Additional numerical investigations on ash vaporization during coal combustion have been conducted\textsuperscript{28, 38-40} based on the work of Quann and Sarofim\textsuperscript{15}. The model of Quann and Sarofim\textsuperscript{15} has been coupled with CFD codes to predict trends in ash vaporization in coal-fired utility boilers\textsuperscript{28, 38-40}. Krishnamoorthy and Veranth\textsuperscript{38} constructed a computational model to assess the average P\textsubscript{CO}/P\textsubscript{CO\textsubscript{2}} ratio inside single char particles during pulverized coal combustion. They predicted that, with all other parameters kept equal, increasing the CO\textsubscript{2} in the bulk gas reduces metal vaporization. This result is relevant to oxy-combustion applications.

### 3.3. Fuels, Experimental Apparatus and Procedure

Coals from three different ranks, bituminous (PSOC-1451), sub-bituminous (DECS-26), and lignite (PSOC-1443), were burned in this study. Their chemical compositions and properties are listed in Table 1. Samples for the three coals were obtained from the Penn State Coal Bank, and were ground and sieved. The particle cut size of 53-90 µm was used herein.
### Table 1. Chemical Composition of the Coals

<table>
<thead>
<tr>
<th></th>
<th>PSOC-1451</th>
<th>DECS-26</th>
<th>PSOC-1443</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Rank and Fuel Source</strong></td>
<td>Bituminous High Volatile A Pittsburgh #8 Pennsylvania</td>
<td>Sub-Bituminous B River Basin Wyodak, Wyoming</td>
<td>Lignite A Titus, Texas</td>
</tr>
<tr>
<td><strong>Proximate Analysis as received, and (upon re-evaluating moisture)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moisture (%)</td>
<td>2.5</td>
<td>26.3 (13.1)</td>
<td>28.5 (18.6)</td>
</tr>
<tr>
<td>Volatile matter (%)</td>
<td>33.6</td>
<td>33.1 (39.0)</td>
<td>44.2 (50.3)</td>
</tr>
<tr>
<td>Fixed Carbon (%)</td>
<td>50.6</td>
<td>35.1 (41.4)</td>
<td>12.0 (13.7)</td>
</tr>
<tr>
<td>Ash (%)</td>
<td>13.3</td>
<td>5.6 (6.5)</td>
<td>15.3 (17.4)</td>
</tr>
<tr>
<td><strong>Ultimate Analysis (on a dry basis)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon (%)</td>
<td>71.9</td>
<td>69.8</td>
<td>56.8</td>
</tr>
<tr>
<td>Hydrogen (%)</td>
<td>4.7</td>
<td>5.7</td>
<td>4.1</td>
</tr>
<tr>
<td>Oxygen (%) (by diff.)</td>
<td>6.9</td>
<td>15.6</td>
<td>15.8</td>
</tr>
<tr>
<td>Ash (%)</td>
<td>13.7</td>
<td>7.6</td>
<td>21.4</td>
</tr>
<tr>
<td>High-temperature ash (HTA) (%)</td>
<td>13.2</td>
<td>6.7</td>
<td>14.3</td>
</tr>
<tr>
<td>Heating Value Dry Fuel (MJ/kg)</td>
<td>31.5</td>
<td>28.2</td>
<td>23.0</td>
</tr>
</tbody>
</table>

For the three coals and their proximate and ultimate analysis data was obtained from the Penn State Coal Sample Bank; upon opening the sealed containers of the supplied coal samples, variations of moisture content with storage in the laboratory were observed for all, but the bituminous, coals. The measured moisture content values are listed (in parentheses) and the remaining proximate analysis values were re-calculated and are also shown (in parentheses).

Combustion experiments were conducted in an electrically-heated (4.8 kW max) drop-tube furnace (DTF), manufactured by ATS; a schematic of this furnace is provided 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 is 20 cm long, as defined by the length of the aluminum silicate heating elements. 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 section of 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 through a water-cooled stainless-steel injector.

![Diagram](image)

**Figure 1. Cross section view 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 water-cooled particle collection probe where a flow of dilution nitrogen was provided.**

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 1-2 s. Combustion occurred under laminar-flow conditions in the 20 cm hot zone of the furnace.
Furnace wall temperatures ($T_w$) were continuously monitored by type-$S$ thermocouples embedded in the wall.

A thirteen stage Nano-Moudi ash impactor, details of which were shown before\textsuperscript{1}, was coupled to the furnace outlet through a water-cooled probe (under $N_2$ dilution/ quenching flow) to collect particulate emissions after combustion occurred. Particles collected upon impaction plates, loaded with aluminum or teflon substrates, as they traveled through the impactor stages. The ash particles formed small heaps as they accumulated upon the substrates. 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 by means of carbon tapes as seen in Figure 2. 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).

![Figure 2. Ash collected on an aluminum substrate (left); examination samples (right) where prepared out of the substrate for SEM-EDS analysis.](image-url)
Table 2. Nominal cut size of the stages in Nano Nano-Moudi ash impactor. Cut-off sizes were determined by the instrument supplier based on the density of ammonium sulfate particles whose density is 1.77 g/cm³. The density of ash particles varies and is not necessarily equal to this value.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Inlet</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>Filter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal Cut Size (nm)</td>
<td>18,000</td>
<td>10,000</td>
<td>5,600</td>
<td>3,200</td>
<td>1,800</td>
<td>1,000</td>
<td>560</td>
<td>320</td>
<td>180</td>
<td>100</td>
<td>56</td>
<td>32</td>
<td>18</td>
<td>10</td>
<td>&gt;10</td>
</tr>
</tbody>
</table>

Tests were conducted with oxidant gases consisting of either air or O₂/CO₂ mixtures. The 30% and the 40% oxygen mole fractions in CO₂ background gas were chosen based on results of previous works⁴¹-⁴³ to represent a likely range of targeted practical oxy-coal combustion conditions. 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 Sarofim¹⁵. The amount of pulverized fuel fed to the DTF during each experiment was calculated by measuring the weights of the fuel contained in the vial at the beginning and end of each run. Every experiment lasted for 20 minutes. Triplicate combustion experiments were conducted at each condition. Furthermore at each condition, the average of the chemical composition data was obtained based on measurements from 5 different locations of the accumulated particles on the loaded substrates.

3.4. Experimental Results

3.4.1. Submicron Ash (PM₁) Composition

The mineral matter elemental compositions of the three coals burned in this study (bituminous, sub-bituminous, and lignite) are provided in Table 3. Moreover, the mineral oxide compositions of high temperature ashes of the same coals are provided in Table 4.
Table 3. Major and trace elemental composition of the bituminous (PSOC1451), the sub-bituminous (DECS26), and the lignite (PSOC1443) coals. Analysis was done based on dry coal. Data was obtained from the Penn State Coal Sample Bank.

<table>
<thead>
<tr>
<th>Major element analysis:</th>
<th>PSOC 1451 (Bituminous)</th>
<th>DECS 26 (Sub-bituminous)</th>
<th>PSOC 1443 (Lignite)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Element as % of mass of dry coal</td>
<td>3.36</td>
<td>1.0</td>
<td>3.2</td>
</tr>
<tr>
<td>Si</td>
<td>1.71</td>
<td>0.6</td>
<td>1.7</td>
</tr>
<tr>
<td>Al</td>
<td>0.09</td>
<td>0.05</td>
<td>0.15</td>
</tr>
<tr>
<td>Ti</td>
<td>0.85</td>
<td>0.23</td>
<td>0.35</td>
</tr>
<tr>
<td>Fe</td>
<td>0.07</td>
<td>0.19</td>
<td>0.24</td>
</tr>
<tr>
<td>Mg</td>
<td>0.28</td>
<td>1.1</td>
<td>1.4</td>
</tr>
<tr>
<td>Ca</td>
<td>0.06</td>
<td>0.09</td>
<td>0.04</td>
</tr>
<tr>
<td>Na</td>
<td>0.22</td>
<td>0.02</td>
<td>0.07</td>
</tr>
<tr>
<td>K</td>
<td>0.02</td>
<td>0.026</td>
<td>0.007</td>
</tr>
<tr>
<td>P</td>
<td>1.36</td>
<td>0.43</td>
<td>0.74</td>
</tr>
<tr>
<td>S</td>
<td>0.08</td>
<td>0.0</td>
<td>1100</td>
</tr>
<tr>
<td>Trace element analysis:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Element as ppm of mass of dry coal</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>71</td>
<td>311</td>
<td>155</td>
</tr>
<tr>
<td>Ba</td>
<td>18</td>
<td>10</td>
<td>215</td>
</tr>
<tr>
<td>Mn</td>
<td>20</td>
<td>3</td>
<td>17</td>
</tr>
<tr>
<td>Cr</td>
<td>0.0</td>
<td>0.12</td>
<td>0</td>
</tr>
<tr>
<td>Hg</td>
<td>9</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>Ni</td>
<td>78</td>
<td>164</td>
<td>158</td>
</tr>
<tr>
<td>Zn</td>
<td>32</td>
<td>6</td>
<td>3</td>
</tr>
</tbody>
</table>
Table 4. Major and trace analysis of the oxide fraction of the High Temperature Ash (HTA) from burning of the bituminous (PSOC1451), the sub-bituminous (DECS26), and the lignite (PSOC1443) coals. Data was obtained from the Penn State Coal Sample Bank.

<table>
<thead>
<tr>
<th>Oxide element analysis: oxide as % of mass of HTA</th>
<th>PSOC 1451 (Bituminous)</th>
<th>DECS 26 (Sub-bituminous)</th>
<th>PSOC 1443 (Lignite)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>54.40</td>
<td>31.7</td>
<td>47.9</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>24.50</td>
<td>16.1</td>
<td>22.2</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>1.14</td>
<td>1.27</td>
<td>1.75</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>9.16</td>
<td>4.84</td>
<td>3.51</td>
</tr>
<tr>
<td>MgO</td>
<td>0.85</td>
<td>4.64</td>
<td>2.79</td>
</tr>
<tr>
<td>CaO</td>
<td>2.97</td>
<td>23.5</td>
<td>14.0</td>
</tr>
<tr>
<td>Na$_2$O</td>
<td>0.61</td>
<td>1.80</td>
<td>0.37</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>2.02</td>
<td>0.40</td>
<td>0.55</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0.34</td>
<td>0.89</td>
<td>0.11</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>2.30</td>
<td>12.7</td>
<td>7.00</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Trace element analysis: element as ppm of mass of HTA</th>
<th>PSOC 1451 (Bituminous)</th>
<th>DECS 26 (Sub-bituminous)</th>
<th>PSOC 1443 (Lignite)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>-</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Ba</td>
<td>540</td>
<td>4657</td>
<td>1080</td>
</tr>
<tr>
<td>Mn</td>
<td>140</td>
<td>155</td>
<td>1500</td>
</tr>
<tr>
<td>Cr</td>
<td>150</td>
<td>45</td>
<td>120</td>
</tr>
<tr>
<td>Hg</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Ni</td>
<td>65</td>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td>Sr</td>
<td>590</td>
<td>2452</td>
<td>1100</td>
</tr>
<tr>
<td>Zn</td>
<td>85</td>
<td>85</td>
<td>20</td>
</tr>
</tbody>
</table>

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 and EMA techniques. A comparison of the results of these two techniques is shown in Table 5 for the PM$_{0.1-0.18}$ from burning of the lignite coal in 40%O$_2$-60%CO$_2$ atmosphere. Results from the EMA and SEM-EDS analyses were comparable to some degree, as seen in Table 5. SEM-EDS predicted higher concentrations than the EMA technique for most of the major elements, particularly for sulfur (S) content. EMA was able to detect titanium (Ti), even though it exists in trace amounts. Despite its ability to detect the trace amounts of Ti, EMA has limitations detecting amounts ranging from 50 to 100 ppm (0.005-0.010 wt %). As a result,
some other trace elements could not be detected by this technique. In this work SEM-EDS was chosen for the routine analysis of all samples, as it was readily-available in the premises and cost-effective. Selected samples were also analyzed by EMA.

Table 5. Chemical composition (mass % of ash content) of submicron ash particles (stage 9, PM\(_{0.1-0.18}\)) from burning of a lignite coal (PSOC 1443) in a 40% O\(_2\) - 60% CO\(_2\) atmosphere.

<table>
<thead>
<tr>
<th></th>
<th>Si(%)</th>
<th>Mg(%)</th>
<th>Fe(%)</th>
<th>Ca(%)</th>
<th>Na(%)</th>
<th>S(%)</th>
<th>Ti(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEM-EDS</td>
<td>6.7</td>
<td>4.4</td>
<td>12.8</td>
<td>3.6</td>
<td>10.1</td>
<td>16.2</td>
<td>0.00</td>
</tr>
<tr>
<td>EMA</td>
<td>4.2</td>
<td>3.2</td>
<td>12.1</td>
<td>2.1</td>
<td>11.1</td>
<td>7.5</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Quann et al.\(^{19, 44}\) and Buhre et al.\(^2\) used PM\(_{0.3}\) to represent the submicron ash particles formed via the vaporization and condensation mechanism, based on their instrument configurations (i.e., reporting on particles collected on the filter stage of 8 stage\(^{19, 44}\) and 7 stage\(^2\) cascade impactors, respectively). In the present work, the ash particulate matter collected on stage 9 (PM\(_{0.1-0.18}\)) was chosen to represent the PM\(_{0.3}\) range based on the assumption that the chemical composition of the PM\(_{0.3}\) ash does not vary significantly with particle diameter in the 0.3>d range, as documented in Refs\(^{20-22}\). This assumption was verified herein by comparing stage 9 (PM\(_{0.1-0.18}\)) and stage 10 (PM\(_{0.056-0.1}\)) ash compositions of the lignite coal as well as stage 9 (PM\(_{0.1-0.18}\)) and stage 11 (PM\(_{0.032-0.056}\)) ash compositions of the sub-bituminous coal. In order to calculate the major elements yield in PM\(_{0.3}\) emissions and compare with the results of Quann and Sarofim\(^{15}\) and Buhre et al.\(^2\), the mass fraction of the major elements obtained from analysis of PM\(_{0.1-0.18}\) (stage 9 ash particles) were multiplied by the mass yields of PM\(_{0.32}\) of this impactor, calculated from the total mass accumulated on stages from 8 to 13. Yields of the vaporized major elements found in the PM\(_{0.32}\) of the three coals burning in either air or in two plausible oxy-fuel atmospheres (30% O\(_2\) - 70% CO\(_2\), 40% O\(_2\) - 60% CO\(_2\)) are shown in Figure 3. Based on the
SEM-EDS analysis, the PM$_{0.32}$ of the bituminous, the sub-bituminous, and the lignite coals were mainly composed of Si, Al, Fe, Mg, Ca, K, Na, and S. As shown in Figure 3, the yields of the elements in these submicron particles (PM$_{0.32}$) from the combustion of all three coals were typically lower under oxy-coal conditions than those under conventional air combustion. The decrease in the yields were typically more pronounced in the 30% O$_2$-70% CO$_2$ atmosphere.

![Figure 3. Yields of the vaporized major elements (based on analysis of stage 9 (PM$_{0.1-0.18}$) with SEM-EDS) of submicron ash particles (PM$_{0.32}$) emitted from combustion of a bituminous (PSOC 1451), a lignite (PSOC 1443), and a sub-bituminous (DECS 26) coal in air and in two plausible oxy-fuel atmospheres (30%O$_2$-70%CO$_2$ and 40%O$_2$-60%CO$_2$). Yields are represented in mg/g$_{coal burned}$ units. Error bars signify standard deviations.]

Increasing O$_2$ mole fraction from 30% to 40% in CO$_2$ background gas increased the yields of the major elements, as shown in Figure 3. This can be attributed to the increase in both the mass fraction of some of these elements in the submicron particles (PM$_{0.32}$) and the total.
mass yields of these submicron particles. Overall, the elemental composition of the High Temperature Ash (HTA) of the parent coals, namely SiO$_2$, MgO, CaO, and K$_2$O (see Table 4), was reflected in the composition of the submicron ash particles, shown in Figure 3.

Mass fractions of the major elements detected in the PM$_{0.1-0.18}$ and PM$_{0.56-1}$ from burning of the three coals in air (21%O$_2$-79%N$_2$), in 60%O$_2$-40%N$_2$, and in three simulated oxy-fuel atmospheres (30%O$_2$-70%CO$_2$ and 40%O$_2$-60%CO$_2$, 60%O$_2$-40%CO$_2$) are provided in Table 6. Sulfur (S) and silicon (Si) had the largest mass fractions of the PM$_{0.1-0.18}$ compositions of the bituminous and lignite coals, whereas in the case of sub-bituminous coal, sulfur (S) and iron (Fe) had the largest mass fractions of these particles’ compositions in air. However, the mass fractions of S were markedly lower in the compositions of large particle submicron particulate matter (PM$_{0.56-1}$) of all coals, while mass fractions of Si and Al were higher. Moreover, in the case of sub-bituminous coal, mass fraction of Ca in the composition of large particle submicron particulate matter (PM$_{0.56-1}$) was drastically higher while that of Fe was much lower in air.

The mass fractions of the elements in PM$_{0.56-1}$ remained relatively unchanged with respect to the oxidizing environment composition. However, the composition of these ash particles was highly-dependent on the parent coal type and its mineral composition. For instance, HTA analysis of the sub-bituminous coal showed that it has the lowest SiO$_2$, Al$_2$O$_3$, and K$_2$O and the highest MgO and CaO contents among the three coals (see Table 4); this was in agreement with the respective major element fractions (Si, Al, K, Mg, and Ca) in the PM$_{0.56-1}$ ashes (see Table 6). A similar relationship can also be observed between the HTA analysis of the bituminous and lignite coals and the SEM-EDS analysis of their PM$_{0.56-1}$ ashes. The PM$_{0.1-0.18}$ ashes of all coals exhibited typically slight decreases in the fractions of Si, Al, Fe, and Ca elements in the oxy-fuel
atmospheres, as compared to air. Finally, increasing the oxygen mole fraction up to 60% in both N\textsubscript{2} and CO\textsubscript{2} background gas, increased the PM\textsubscript{0.1-0.18} elemental fractions of Si, Al, and Ca and decreased those of Na, K, and S. Moreover, a significant increase in Ca mole fraction caused a major decrease in the Fe mole fraction in the PM\textsubscript{0.1-0.18} composition of the sub-bituminous coal.

Table 6. Comparison of the chemical compositions, given as mass\% of stage 9 (PM\textsubscript{0.1-0.18}) and stage 6 (PM\textsubscript{0.56-1}) ash particles, based on SEM-EDS, emitted from combustion of a bituminous (PSOC 1451), a sub-bituminous (DECS 26), and a lignite (PSOC 1443) coal in air, 60%O\textsubscript{2}-40%N\textsubscript{2} and three simulated oxy-fuel atmospheres (30%O\textsubscript{2}-70%CO\textsubscript{2}, 40%O\textsubscript{2}-60%CO\textsubscript{2}, and 60%O\textsubscript{2}-40%CO\textsubscript{2}).

<table>
<thead>
<tr>
<th>Major elements</th>
<th>In Ambient Gases</th>
<th>PSOC 1451 (Bituminous)</th>
<th>DECS 26 (Sub-bituminous)</th>
<th>PSOC 1443 (Lignite)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Stg 9 PM\textsubscript{0.1-0.18}</td>
<td>Stg6 PM\textsubscript{0.56-1}</td>
<td>Stg9 PM\textsubscript{0.1-0.18}</td>
</tr>
<tr>
<td>Si</td>
<td>Air</td>
<td>12.2</td>
<td>23.6</td>
<td>1.9</td>
</tr>
<tr>
<td></td>
<td>60%O\textsubscript{2}-40%N\textsubscript{2}</td>
<td>27.8</td>
<td>-</td>
<td>3.4</td>
</tr>
<tr>
<td></td>
<td>30%O\textsubscript{2}-70%CO\textsubscript{2}</td>
<td>11.8</td>
<td>18.7</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>40%O\textsubscript{2}-60%CO\textsubscript{2}</td>
<td>12.0</td>
<td>22.9</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>60%O\textsubscript{2}-40%CO\textsubscript{2}</td>
<td>30.4</td>
<td>-</td>
<td>3.6</td>
</tr>
<tr>
<td>Al</td>
<td>Air</td>
<td>7.4</td>
<td>15.6</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>60%O\textsubscript{2}-40%N\textsubscript{2}</td>
<td>7.6</td>
<td>-</td>
<td>5.1</td>
</tr>
<tr>
<td></td>
<td>30%O\textsubscript{2}-70%CO\textsubscript{2}</td>
<td>4.7</td>
<td>12.7</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>40%O\textsubscript{2}-60%CO\textsubscript{2}</td>
<td>7.0</td>
<td>15.5</td>
<td>1.3</td>
</tr>
<tr>
<td></td>
<td>60%O\textsubscript{2}-40%CO\textsubscript{2}</td>
<td>7.6</td>
<td>-</td>
<td>3.9</td>
</tr>
<tr>
<td>Fe</td>
<td>Air</td>
<td>11.4</td>
<td>16.0</td>
<td>22.8</td>
</tr>
<tr>
<td></td>
<td>60%O\textsubscript{2}-40%N\textsubscript{2}</td>
<td>11.4</td>
<td>-</td>
<td>8.9</td>
</tr>
<tr>
<td></td>
<td>30%O\textsubscript{2}-70%CO\textsubscript{2}</td>
<td>8.4</td>
<td>27.2</td>
<td>17.5</td>
</tr>
<tr>
<td></td>
<td>40%O\textsubscript{2}-60%CO\textsubscript{2}</td>
<td>9.5</td>
<td>17.1</td>
<td>21.0</td>
</tr>
<tr>
<td></td>
<td>60%O\textsubscript{2}-40%CO\textsubscript{2}</td>
<td>11.8</td>
<td>-</td>
<td>8.6</td>
</tr>
<tr>
<td>Mg</td>
<td>Air</td>
<td>0.5</td>
<td>0.8</td>
<td>10.8</td>
</tr>
<tr>
<td></td>
<td>60%O\textsubscript{2}-40%N\textsubscript{2}</td>
<td>0.5</td>
<td>-</td>
<td>6.6</td>
</tr>
<tr>
<td></td>
<td>30%O\textsubscript{2}-70%CO\textsubscript{2}</td>
<td>0.7</td>
<td>0.7</td>
<td>7.4</td>
</tr>
<tr>
<td></td>
<td>40%O\textsubscript{2}-60%CO\textsubscript{2}</td>
<td>1.3</td>
<td>0.8</td>
<td>12.0</td>
</tr>
<tr>
<td></td>
<td>60%O\textsubscript{2}-40%CO\textsubscript{2}</td>
<td>0.5</td>
<td>-</td>
<td>8.7</td>
</tr>
<tr>
<td>Ca</td>
<td>Air</td>
<td>1.5</td>
<td>2.0</td>
<td>7.1</td>
</tr>
<tr>
<td></td>
<td>60%O\textsubscript{2}-40%N\textsubscript{2}</td>
<td>2.2</td>
<td>-</td>
<td>32.2</td>
</tr>
<tr>
<td></td>
<td>30%O\textsubscript{2}-70%CO\textsubscript{2}</td>
<td>1.4</td>
<td>3.9</td>
<td>6.9</td>
</tr>
<tr>
<td></td>
<td>40%O\textsubscript{2}-60%CO\textsubscript{2}</td>
<td>1.5</td>
<td>4.6</td>
<td>10.7</td>
</tr>
<tr>
<td></td>
<td>60%O\textsubscript{2}-40%CO\textsubscript{2}</td>
<td>2.8</td>
<td>-</td>
<td>27.9</td>
</tr>
<tr>
<td>Na</td>
<td>Air</td>
<td>4.0</td>
<td>2.3</td>
<td>8.5</td>
</tr>
<tr>
<td></td>
<td>60%O\textsubscript{2}-40%N\textsubscript{2}</td>
<td>2.9</td>
<td>-</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>30%O₂-70%CO₂</td>
<td>40%O₂-60%CO₂</td>
<td>60%O₂-40%CO₂</td>
<td>K</td>
</tr>
<tr>
<td>------------------</td>
<td>--------------</td>
<td>--------------</td>
<td>--------------</td>
<td>-----------</td>
</tr>
<tr>
<td>Air</td>
<td></td>
<td></td>
<td></td>
<td>2.9</td>
</tr>
<tr>
<td>60%O₂-40%N₂</td>
<td>2.3</td>
<td>1.9</td>
<td>1.4</td>
<td>1.5</td>
</tr>
<tr>
<td>30%O₂-70%CO₂</td>
<td>5.2</td>
<td>2.7</td>
<td>2.4</td>
<td>1.7</td>
</tr>
<tr>
<td>40%O₂-60%CO₂</td>
<td>3.9</td>
<td>5.0</td>
<td>1.4</td>
<td>0.9</td>
</tr>
<tr>
<td>60%O₂-40%CO₂</td>
<td>1.4</td>
<td>-</td>
<td>2.5</td>
<td>-</td>
</tr>
<tr>
<td>40%O₂-60%CO₂</td>
<td>1.9</td>
<td>2.8</td>
<td>15.5</td>
<td>4.6</td>
</tr>
<tr>
<td>60%O₂-40%CO₂</td>
<td>10.5</td>
<td>-</td>
<td>12.7</td>
<td>-</td>
</tr>
</tbody>
</table>

3.5. Discussion

3.5.1. Submicron Ash (PM₁) Composition

PM₀.₃₂ was considered in this study as representative of ultrafine ash particles which were assumed to be formed by vaporization of the mineral inclusions followed by condensation⁹, 2¹, 2³-⁴⁵, 2⁶, 4⁷. Based on the experimental studies conducted by Yu et al.²¹, ²² and Teramae and Takarada²⁰, a constant elemental mass fraction size distribution throughout the size range of these ultrafine particles was assumed. Yu et al.²¹, ²² and Teramae and Takarada²⁰ reported the mass fraction size distribution of common elements found in the ash to be tri-modal, as mentioned earlier. Accordingly, Si, Al, and S presented in Refs ²⁰-²², exhibited constant mass fractions with size for ash particles below 0.3 µm (ultrafine particles). In ash particles with sizes between 0.3 and 3 µm (central mode) Si and Al increased with increasing size whereas S decreased. Similar results were observed in this study, the mass fractions of Si and Ca were increased while those of Na and S were decreased (see Table 6 and Figure 4). Finally, in coarse mode ash particles (above 3 µm), again the mass fractions of Si, Al, and S remained constant with size.
Figure 4. 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), a sub-bituminous (DECS 26), and a lignite (PSOC 1443) coal in air.

The yields of Si found in submicron ash particles of all three coals ranged from 10 to 126 µg/g$_{\text{coal burned}}$ in air combustion, shown in Fig. 3, which are lower than the value of 280 µg/g$_{\text{coal burned}}$ reported elsewhere for a sub-bituminous coal burning under similar conditions$^{10}$. This difference can be attributed to the particle sizes chosen to represent submicron ashes, and to the Si contents of the corresponding parent coals. Suriyawong et al.$^{10}$ assumed that the submicron mode is represented by PM$_{0.5}$, whereas in this study the submicron mode was assumed to be represented by PM$_{0.32}$, following the practice of Quann et al.$^{19,44}$ and Buhre et al.$^{2}$. This was also supported by the nature of the ash particle size distributions (PSDs) from the same coals, presented in Kazanc and Levendis$^{9}$, which showed an ultrafine particle mode around 0.2 µm. Had PM$_{0.5}$ also been used in this study to represent submicron ash emissions, then the corresponding Si yields would have been in the range of 13-321 µg/g$_{\text{coal burned}}$. On the other hand, in the study of Quann et al.$^{19,44}$, the Si yield found in the PM$_{0.3}$ spanned from 40 to 350 µg/g$_{\text{coal burned}}$, which is higher than the corresponding range in this study, see Fig. 2 therein and Fig. 3 herein. This may be explained by the higher furnace temperature (1750 K) used in the study of Quann et al.$^{19,44}$ as compared to this study (1400 K).
The yields of major elements in ultrafine ash particles (PM$_{0.32}$) collected from the combustion of all three coals typically increased with increasing oxygen mole fraction in either N$_2$ or CO$_2$ background gases. This was attributed to increasing particle temperatures with increasing O$_2$ mole fractions, as illustrated in Table 7, which lists data collected in this laboratory$^{17}$. Coal char temperatures typically vary between 1700 and 2600 K, under the combustion conditions tested herein. On the other hand, vaporization temperatures of metal sub-oxides and other elements in the ash vary widely, as shown in Table 8, from 718 K for elemental sulfur to 3873 K for MgO and, even, 4123 K for CaO. Compounds that have a vaporization temperature that is much lower or much higher than the aforementioned 1700-2600 K char combustion temperature range are not affected much by temperature variations within this range. The former vaporize before any of the temperatures in this range are reached, whereas the latter do not significantly vaporize until much higher temperatures are reached. It is the elements with vaporization temperatures inside this range that are affected the most by the magnitude of the combustion temperature change, as oxygen mole fraction varies. Those elements are notably Si, Ca and most likely Al, based on the boiling points of their reduced oxides (SiO, Ca, AlO). Hence, as the oxygen mole fraction increases, the mass fraction of these elements in the fine particle ashes (PM$_{0.1-0.18}$) typically increases, as seen in Table 6 and Figure 5, at the expense (percentage-wise) of the remaining elements (mostly Na, K, S, but also in some cases Fe and Mg).
Figure 5. Comparison of the chemical compositions, given as mass%, of stage 9 (PM_{0.1-0.18}) ash particles, based on SEM-EDS, emitted from combustion of a bituminous (PSOC 1451), a sub-bituminous (DECS 26), and a lignite (PSOC 1443) coal in air and in 60%O_2-40%N_2 environments.

The comparison of the ultrafine particle ash (PM_{0.1-0.18}) composition in air and in oxy-fuel combustion conditions is more complicated and trends are less clear, as two influential parameters, particle temperature and background gas partial pressure, change simultaneously. However, the particle temperature can be nearly-equalized, when combustion of chars in air is contrasted to combustion in 30%-40%O_2/CO_2, see Table 7. In such cases the effect of the background gas on the composition these fine particles can be isolated and assessed. In such cases, ash components containing Si, Ca Al, Fe Mg, etc. are less expected to form in CO_2-containing atmospheres, based on the mechanisms of formation of their reduced oxides: SiO, Ca, AlO, FeO, MgO, etc. Indeed, when nitrogen was replaced by carbon dioxide and the oxygen mole fraction was appropriately elevated to even out the combustion temperatures, the mass fraction of these elements in the ultrafine particle ashes (PM_{0.1-0.18}) typically decreased, see Table 6, at the expense (percentage-wise) of the remaining elements (mostly Na, K and S).
Table 7. Experimentally-observed char burnout times, as well as maximum and average deduced char combustion temperatures of the bituminous (PSOC 1451), sub-bituminous (DECS 26), and lignite (PSOC 1443) coals in various environments.

<table>
<thead>
<tr>
<th>Coals Burned</th>
<th>In Ambient Gases</th>
<th>Observed Burnout times (ms)</th>
<th>Maximum char combustion temperatures (K)</th>
<th>Average char combustion temperatures (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bituminous (PSOC 1451)</td>
<td>Air</td>
<td>58</td>
<td>1825</td>
<td>1713</td>
</tr>
<tr>
<td></td>
<td>40% O₂-60%N₂</td>
<td>30</td>
<td>2117</td>
<td>1990</td>
</tr>
<tr>
<td></td>
<td>60% O₂-40%N₂</td>
<td>20</td>
<td>2462</td>
<td>2350</td>
</tr>
<tr>
<td></td>
<td>30% O₂-70%CO₂</td>
<td>95</td>
<td>1821</td>
<td>1710</td>
</tr>
<tr>
<td></td>
<td>40% O₂-60%CO₂</td>
<td>70</td>
<td>2090</td>
<td>1880</td>
</tr>
<tr>
<td></td>
<td>60% O₂-40%CO₂</td>
<td>35</td>
<td>2430</td>
<td>2310</td>
</tr>
<tr>
<td>Sub-bituminous (DECS 26)</td>
<td>Air</td>
<td>37</td>
<td>2131</td>
<td>2020</td>
</tr>
<tr>
<td></td>
<td>40% O₂-60%N₂</td>
<td>25</td>
<td>2418</td>
<td>2300</td>
</tr>
<tr>
<td></td>
<td>60% O₂-40%N₂</td>
<td>17</td>
<td>2665</td>
<td>2540</td>
</tr>
<tr>
<td></td>
<td>30% O₂-70%CO₂</td>
<td>62</td>
<td>1728</td>
<td>1680</td>
</tr>
<tr>
<td></td>
<td>40% O₂-60%CO₂</td>
<td>32</td>
<td>2084</td>
<td>1975</td>
</tr>
<tr>
<td></td>
<td>60% O₂-40%CO₂</td>
<td>14</td>
<td>2380</td>
<td>2275</td>
</tr>
<tr>
<td>Lignite (PSOC 1443)</td>
<td>Air</td>
<td>47</td>
<td>2069</td>
<td>1930</td>
</tr>
<tr>
<td></td>
<td>40% O₂-60%N₂</td>
<td>31</td>
<td>2204</td>
<td>2140</td>
</tr>
<tr>
<td></td>
<td>60% O₂-40%N₂</td>
<td>20</td>
<td>2600</td>
<td>2508</td>
</tr>
<tr>
<td></td>
<td>30% O₂-70%CO₂</td>
<td>50</td>
<td>1941</td>
<td>1860</td>
</tr>
<tr>
<td></td>
<td>40% O₂-60%CO₂</td>
<td>42</td>
<td>2033</td>
<td>1920</td>
</tr>
<tr>
<td></td>
<td>60% O₂-40%CO₂</td>
<td>24</td>
<td>2550</td>
<td>2465</td>
</tr>
</tbody>
</table>

Table 8. Vaporization temperatures of some common oxides as well as sub-oxides and metals (reduced oxides) found in their ashes (from Ref. and other web-based sources).

<table>
<thead>
<tr>
<th></th>
<th>CaO</th>
<th>Ca</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>SiO</th>
<th>FeO</th>
<th>MgO</th>
<th>Mg</th>
<th>Na₂O</th>
<th>Na</th>
<th>K</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>T_{vaporization} (K)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4123</td>
<td>1757</td>
<td>3253</td>
<td>2500</td>
<td>2153</td>
<td>3687</td>
<td>3873</td>
<td>1380</td>
<td>1405</td>
<td>1156</td>
<td>1032</td>
<td>718</td>
</tr>
</tbody>
</table>

As shown in Table 6, the PM_{0.56-1} (stage 6) of the all three coals in this study were mainly composed of Si and Al regardless of the combustion conditions, an observation which is in line with related works in the literature (Buhre et al., Yu et al., Teramae and Takarada). On the
contrary, the PM$_{0.1-0.18}$ (stage 9) particles were mostly composed of S, which agrees with the findings of Buhre et al.$^2$, Yu et al.$^{21, 22}$ and Teramae and Takarada$^{20}$. According to Buhre et al.$^2$, sulfur is present in the form of sulfates of the alkali and alkaline earth metals, however, a portion may be present in the form of sulfuric acid. The mass fraction of sulfur decreased in the PM$_{0.1-0.18}$ with increasing oxygen mole fraction in both background gases, see Table 6, as in the findings of Buhre et al.$^2$. The average mass fraction of sulfur in submicron particles (<0.3 µm) in the study of Buhre et al.$^2$, calculated from Table 4 therein for five different bituminous coals, was 17.8% in air. That number correlates well with the 17.3% and 17.5% mass fractions of sulfur in PM$_{0.1-0.18}$ emissions from burning of bituminous and sub-bituminous coals herein. Although the Fe content of the sub-bituminous coal is the lowest of all coals, the PM$_{0.1-0.18}$ of this coal has the highest Fe mole fraction in air and in moderate oxy-fuel conditions (average of 20.4%), which is parallel to the findings of Quann et al.$^{19}$ and Jia and Lighty$^{30}$ in the case of sub-bituminous coals burned therein. Quann et al.$^{19}$ attributed this phenomenon to the form of the iron found in sub-bituminous coal. Pyrite (FeS$_2$) can be found in coal either as an extraneous mineral (pyrite) or as an inclusion in the char organic matrix. The former form burns exothermically and was suggested to contribute more to submicron particle formation, however the latter form was assumed to undergo reduction reaction to form more volatile sub-oxides$^{19}$. According to this explanation, possible high content of the pyrite in extraneous mineral form in the sub-bituminous coal may lead to the high Fe mole fraction in PM$_{0.1-0.18}$. Moreover, as oxygen mole fraction increased to 60% in either N$_2$ or CO$_2$, the Fe mole fraction decreased and the Ca mole fraction increased significantly in the sub-bituminous coal PM$_{0.1-0.18}$. This is due to the higher sensitivity of Ca to the temperature increase as compared to that of Fe, as discussed above. The yield of Fe was not substantially affected by the increase in oxygen mole fraction; however, as the yield and
percentage of Ca increased markedly with increasing oxygen mole fraction, the percentage of the Fe decreased in the PM$_{0.1-0.18}$ of the sub-bituminous coal.

3.5.2. Comparison of experimental data with predictions from the vaporization model of Quann and Sarofim$^{15}$

As shown in Figure 3, the major element yields in the PM$_{0.32}$ were higher from combustion of all three coals in air than from combustion in CO$_2$-containing environments. This is in line with the reduction mechanism of Quann and Sarofim$^{15}$, where refractory metal oxides (MO$_n$(s)) are reduced by CO (generated from the char oxidation) to more volatile metal sub-oxides (MO$_{n-1}$(v)) and CO$_2$. In oxy-combustion, however, the presence of high partial pressures of CO$_2$ in the bulk gas is expected to impede such reduction reactions that result in vaporization of metal oxides and, consequently, to impede the formation of submicron ash.

MO$_n$(s) + CO = MO$_{n-1}$(v) + CO$_2$  ... (1)

For example: SiO$_2$(s) + CO = SiO(v) + CO$_2$

P$^e_m$ = ($K_e$ × P$_{CO}$)/P$_{CO2}$  ... (2)

$K_e$ = (P$^e_m$ × P$_{CO2}$)/(a$_m$ × P$_{CO}$),  a$_m$=1  ... (3)

P$_{CO}$ = (2 × P$_{O2}$)/(1 + P$_{O2}$)  ... (4)  the derivation of this equation is shown in Appendix 1.

A range of the partial pressures of SiO at the char surfaces was calculated based on Quann and Sarofim’s ash vaporization model$^{15}$ using the time-independent values for the partial pressure of CO (P$_{CO}$) calculated from Eqn. (4).
Alternatively, time-dependent values for the partial pressure of CO were derived from the predictions of a comprehensive multi-scale, multi-phase and multi-component model which was able to describe combustion and gasification of coal particles, see Maffei et al. The model solved energy and mass balance equations for gas and solid phases, together with empirical sub-models used for the closure of the balance equations. Various kinetic mechanisms were considered to describe the different reaction steps. Pyrolysis was treated as a primary process by which the coal produced residual char, heavy volatile species (tar) and permanent gaseous products. The released volatiles mixed with the surrounding gas in the drop tube reactor and underwent secondary gas phase reactions. The char solid residue interacted with surrounding gases by heterogeneous reactions. A detailed description of this combustion model has been reported elsewhere. Herein the Quann and Sarofim’s ash vaporization model was coupled with the aforesaid combustion model and the evolution times of the SiO partial pressures were calculated by incorporating the thermodynamic equilibrium approach for the formation of metal sub-oxides shown above (Eqns. 1-3). Temporal and spatial evolution of profiles of CO and CO₂, illustrated in Fig. 7, and profiles of temperature within a coal particle were computed by the combustion model. Hence, in this case, Eqn. 4 was not used. The average partial pressure of SiO was evaluated throughout a particle’s burnout time as an integral average, defined by:

\[
\overline{P_{SiO}} = \frac{\int_{t_0}^{t_f} P_{SiO} \, dt}{t_f - t_0} \quad \cdots \quad (5)
\]

where \(P_{SiO}\) is the instantaneous partial pressure of SiO, \(t_0\) and \(t_f\) are the limits of the integration, respectively. The initial time of SiO formation was taken as the onset of ignition and the final time was taken as the particle extinction.
Results of both calculations are shown in Figure 6. The lower and upper limits of the Quann and Sarofim’s ash vaporization model were calculated based on a perturbation analysis of physical properties of the coals, i.e. pore radius, porosity, tortuosity and Thiele modulus. The partial pressure of the SiO was assumed to be linearly-dependent on the initial radius of the char and on the effective pore radius therein, see Equations A3-2 and A3-12 in Appendix 3; however it is inversely proportional to tortuosity and to the ash inclusion size of the mineral oxide, see Equations A3-2, A3-7, and A3-12 in Appendix 3. Quann used a (micropore) pore radius of 25 Å in his work for all coal types, however larger pore sizes (messo- or macro-pores) may be more effective in transport phenomena. Sahu et al. reported a macro-pore radius of 0.15 µm for the particular bituminous coal in this study. As it is not known in priori which is the most effective pore size range in this process, the pore size of the char was perturbed by three orders of magnitude in the model to cover the entire range between the aforesaid sizes. As shown in Figure 6, the upper limit of the Quann and Sarofim’s ash vaporization model range, which was calculated with a pore size of 0.15 µm, showed a better agreement with the experimental values. This can be explained by the enhanced transport of volatile species in such macropores. As in the size cut used herein the coal particle diameter varied between 53 and 90 µm, the radius of the char was varied in the range of 25-45 µm in the calculations. As there is no clear information on the tortuosity in the literature, it was varied between 1.5 and 3 based on Ref. Quann mentioned a range of 0.25 to 1 µm for the mineral inclusion radius, hence this range was also covered in this calculations of the model.
Figure 6. Comparison of the partial pressures of SiO ($P_{\text{SiO}}$) at the char surface; a) calculated from experimental data, b) derived from Quann and Sarofim’s model\cite{15} predictions, and c) computed from Quann and Sarofim’s model\cite{15} coupled to a detailed char combustion code\cite{16,49}. Values are represented with respect to maximum average char temperature.
Experimentally-derived partial pressures of SiO ($P_{\text{SiO}}$) at the surface of burning chars were calculated as exemplified in Appendix 3; they were superimposed on Fig. 6, with respect to measured temperatures of chars, averaged over their burnout histories listed in Table 7. As shown in Figure 6, experimental $P_{\text{SiO}}$ values typically lie in the range of Quann and Sarofim’s ash vaporization model$^{15}$ predictions in both N$_2$ and CO$_2$ environments. When Quann and Sarofim’s ash vaporization model$^{15}$ was coupled with the combustion model of Maffei et al. $^{16,49}$ the results also show a reasonable agreement with the experimental data, in particular with those obtained at the lower oxygen mole fractions; however, at higher oxygen mole fractions, the experimental data was over-predicted, particularly in O$_2$/N$_2$ environments.

The upper limit of the model calculations of Quann and Sarofim’s ash vaporization model coupled with the combustion model of Maffei et al. $^{16,49}$ represents maximum $P_{\text{SiO}}$ calculated at peak temperatures; the lower limit represents average time-integrated $P_{\text{SiO}}$ values throughout char burnout, based on Eqn. 5. This model$^{16}$ showed higher sensitivity to temperature than both Quann and Sarofim’s ash vaporization model$^{15}$ and the experimental data. In O$_2$/CO$_2$ environments, both approaches showed similar temperature dependence for the calculated SiO partial pressure. The slope of the experimentally obtained $P_{\text{SiO}}$ versus temperature was lower than those predicted by the models, particularly in the case of the CO$_2$ background gas.

According to Quann and Sarofim$^{15}$ for coal particle combustion in air and in other O$_2$/N$_2$ environments the only source of carbon dioxide in the bulk gas is the reduction reaction shown in Equation (1); therefore, the mole fraction of CO$_2$ is equal to the mole fraction of mineral oxide (i.e. SiO), which is a very low value compared to the calculated CO mole fraction. On the contrary, the combustion model of Maffei et al.$^{16,49}$ considers various CO$_2$ formation
mechanisms, as a consequence of the different reaction steps of pyrolysis\textsuperscript{50} and heterogeneous reactions\textsuperscript{16} involved in the coal combustion process. In air combustion, the CO\textsubscript{2} mole fraction evaluated by this combustion model\textsuperscript{16} is shown in Fig. 7. It is higher than that computed by the Quann and Sarofim’s approach\textsuperscript{15} which turns out to be nearly zero.

![Graph showing temporal evolution of mole fractions of O\textsubscript{2}, CO, CO\textsubscript{2}, and H\textsubscript{2}O at the surface of a sub-bituminous coal char particle during burning in air. Quann and Sarofim’s CO value is superimposed to the pertinent graph with a black horizontal line.](image)

Figure 7. Temporal evolution of the mole fractions of O\textsubscript{2}, CO, CO\textsubscript{2}, and H\textsubscript{2}O at the surface of an 85 μm sub-bituminous coal char particle during burning in air. Quann and Sarofim’s CO value is superimposed to the pertinent graph with a black horizontal line.

Figure 7 shows the profiles of several species within a sub-bituminous coal particle burning in air. During the high heating rate devolatilization process, coal expediently releases volatile matter as gas (e.g. CO, CO\textsubscript{2}) and tar and this causes a sharp reduction of O\textsubscript{2} mole fractions. The successive peaks, at about 15 ms, correspond to a further release of CO, CO\textsubscript{2} and H\textsubscript{2}O, derived from chemi-adsorbed species in the metaplastic phase. Once the pyrolysis process is nearly-concluded, O\textsubscript{2} penetrates within the particle and reacts with the solid residue. The O\textsubscript{2} mole fraction profile in Fig 7a shows that the particle combustion is partially controlled by O\textsubscript{2} diffusion from the bulk to the core of the particle. Due to the diffusion limitations, O\textsubscript{2} can arrive to the particle core only after ~50 ms, upon complete conversion of the external particle shells. CO is the main gaseous product of the heterogeneous reactions. The CO, CO\textsubscript{2} peaks observed at
~35 ms and ~50 ms are the products of the combustion reaction of different solid residue components.

In the Quann and Sarofim ash vaporization model the CO mole fraction was calculated based on the assumption of stoichiometry for Reaction (1), as outlined in Appendix 2. The calculated CO mole fraction using Eq. 4 in air was higher than the predictions of Maffei et al., see Fig. 7. The char temperatures that were input to Quann and Sarofim’s model were pyrometrically measured in this laboratory, whereas the char temperatures of Maffei et al. were computed using their combustion code. The discrepancy in the temperature ranges in Figure 6 stems from the aforesaid difference in these two approaches.

Experimentally-observed average coal char particle temperatures and total char burnout times, shown in Table 7, were used to calculate partial pressures of the metal oxides; however the reader should keep in mind that most of the ash vaporization may occur in a short period of time during a char particle’s burnout when maximum temperature is achieved. Increasing temperatures and decreasing burnout times in calculations would increase the experimental values of the partial pressures of most metal sub-oxides and the predictions of the same using Quann and Sarofim’s ash vaporization model.

According to combustion observations made in this laboratory, the radius of bituminous coal chars changes little during burnout, therefore constant radius is assumed for this coal in the calculations shown in Appendix 3. However, the radii of sub-bituminous and lignite coals in this study were observed to be shrinking during char burnout, therefore a shrinking core model was used for these two coals to calculate their time average radiiuses using Eqn. A4-(1b).
The partial pressure of SiO ($P_{SiO}$) was mostly affected by char temperature and CO$_2$ bulk mole fraction, see Appendix 3. Increasing temperature increased $P_{SiO}$, however increasing bulk CO$_2$ mole fraction decreased $P_{SiO}$. As seen from both experimental and model results in Fig. 6, $P_{SiO}$ were lower under oxy-combustion conditions as compared to air. To understand the effect of CO$_2$ on $P_{SiO}$, char temperatures in air and oxy-conditions need to be matched. In the case of the bituminous coal, air and 30%O$_2$–70%CO$_2$ atmospheres resulted in similar deduced char particle temperatures (see Table 7). However in the cases of sub-bituminous and lignite coals the char temperatures matched better in air and 40%O$_2$–60%CO$_2$ atmospheres. In these cases, temperature effect were nearly-cancelled and the decrease of $P_{SiO}$ in oxy-combustion conditions as compared to those in air, see Fig. 6, was attributed to the replacement of N$_2$ with CO$_2$ background gas, which impedes the formation of the volatile sub-oxide ($SiO_2(s) + CO = SiO(v) + CO_2$).

### 3.6. Conclusions

This study addressed the chemical properties of the PM$_1$ emissions from burning pulverized coals of three different ranks in a laboratory-scale drop-tube furnace, electrically-heated to 1400K, in various O$_2$/N$_2$ and O$_2$/CO$_2$ atmospheres. Particulate matter (ashes) were collected using a cascade thirteen-stage impactor, yields were measured gravimetrically and chemical compositions of the PM$_1$ ashes were obtained by utilizing SEM-EDS and EMA analyses:

- The yields of the elements of submicron particles (PM$_1$) from all three coals were lower when combustion occurred in CO$_2$, instead of in N$_2$ background gases.
The chemical composition of the PM_{0.56-1} sub-category was similar in CO_2, and in N_2 background gases.

The composition of the ultrafine PM_{0.01-0.18} sub-category was affected by replacing N_2 with CO_2, and mass fractions of Si, Ca Al, decreased whereas Na, K and S increased.

The composition of the ultrafine PM_{0.01-0.18} sub-category was affected when the O_2 mole fraction increased in either N_2 or CO_2; the mass fractions of Si, Ca and Al increased at the expense mostly of Na, K and S but, also, in most cases of Fe and Mg.

PM_{0.56-1} (stage 6) of the three coals in this study was mainly composed of Si and Al (and Ca for sub-bituminous), regardless of the combustion conditions.

PM_{0.1-0.18} particles of all coals were highly-enriched in S regardless of the combustion conditions.

PM_{0.1-0.18} particles of the sub-bituminous were highly-enriched in Fe in air and moderate oxy-fuel environments. Ca was the predominant element at high O_2 environments.

The composition of both PM_{0.1-0.18} and PM_{0.56-1} showed a strong correlation with the composition of the ash content (HTA) of the respective coals.

The experimental data were compared with the prediction of an ash vaporization model without and with coupling with a particle combustion model. The experimental values of the partial pressure of the volatile sub-oxide SiO (P_{SiO}) at the char surface were in the range of the model predictions, given the considerable uncertainty in pertinent key char properties.

Submicron ashes are of major concern in coal-fired power plants, since conventional particulate control devices have very low capture efficiencies in this particle size range. In
conventional coal power plants PM\textsubscript{1} emissions are then released to the atmosphere and are classified as health hazardous. In oxy-coal power plants they will be re-circulated to the boiler and they will also be channeled to the carbon capture and sequestration apparatus; therefore, they will have potential detrimental long-term effects on both accounts causing erosion, corrosion, slagging and fouling. This research has provided data on PM size and composition under both conventional (air) and oxy-coal combustion conditions. The most encouraging result for oxy-coal combustion (a clean-coal related) technology, is that replacement of N\textsubscript{2} with CO\textsubscript{2} has a beneficial effect on lowering the amounts of generated submicron ashes, and thus lessening the prospects of the aforementioned detrimental phenomena.

**Acknowledgements**

The authors acknowledge financial assistance from the NSF award CBET-0755431. The authors are thankful late Prof. Adel Sarofim for invaluable advise. Technical assistance in SEM analysis by Mr. William Fowle is acknowledged. Profs. Eliseo Ranzi, Tiziano Faravelli and Sauro Pierucci are also thanked for use of the particle combustion model, which was developed under their direction.
3.7. Appendix 1

Techniques used to analyze chemical composition of submicron ash particles in the literature.


<table>
<thead>
<tr>
<th>Reference</th>
<th>Techniques</th>
<th>Substrates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quann et al.(^{31, 44})</td>
<td>INAA</td>
<td>EMA SEM-EDS Teflon filters</td>
</tr>
<tr>
<td>Buhre et al.(^{2, 27})</td>
<td>PIXE PIGE</td>
<td>Polycarbonate and Teflon filters</td>
</tr>
<tr>
<td>Carbone et al.(^{56})</td>
<td>SEM-EDS</td>
<td>Gold foils</td>
</tr>
<tr>
<td>Yu et al.(^{21, 22})</td>
<td>XRF</td>
<td>Teflon filters</td>
</tr>
<tr>
<td>Suriyawong et al.(^{10})</td>
<td>XRF</td>
<td>Teflon filters</td>
</tr>
<tr>
<td>Sheng et al.(^{11})</td>
<td>XRF</td>
<td>Aluminum foils</td>
</tr>
<tr>
<td>Teramae and Takarada(^{20})</td>
<td>SEM-EDS</td>
<td>Teflon filters</td>
</tr>
</tbody>
</table>
3.8. Appendix 2

Calculation of the CO mole fraction at the char surface.

This derivation was provided to us by the late Prof. Adel Sarofim, who developed it from scratch during his trip to the Clearwater Conference in June of 2011.

$L =$ Boundary layer thickness

$C_T =$ Total molar concentration (mol/vol)

$N_T =$ Total molar flux (moles/(cm$^2$.s))

$N_{O2}, N_{CO} =$ molar fluxes

$D =$ Diffusivity (cm$^2$/s)

$y_{O2} =$ mole fraction of O$_2$

$2C + O_2 = 2CO$  \hspace{1cm} \text{(A2-1)}$ $\text{oxidation reaction of the char carbon.}$

$N_{O2} = N_T \times y_{O2} - D \times C_T \times (dy_{O2}/dx)$

$N_{CO} = -2N_{O2}$ from the stoichiometry of reaction (A2-1)

Express total molar flux ($N_T$) in terms of oxygen molar flux ($N_{O2}$) based on stoichiometry.

$N_T = N_{CO} + N_{O2} = -2N_{O2} + N_{O2} = -N_{O2}$ \hspace{0.5cm} \text{total molar flux in terms of oxygen molar flux.}$

$N_{O2} = - (N_{O2} \times y_{O2}) - (D \times C_T \times (dy_{O2}/dx))$ \hspace{0.5cm} \text{oxygen molar flux equation; fist part is convective flux and second part is diffusive flux.}$

$N_{O2} \times (1 + y_{O2}) = - D \times C_T \times (dy_{O2}/dx)$
\( \text{NO}_2 = -D \times C_T \times (1/1+y_{O2}) \times (dy_{O2}/dx) \) …rearrange to integrate both sides.

\( \text{NO}_2 \times dx = -D \times C_T \times (dy_{O2}/1+y_{O2}) \)

\( \text{NO}_2 \times L = -D \times C_T \times \ln(1+y_{O2}) \)

Boundary conditions: \( y_{O2} = 0 \) at \( x=0 \), \( y_{O2} = y_{O2,\infty} \) at \( x=L \)

\( \text{NO}_2 = (-D \times C_T/L) \times \ln(1+y_{O2,\infty}) \)…………………(A2-2)

Express total molar flux (\( N_T \)) in terms of carbon monoxide molar flux (\( N_{CO} \)) based on stoichiometry.

\( N_T = N_{CO} + N_{O2} = N_{CO} - \frac{1}{2} N_{CO} = \frac{1}{2} N_{CO} \) …total molar flux in terms of carbon dioxide molar flux.

\( N_{CO} = N_T \times y_{CO} - D \times C_T \times (dy_{CO}/dx) \) …oxygen molar flux equation; fist part is convective flux and second part is diffusive flux.

\( N_{CO} = \frac{1}{2} N_{CO} \times y_{CO} - D \times C_T \times (dy_{CO}/dx) \)

\( N_{CO} \times (1 - \frac{1}{2} y_{CO}) = - D \times C_T \times (dy_{CO}/dx) \) …rearrange to integrate both sides.

\( N_{CO} \times dx = - D \times C_T \times (dy_{CO}/(1- \frac{1}{2} y_{CO})) \)

Boundary conditions: \( y_{CO} = y_{CO,s} \) at \( x=0 \), \( y_{CO} = 0 \) at \( x=L \)

\( N_{CO} = -\frac{2}{L} \times D \times C_T \times \ln(1- \frac{1}{2} y_{CO,s}) \)……………………………………(A2-3)

\( \text{NO}_2 = -\frac{1}{2} N_{CO} \) …insert equation (1-2) and (1-3) in this expression.

\( (-D \times C_T/L) \times \ln(1 + y_{O2,\infty}) = (D \times C_T/L) \times \ln(1- \frac{1}{2} y_{CO,s}) \) …'(D \times C_T/L)' term cancels out.
\[ \ln(1 + y_{O_2, \infty}) = -\ln(1 - \frac{1}{2} y_{CO,s}) \]

\[ \ln[(1 + y_{O_2, \infty}) \times (1 - \frac{1}{2} y_{CO,s})] = 0 \]

\[ (1 + y_{O_2, \infty}) \times (1 - \frac{1}{2} y_{CO,s}) = 1 \]

\[ 1 - \frac{1}{2} y_{CO,s} = \frac{1}{1 + y_{O_2, \infty}} \]

Finally, the CO mole fraction at the char surface can be calculated as:

\[ y_{CO,s} = \frac{2y_{O_2, \infty}}{(1 + y_{O_2, \infty})} \] \hspace{1cm} \text{\textbf{\textit{(A2-4)}}}
Sample calculation of SiO mole fraction at the char surface ‘\(x_{ms}\)’, also denoted as \(P_{me}\) because the total pressure is 1 atm, from burning of the bituminous coal in air atmosphere based on the model of Quann and Sarofim \(^{21}\) is performed and details of the calculation are demonstrated below.

Reduction reaction used in this model is as follows:

\[
SiO_2(c) + CO = SiO(v) + CO_2 \quad \text{(A3-1)}
\]

Parameters used in this model:

\[
\begin{align*}
rm & := 0.25 \cdot 10^{-4} \text{cm} \quad \text{radius of mineral inclusion } 0.25<rm<1 \mu \text{m} \\
(rp & := 45 \cdot 10^{-4} \text{cm} \quad \text{mean radius of the particle.}\nre & := 0.15 \cdot 10^{-4} \text{cm} \quad \text{mean radius of the pore (Sahu et. al\(^{51}\)).}\n\tau & := 1 \quad \text{tortuosity.}\n\varepsilon & := 0.4 \quad \text{porosity (Sahu et. al\(^{51}\)).}\nTp & := 1713-K \quad \text{average char combustion temperature for bituminous\(^{50}\).}\nTm & := \frac{(Tp + 1400K)}{2} \quad \text{mean char temperature.}\n\end{align*}
\]

\[Tm = 1.556 \times 10^3 \text{K}\]
\[ x_{O2b} := 0.21 \quad \text{oxygen bulk mole fraction.} \]

\[ \rho_a := 2.648 \frac{g}{cm^3} \quad \text{inclusion (SiO}_2\text{) density.} \]

\[ \rho_0 := 1.18 \frac{g}{cm^3} \quad \text{coal density (Sahu et. al\textsuperscript{51}), \rho_0=1.1} \frac{g}{cm^3} \quad \text{for the lignite in this study.} \]

\[ \rho_c := 0.75 \frac{g}{cm^3} \quad \text{char density, 0.59 (Sahu et. al\textsuperscript{51})-0.9} \frac{g}{cm^3} \quad \text{(Sahu et. al\textsuperscript{51}).} \]

\[ M := 60 \frac{g}{mol} \quad \text{molecular weight of the mineral inclusion (SiO}_2\text{).} \]

**Calculation of the SiO mole fraction at the char surface**

\[
x_{msa} = \left[\begin{array}{c}
t \frac{tb}{\alpha \cdot DO2} \\
\frac{1}{\alpha \cdot DO2} + \frac{Dt}{1 - \frac{1}{tb}} \\
0
\end{array}\right] \cdot \left[\begin{array}{c}
\phi \cdot \left(1 - \frac{1}{tb}\right) \\
\tanh \phi \cdot \left(1 - \frac{1}{tb}\right) \\
\phi \cdot \left(1 - \frac{1}{tb}\right)
\end{array}\right] \cdot \left[\begin{array}{c}
\frac{1}{2} \\
\frac{1}{2} \\
\frac{1}{2}
\end{array}\right] \cdot \left[\begin{array}{c}
x_{me} \\
-1 \\
-1
\end{array}\right] \cdot \left[\begin{array}{c}
1 \\
1 \\
1
\end{array}\right] \cdot \frac{1}{tb} \cdot dt \quad \text{...(A3-2)}
\]
To solve this integral \( t_b, x_{me}, D_e, DO_2, \alpha, \) and \( \varphi \) should be found.

\( t_b = 0.07 \, \text{s} \) \hspace{1cm} \text{average char burnout time from Khatami et al.}^{50}

**Calculation of the local equilibrium SiO mole fraction at the inclusion surface, \( x_{me} \)**

\[
P_{me} = x_{me} \cdot P_{atm} \hspace{1cm} P_{atm} = 1 \, \text{atm}
\]

\[
x_{me} = P_{me}
\]

\( x_{me} \) \hspace{1cm} \text{equilibrium mole fraction of the SiO at the inclusion surface}

\[
K_{eq} = \frac{(P_{me} \cdot P_{CO_2})}{(a_m \cdot P_{CO})} \hspace{1cm} \text{(A3-3)}
\]

\( K_{eq} \) \hspace{1cm} \text{equilibrium constant for the reaction (3-1)}

In case of combustion in air, the only source of \( CO_2 \) is from the reduction reaction (1); \( P_{me} = P_{CO_2} \)

\[
x_{me} := \sqrt{Keq \cdot PCOs} \hspace{1cm} \text{(A3-4)}
\]

\( x_{me} \) \hspace{1cm} \text{equilibrium partial pressure of the SiO at the inclusion surface from chemical reaction (3-1)}

\[
\ln (K_{eq}) = A + B \times 10^4/T_p \hspace{1cm} \text{(A3-5)}
\]

\( K_{eq} \) \hspace{1cm} \text{equilibrium constant equation and coefficients from Senior et al.}^{33}

\[
A = 18.8256
\]

\[
B = -5.9700
\]

\[
Keq := e^{A + B \cdot \frac{10^4 \cdot K}{T_p}}
\]

\[
PCOs := 2 \cdot \frac{xO_2b}{1 + xO_2b} \hspace{1cm} \text{(A3-6)}
\]

\( PCOs \) \hspace{1cm} \text{derived in the Appendix 1 from the stoichiometry.}

\[
x_{me} = 1.951 \times 10^{-4}
\]
Calculation of the effective diffusivity, $D_e$

$$D_e := \frac{D_p}{\tau} \quad \text{...(A3-7)}$$

effective diffusivity of a molecule in a porous char for

Knudsen diffusion (Quann\textsuperscript{13}, eqn 6.14)

$$D_p := 9700 \cdot \left(\frac{g}{\text{K-mol}}\right)^{0.5} \cdot \frac{\text{cm}}{s} \cdot \text{re} \left(\frac{T_m}{M}\right)^{0.5} \quad \text{pore diffusivity (Quann\textsuperscript{13}, eqn 6.15)}$$

$$D_p = 0.741 \frac{\text{cm}^2}{s}$$

$$D_e = 0.296 \frac{\text{cm}^2}{s}$$

Calculation of the oxygen diffusivity, $D_O^2$

$$D_O^2 := 0.181 \cdot \left(\frac{T_m}{273\text{K}}\right)^{1.75} \cdot \frac{\text{cm}^2}{s} \quad \text{...(A3-8)}$$

oxygen diffusivity

$$D_O^2 = 3.808 \times 10^{-4} \frac{\text{m}^2}{s}$$

Calculation of the Stefan flow factor, $\alpha$

$$\alpha := \frac{\ln(1 + xO2b)}{1 - e^{-\frac{D_O^2}{DM}}} \quad \text{...(A3-9)}$$

Stefan flow factor (Quann\textsuperscript{13}, pg 62)

Calculation of the Ash diffusivity, $D_M$, from Senior's thesis\textsuperscript{53}, table 4.1

$$c \cdot DM = a \cdot T_p + b \quad \text{...(A3-10)}$$

$$a := 9.11 \times 10^{-9} \frac{\text{mole}}{\text{cm} \cdot \text{s} \cdot \text{K}}$$

constants obtained from Senior\textsuperscript{53} table 4.1
b := 7.363 \cdot 10^{-6} \frac{\text{mole}}{\text{cm} \cdot \text{s}}

\text{Patm} := 101.3 \cdot 10^3 \cdot \text{Pa}

R := 8.314 \cdot \text{m}^3 \cdot \frac{\text{Pa}}{\text{K} \cdot \text{mol}}

c := \frac{\text{Patm}}{R \cdot T_p} \quad \text{(A3-11)}

\text{concentration of the mineral inclusion (SiO}_2\text{).}

c = 6.676 \frac{\text{mol}}{\text{m}^3}

\text{DM} = 3.229 \times 10^{-4} \frac{\text{m}^2}{\text{s}}

\text{ash diffusivity.}

\text{Then } \alpha \text{ can be calculated as; } \alpha = 0.986

\text{Calculation of the Thiele modulus, } \phi

\phi := \left| 3 \cdot \sqrt{0.5} \cdot \frac{\text{rp}}{\text{rm}} \right| \quad \text{initial thiele modulus (Quann}^{13}, \text{pg 66)}, (5 < \phi < 20 \text{ for all coals, Quann}^{13}).

\text{Calculation of the inclusion volume fraction, } \theta

\theta := \frac{\text{Wt\%metaloxide} \cdot \phi \cdot c}{\text{pa}} \quad \text{(A3-13)}

\text{inclusion (SiO}_2\text{) volume fraction.}

\text{Wt\%metal} := 3.36

\text{weight percent of the mineral (Si) in the bituminous.}

\text{Wt\%metaloxide} := \left( \frac{\text{Wt\%metal}}{28} \right) \cdot \frac{(28 + 32)}{100}

\text{weight percent of the SiO}_2\text{ in the coal.}

\text{Wt\%metaloxide} = 0.072

\theta = 0.02
Then $\phi$ can be calculated as; $\phi = 48.771$

Finding all parameters, Eq. (2-2) can be solved as follows;

$$x_{msa} = 1.353 \times 10^{-4}$$

average mole fraction of inorganic vapor species at the char surface (Quann$^{13}$, eqn 1.7)
Calculation methodology of the experimental SiO mole fraction at the char surface \( x_{ms} \) by equating vaporization rate \( V_c \) to the external diffusion rate.

Total vaporization rate \( V_c \) is equal to the external diffusion rate;

\[
V_c = 4\pi r_p c D_{O2} \alpha_1 x_{ms} \quad \text{(A4-1)}
\]

Solve equation (1) for \( x_{ms} \):

- \( r_p = r_0 \), \( \text{(A4-1a)} \) char radius is assumed to be constant throughout the combustion for bituminous coal.

- \( r_p = r_0 \times (1-t/t_b)^{0.5} \), \( \text{(A4-1b)} \) from Quann and Sarofim \(^{21} \), radii are assumed to be shrunk throughout the combustion for sub-bituminous and lignite coals.

- \( c \) is concentration of the SiO, see App.3 Eq. A3-11.

- \( D_{O2} \) is oxygen diffusivity, see App3 Eq.A3-8.

- \( \alpha_1 \) is Stefan flow factor, see App.3 Eq.A3-9.

- \( t_b \) is char burnout.

\[
N_v = \int_0^{t_b} V_c \, dt \quad \text{(A4-2)}
\]

mole vaporized per coal particle

\[
f_v/t_b = N_v/(N_0 \times t_b) \quad \text{(A4-3)}
\]

experimentally determined fractional vaporization rate

\[
N_0 = (\theta \times \rho_s \times 4\pi r_0^3)/(3M) \quad \text{(A4-4)}
\]

initial moles of the metal in the char particle \( (N_0) \)

- \( \theta \) is volume fraction of the mineral inclusion (SiO).

- \( \rho_s \) is inclusion \( (\text{SiO}_2) \) density.

- \( r_0 \) is initial char radius.

- \( M \) is molecular weight of the inclusion \( (\text{SiO}_2) \).

Plug equation (4-2) and (4-4) into equation (4-3) and solve for total vaporization rate \( V_c \) which includes experimental fractional vaporization rate \( f_v/t_b \). Then equate it to equation (4-1) and solve for \( x_{ms} \).
Then mole fraction of the metal oxide (SiO) at the char surface ‘$x_{ms}$’ can be solved as follows;

- for bituminous coals;

$$x_{ms} = \left(\frac{f_v}{t_b}\right) \times \left[\left(\frac{\rho_x \times r_0^2}{3M \times c \times D_{O2} \times \alpha}\right)\right] \quad \text{(A4-5)}$$

- for sub-bituminous and lignite coals;

$$x_{ms} = \left(\frac{2}{3}\right) \times \left(\frac{f_v}{t_b}\right) \times \left[\left(\frac{\rho_x \times r_0^2}{\left(M \times c \times D_{O2} \times \alpha\right)}\right)\right] \quad \text{(A4-6)}$$
3.11. References


CHAPTER 4
4. Characterization of Particulate Matter Emitted from Combustion of Various Biomasses in O$_2$/N$_2$ and O$_2$/CO$_2$ Environments

Abstract

Oxy-fuel combustion is a viable technology for new and existing coal-fired power plants, as it facilitates carbon capture and thereby, can reduce carbon dioxide emissions. The use of biomass as an energy source is another popular strategy to reduce carbon dioxide emissions as they are considered nearly carbon dioxide neutral. If the use of biomass is combined with oxy-fuel combustion, negative net emissions of carbon dioxide are possible. This work examined the particulate emissions from combustion of pulverized biomass residues burning in either conventional or oxy-fuel environments. Combustion of three biomasses (olive residue, corn residue, and torrefied pine sawdust) occurred in a laboratory-scale laminar-flow drop tube furnace (DTF) heated to 1400 K. The O$_2$ mole fraction was increased from 20% to 60% in N$_2$ environments while a range of 30% to 60% O$_2$ mole fractions were used in CO$_2$ environments to represent plausible dry oxy-fuel combustion conditions. Submicron particulate matter (PM$_1$) emission yields of all three fuels were typically lower in O$_2$/CO$_2$ environments than in O$_2$/N$_2$ environments. When the oxygen mole fraction was increased, the PM$_1$ yields typically increased. The mass fractions of submicron particulate matter (PM$_1$/PM$_{18}$) collected from biomass combustion were higher than those of coal combustion. PM$_1$ constituted approximately 50 wt% of the collected ash particles in PM$_{18}$ in each environment, whereas the corresponding submicron emissions from coal constituted approximately 20 wt%. Changing the background gas had little effect on the chemical composition of the PM$_1$ particles. Unlike the submicron particles collected from coal which contained high amounts of silicon and aluminum, high amounts of alkalis
(potassium, calcium, and sodium) and chlorine were the major elements observed in PM$_1$ from the biomasses. In addition, phosphorous and sulfur also existed in high amounts in PM$_1$ of corn residue. Super-micron particles (PM$_{1-18}$) yields exhibited no clear trend when the background gas was changed or when the oxygen mole fraction was increased. The composition of these particles reflected the bulk ash composition of the parent fuels. Olive residue resulted in by far the largest particulate yields, while torrefied pine sawdust had the lowest. The yields of these two biomasses were analogous with the ash contents of the parent fuels. The particulate yields of corn residue, however, were lower than expected when compared to the parent fuel’s ash content. This was attributed to the high phosphorous and sulfur contents of this fuel which might have increased its deposition tendencies in the laboratory furnace.

4.1. Introduction

In 2011, the use of coal accounted for 30% of the total global energy consumption; a growth of 5.4% over 2010$^1$. Although coal is second to oil as a primary world energy source, it is the primary source of electricity; generating 40% of the electricity in the world$^{1-3}$. As the world’s needs are projected to increase, coal will remain to be an important source of electricity into the foreseeable future, with an annual projected growth of 1.4% through 2030 (total growth of $\sim$26%)$^3$. In addition to being the predominant source of electricity, the combustion of coal is also responsible for the majority of emissions of the greenhouse gas carbon dioxide. Approximately 43% of the total global carbon dioxide emissions can be attributed to coal$^4$; increasing the concerns over environmental impacts, such as climate change and global warming, and prompting the development of strategies to either reduce and/or capture and sequester these emissions. Carbon Capture and Storage (CCS) in conjunction with oxy-fuel combustion is one
such technology that can capture more than 90% of carbon dioxide emissions generated from the use of coal and other fossil fuels in electricity generation\textsuperscript{5}. In oxy-fuel combustion, the required oxygen is separated from air prior to combustion through the use of an air-separation unit (ASU). Combustion of the fuel then takes place in oxygen diluted with re-circulated flue gas rather than air; a technique that generates an effluent highly concentrated with carbon dioxide that can then be captured and stored in underground reservoirs\textsuperscript{5}. If the flue gas is dried, then combustion takes place in O\textsubscript{2}/CO\textsubscript{2} environments.

The use of renewable energy sources, such as biomass, is another strategy that has become popular and been utilized in recent years as a means to contain carbon dioxide emissions. For example, the official Danish energy policy encourages the combustion of straw and other biomass fuels to manage the amount of CO\textsubscript{2} emitted to the atmosphere\textsuperscript{6}, while two medium sized power plants, (\textasciitilde 16 MW each) exclusively fired with pulverized orujillo (a waste residue of the olive oil industry), have recently been built in Spain\textsuperscript{7-9}. In addition, bagasse (a by-product of the sugar cane industry) supplied 3\% of the Brazilian energy matrix in 2009\textsuperscript{10}. These are not the only countries utilizing biomass as an energy source. In fact in 2010, 8.5\% of the total global energy consumption was attributed to traditional biomass, i.e. waste wood and manure\textsuperscript{4}. In addition, during the same year, the use of biomass accounted for 1.5\% of the world’s generated electricity\textsuperscript{2}. The world’s energy consumption generated from biomass is projected to grow by 136\% by 2030\textsuperscript{3}. The increased interest in biomass as an energy source is attributed to its effect on greenhouse gases. In regards to its carbon emissions, biomass may be considered nearly-neutral since the carbon dioxide emissions released from converting biomass to energy are equivalent to the amount of carbon dioxide absorbed by the plants during their growing cycles\textsuperscript{4, 11, 12}. The energy used in the growing, harvesting, and transportation processes results in
CO₂ emissions that are detractors. Nevertheless, when fired with primary fossil fuels, such as coal, the use of biomass reduces the net production of carbon dioxide\textsuperscript{11, 12}. What is more, if co-firing of biomass and coal is combined with oxy-fuel combustion and CCS, then the outcome of negative net emissions of carbon dioxide may be achieved\textsuperscript{5, 11}, i.e., removal of carbon dioxide from the atmosphere.

As an energy source, biomass combustion may take place in conventional boilers where combustion takes place with air or within future oxy-fuel fired boilers where, as previously stated, combustion takes place in oxygen and recycled combustion gases (containing mostly CO₂). Emissions from conventional boilers are heavily regulated and scrutinized for pollutants. In particular, submicron particles (PM\textsubscript{1}), which cannot be captured by environmental cleanup equipment, are especially health hazardous and have adverse environmental effects. For the most part, emissions from future oxy-fuel fired boilers will not be emitted to the atmosphere. They will instead be sequestered in underground reservoirs. However, as seen in Figure 1, typical oxy-combustion plants will still require environmental cleanup equipment to remove ash and other pollutants. If pollutants are not removed, they could be a) partly recycled to the boiler through the flue gas recirculation stream which could be detrimental to its operation and b) partly channeled to the CO₂ compressor, interfering with its operation. In both cases, deposition and corrosion tendencies of the pollutants are of particular interest as they affect the system operation. In addition, Tan and Croiset\textsuperscript{13} stated that during high peak hours it is possible for an oxy-fuel power plant to emit flue gases into the atmosphere by shutting down the flue gas recovery train in order to make the power available for use. As a result, it is necessary to ensure levels of pollutants emitted are low. Again, as environmental cleanup equipment has low efficiency in capturing submicron particles, it is of technical interest to study both the physical
and chemical nature of these pollutants from the oxy-combustion of biomass. Hence, the aim of this work is to study the particulate emissions, both the physical and chemical aspects, from the combustion of biomass in air and typical oxy-fuel environments.

Figure 1: Typical oxy-fuel combustion plant configuration\textsuperscript{14}.

4.2. Literature Review

Studies are prevalent on the combustion characteristics and emissions (particulate and gaseous) of a variety of biomasses and their blends with coal in air. The study of the combustion of biomass and its blends in oxy-fuel environments, however, is only just emerging. The oxy-fuel combustion characteristics of biomass and their blends with coal have been outlined by Riaza et. al\textsuperscript{15} and Yuzbasi et. al.\textsuperscript{16} Riaza et al.\textsuperscript{17} have also recently outlined the combustion characteristics of a variety of neat biomasses in oxy-fuel environments. The gaseous emissions of the combustion of biomass and its blends with coal in oxy-fuel environments have been studied by Kazanc et. al\textsuperscript{18} while Fryda et. al\textsuperscript{11} performed a comparative study of ash formation and deposition of selected coal/biomass blends under both oxy-fuel and air conditions. Information
on the characteristics of the particulate emissions generated by the combustion of biomasses within oxy-fuel environments, however, is limited.

4.2.1. Ash Yields and Particle Size Distributions

Many laboratory and field studies have been conducted throughout the years to study the characteristics of the particulate emissions resulting from the combustion of neat biomasses and blends with coals in air. Jiménez and Ballester\textsuperscript{9} burned orujillo (a residual by-product of the olive oil production industry) and its blends with coals and coke in an entrained flow reactor with a co-flowing gas stream consisting of combustion products from a natural gas/air burner to ensure particles burned in an environment representative of those found in industrial pulverized fuel boilers. In that study, for the blend of orujillo and coal, a multimodal distribution was observed within the bulk ash, with a submicron mode peak centered at approximately 200nm, while a bimodal distribution was observed in PM\textsubscript{10} with peaks at ~200nm and ~3micrometers for the combustion of orujillo alone. The submicron particles represented approximately 3\% (wt\%) of the total particulate matter emissions, with the similarity between the diameters of the lower peaks indicating that orujillo was the main source for these submicron particles. In addition, experiments with blends of orujillo and coals resulted in a higher content of coarse particulates than for orujillo alone. A similar study conducted by Jiménez and Ballester\textsuperscript{8}, in which orujillo was burned alone, confirmed that approximately 3\% (wt\%) of the total particulate matter emissions was contained in the submicron mode. However, in that study, they reported the particulate size distribution was bimodal with a submicron peak centered at ~155nm. While Jiménez and Ballester\textsuperscript{9} reported multimodal particle size distributions (PSD’s) for the combustion of orujillo and its blends, Christensen and Livbjerg\textsuperscript{6} observed a unimodal size
distribution with a submicron peak of ~300 nanometers when they examined the particulate emissions of a 25 MW straw-fired power plant. This is in qualitative agreement with their model calculations, conducted by the Plug Flow Aerosol Condensor Model, which simulates the formation and evolution of aerosols in the potassium/chlorine/sulfur system during flue gas cooling. From this model, a submicron mode was observed at a geometric mean diameter of 120 nanometers. In this study, the observed submicron mass concentrations were much higher than those of typical coal combustion aerosols measured before the particle collecting devices. Similarly, Johnasson et al. observed a particle mass size distribution consisting predominantly of submicron particles with a mode between 80-200 nanometers when he observed the combustion of wood pellets and wood briquettes in two size classes of boilers (small boilers for domestic heating and slightly larger boilers used for district heating). In addition, a second mode was observed, existing around 2-3 micrometers, when combustion of wood briquettes occurred in a district heating boiler. A super-micron mode was also observed for the emissions from the pellet burner. In addition, Johansson and his co-workers determined that the number size distribution was unimodal, with a submicron peak centered between 80 – 300 nanometers. They determined that this distribution shifts to larger sizes at low excess air and low boiler loads as well as in the combustion of low density briquettes; indicating oxygen concentration and fuel type may play a role in the ash particle distribution.

The effect of increasing the oxygen mole fraction in N₂ environments on the particulate emissions has been briefly studied. Wang et al. investigated the emission properties from the co-combustion of two typical Chinese coals and two types of biomass (sawdust and straw) as well as the effect of increasing the oxygen mole fraction of the environment on the particulate emission behavior. In their study, during the combustion of the four different coal/biomass
blends at oxygen mole fractions of 20% and 50%, a similar bimodal size distribution with mode
peaks at ~0.1 micrometers and~ 4.3 micrometers was observed in the PM$_{10}$. The mass fraction of
submicron particles accounted for approximately two thirds of the PM$_{10}$ in an atmosphere of 20%
O$_2$ in N$_2$. Increasing the oxygen mole fraction to 50% caused the mass fraction of submicron
particles (PM$_1$) to decrease (to ~50 %) while the percentage of super-micron (PM$_{1-10}$) particles in
PM$_{10}$ increased greatly. They concluded that at higher oxygen mole fractions and thus higher
combustion temperatures, the large molten coal ash particles captured the very fine particulates
which resulted in the decrease in submicron particles. Moreover, by increasing the oxygen mole
fraction from 20% to 50%, the overall total PM$_{10}$ yields increased. They suggested that at higher
oxygen mole fractions larger ash particles were more likely to fragment, forming much more
PM$_{10}$. Wang and his co-workers$^{12}$ also observed a weak relation to fuel type. The co-combustion
of a Chinese coal with sawdust resulted in the lowest concentration of emissions which was
attributed to its low ash content.

Few studies exist on the emissions generated by the combustion of biomass and
biomass/coal blends within oxy-fuel environments. Fryda et. al$^{11}$ studied the deposition
properties of two different coals (Russian and South African coals) and their blends with shea
meal, a cocoa residue, in air and in an oxy-fuel environment (30% O$_2$ – 70% CO$_2$) by analyzing
ash deposited on a probe maintained at 660 °C (933 K) and a filter located at the end of a drop
tube reactor, downstream of the probe. For each coal and its blend, the deposition tendencies
were lower in air than in oxy-fuel environments. In addition, higher amounts of fine ash (fly ash)
were captured on the filter in air environments than in oxy-fuel environments. In conclusion, it
was observed that in oxy-fuel environments more coarse ash was deposited while less fly ash
was found on the filter as opposed to air. Fryda et. al$^{11}$ also observed that when shea meal was
blended with the coals, the deposition tendencies were reduced in both environments when compared to the combustion of coal. Moreover, the blends showed lower fouling factors in comparison to the coals, which is in agreement with the lower deposition propensities exhibited by the blends. In summary, when coal was combined with biomass, the formation of deposits was less than when coal was combusted in both environments. In addition, deposition was seen to be more likely to occur when combustion of both neat coals and blends of coal and biomass occurs in oxy-fuel environments. There are many mechanisms for particles to deposit upon combustion surfaces. According to Baxter\textsuperscript{20}, four major deposition mechanisms exist: inertial transport including impaction and sticking, thermophoresis, condensation, and chemical reactions. In inertial impaction, the inertia of the particles is large and allows them to more readily impact and collect on the combustion surfaces while thermophoresis is related to the large temperature gradients between the hot gas stream and cold combustion surfaces. Fryda et al\textsuperscript{11} suggested that through thermophoresis, alkalis present in the shea meal condensed on the probe, forming a thin film which allowed for further deposit growth through inertial impaction. They also suggested that inertial impaction is dependent on the variation in the physical gas properties. For example, the gas density is higher in $\text{O}_2/\text{CO}_2$ environments than in $\text{O}_2/\text{N}_2$ environments which may explain the higher deposition tendencies they observed in oxy-fuel environments. Deposition caused by condensation involves physical transportation of the vaporized ash particles in the gas stream to the combustion surface at which the particles undergo a phase change. Heterogeneous chemical reactions involve the interaction between flue gases and materials in the deposit. One such example is sulfation, during which materials, such as potassium and sodium, found in the deposit as hydroxides and possibly chlorides, react with the sulfur in the flue gas.
4.2.2 Chemical Composition of Ash Particles

In addition to particle size distributions and morphology, field and laboratory studies have also reported the chemical composition of emitted particles resulting from combustion in air. In addition to studying the size distribution of the combustion of orujillo\textsuperscript{8,9} and its blends\textsuperscript{9}, Jiménez and Ballester also studied the chemical composition of the resulting particulate emissions\textsuperscript{9} for various particulate geometric mean sizes, as collected by their impactor. They observed that the chemical composition of particulate emissions with geometric mean diameters below 540 nanometers of pulverized orujillo combustion were consistent and mostly composed of potassium chloride (KCl) and potassium sulfate (K\textsubscript{2}SO\textsubscript{4}) in almost the same mass proportions. The formation mechanism that they proposed addressed the reason for the composition of the submicron particles. Through thermodynamic equilibrium equations, they suggested that at high temperatures potassium hydroxide (KOH), sulfur dioxide (SO\textsubscript{2}), and hydrogen chloride (HCl) existed in the gas phase and were the only stable species. When the temperature decreased, KOH reacted with the SO\textsubscript{2} and through nucleation formed K\textsubscript{2}SO\textsubscript{4} while KOH and HCl reacted to form KCl which then condensed. Small amounts of phosphorous (P) were also observed which was present as potassium phosphate and accounted for less than 7\% of the mass\textsuperscript{8}. When orujillo was co-fired with coal, KCl disappeared from the particles, substituted by more K\textsubscript{2}SO\textsubscript{4}\textsuperscript{9}. In contrast, the coarse particulate emissions (with diameters larger than 540 nanometers) retained the original fuel characteristics, consisting of calcium (Ca), silicon (Si), potassium (K), aluminum (Al), iron (Fe), and phosphorous (P)\textsuperscript{8}. The study conducted by Christensen and Livbjerg\textsuperscript{6} showed a fairly uniform composition for particles with a mean particle diameter less than 1 micrometer consisting of K, Cl, sulfur (S), and P with KCl and K\textsubscript{2}SO\textsubscript{4} accounting for 80-90\% (wt \%) of the total mass. In addition to the elements found in smaller particles, larger particles were found to
contain elements such as Si, magnesium (Mg), Ca, sodium (Na), titanium (Ti), and Fe, indicating these particles may not have formed from gas-to-particle conversion but by fragmentation. The submicron chemical composition of the particles observed by Johansson et al.\textsuperscript{19} were similar to those of previous works, with the majority of the particles consisting of potassium sulfates and potassium chlorides. Small amounts of zinc (Zn), Mg, and Na were also observed in the submicron particles.

Wang et al.\textsuperscript{12} observed that during the co-combustion of biomass and coal, the majority of alkalis, sulfur, and chlorine were present in the submicron particles, which was in agreement with these studies\textsuperscript{6,8,9}. They also observed that by increasing the oxygen mole fraction from 20\% to 50\%, the S/Cl ratio increased along with the sulfating extent in submicron particles. The alkali content in these particles, however, was found to decrease which may be attributed to the fact that aluminosilicates react with alkali chlorides leading to the incorporation of more alkalis in super-micron particles. An exception to this was the blends of the biomasses with a Chinese coal which had a higher calcium content than the other coal burned in this study. The high calcium content in this coal enhances potassium release by competing for silicates and phosphates and as a result more potassium is vaporized and condensed, forming more fine particles. With the increased oxygen mole fraction, the alkali content in the super-micron particles were observed to increase significantly with alkalis bound as chlorides, sulfates, or salts.

Fryda et al.\textsuperscript{11} calculated the relative enrichment of an element in the sampled ash relative to its concentration in the fuel (enrichment factor). For each environment, air and oxy-fuel, the resulting enrichment factors were similar. For coal and biomass blends, the deposit and fly ash samples are slightly depleted in potassium, indicating that potassium enters the gas phase due to
the increased presence of Cl in the blends. The increased Cl facilitates the volatilization of elements that would normally deposit, mobilizing elements such as potassium which end up in larger concentrations in the fly ash. The depletion of chlorine on the probe surface and minor amounts found in the fly ash samples of the coal/biomass blends supports this finding. Sulfur, like potassium, is depleted in both the deposit and fly ash, indicating that under high temperatures, it enters the gas phase and interacts with alkalis. At the deposition probe temperature, for example, sulfur dioxide reacts with alkalis introduced by the biomass, such as K and Ca, to form sulfates which exist in the solid phase and are prone to deposit. Fryda et al.\textsuperscript{11} concluded that blending of coals with biomass in both combustion conditions did not change the ash chemistry.
4.3. Experimental Setup

Three different biomass, olive waste (OR), torrefied pine sawdust (TOPI), and corn residue (CR), were burned in this study. Their chemical compositions and properties are listed in Table 1.

**Table 1: Biomass Type and Chemical Composition.** The proximate and ultimate analysis data for the olive residue and torrefied pine sawdust was obtained from the laboratories of the Instituto Nacional del Carbón (INCAR-CSIC)\(^\text{17}\) in Spain. The proximate analysis for the corn residue was provided by Giuntoli et. al\(^\text{21}\) while the ultimate analysis was obtained from Alves et. al.\(^\text{22}\)

<table>
<thead>
<tr>
<th>Biomass Type</th>
<th>OR</th>
<th>TOPI</th>
<th>CR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Olive Waste</td>
<td>Torrefied Pine Sawdust</td>
<td>Corn Residue</td>
</tr>
<tr>
<td><strong>Proximate Analysis (wt %, db)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volatile Matter</td>
<td>71.9</td>
<td>81.4</td>
<td>78.2</td>
</tr>
<tr>
<td>Fixed Carbon</td>
<td>20.5*</td>
<td>18.3*</td>
<td>14.7</td>
</tr>
<tr>
<td>Ash</td>
<td>7.6</td>
<td>0.4</td>
<td>7.1</td>
</tr>
<tr>
<td>Moisture (wt %, ar)</td>
<td>9.2</td>
<td>5.2</td>
<td>8.9</td>
</tr>
<tr>
<td><strong>Ultimate Analysis (wt %, daf)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>54.3</td>
<td>52.8</td>
<td>48.2</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>6.6</td>
<td>6.0</td>
<td>7.5</td>
</tr>
<tr>
<td>Oxygen</td>
<td>37*</td>
<td>40.9*</td>
<td>17.8</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1.9</td>
<td>0.3</td>
<td>3.7</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.2</td>
<td>0.0</td>
<td>6.7</td>
</tr>
<tr>
<td>HHV (MJ/kg)</td>
<td>19.9</td>
<td>20.5</td>
<td>19.8</td>
</tr>
</tbody>
</table>

* Determined by difference

The olive residue and the torrefied pine sawdust were obtained from the Instituto Nacional del Carbón (INCAR-CSIC) and was used in a recent study\(^\text{17}\). Olive residue is commonly used today as a low cost renewable fuel for domestic and industrial heating and is a byproduct of the olive oil production industry. More specifically it is the part of the olive that remains after the oil
has been extracted. This type of biomass used herein and in recent studies\textsuperscript{17} is used in fuel blends with coal and petcoke at ELCOGAS, S.A, an IGCC power station located in Ciudad Real, Spain. The torrefaction process of the pine sawdust was performed at INCAR-CSIC. The parent sample was obtained from Pellets Asturias, S.L., a pellets industry situated in Austria, Spain. The torrefaction was performed in the laboratory using a horizontal quartz reactor, where 10-15 grams of biomass were heated to 280°C (553 K) at a rate of 10 K per minute under a nitrogen flow rate of 50 mL per minute. The samples were kept at the final temperature for 20 minutes. The corn residue sample, also known as dried distillers grains (DDGS), was provided by a North American ethanol-producing company and used in a recent study\textsuperscript{22}. The corn residue and torrefied pine sawdust were ground and sieved to a cut size of 53-90 µm while a cut size of 75-150 µm was used for olive residue. Photos of each biomass, as received and the sieved samples used herein are demonstrated in Table 2.

Table 2: Photographs of the olive residue, torrefied pine sawdust, and corn residue. First row demonstrates the particles as received and second row indicates ground powders.

<table>
<thead>
<tr>
<th>Olive Residue</th>
<th>Torrefied Pine Sawdust</th>
<th>Corn Residue</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Olive Residue" /></td>
<td><img src="image2.png" alt="Torrefied Pine Sawdust" /></td>
<td><img src="image3.png" alt="Corn Residue" /></td>
</tr>
</tbody>
</table>
Ashing experiments were performed to verify the ash content of each biomass. Each fuel was burned in a ceramic boat inserted within a muffle furnace operated at an air temperature of 900 °C (1173 K) for one hour. Each sample was weighed prior to and after each experiment to calculate the resulting ash content (wt %). Duplicate experiments were conducted.

Combustion experiments were conducted in an electrically-heated (4.8 kW max) drop-tube furnace (DTF), manufactured by ATS; a schematic of this furnace is provided in Figure 2. 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 is 20 cm long, as defined by the length of the aluminum silicate heating elements. 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). Particles were entrained in a metered stream of oxidant gases and entered a long section of capillary tubing with an inner diameter of 1.14 mm (MicroGroup). The tubing was vibrated to its natural frequency by one vibrator (Vibro-Graver by Alltech) to ensure an unimpeded flow of particles to the injector. The fuel particles then entered the furnace through a water-cooled stainless-steel injector.
Figure 2: Cross section view 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 water cooled particle collection probe where a flow of dilution Nitrogen was provided.

The input flow rate of the particle fluidizing gas was 4 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 1-2 s. Combustion occurred under laminar-flow conditions in the 20 cm hot zone of the furnace.
Furnace wall temperatures \( T_w \) were continuously monitored by type-S thermocouples embedded in the wall.

A thirteen stage Nano-Moudi cascade impactor was coupled to the furnace outlet through a water-cooled probe (under \( \text{N}_2 \) dilution/ quenching flow) to collect particulate emissions after combustion occurred. All products of combustion, gaseous and particulate, were collected at the exit of the furnace by a water-cooled probe, consisting of three coaxial layers, placed along the furnace axis. The outer two layers channeled cooling water along the entire length of the probe while the inner layer consisted of porous stainless steel tubing. Within the probe, nitrogen gas was transported inward through the porous wall in order to prevent surface deposition. This allowed the furnace flue gases to be thermally quenched, chemically inerted, and diluted in order to minimize further reactions. The nitrogen also served as makeup flow, necessary for proper operation of the cascade impactor. A pressure gage was utilized to monitor the pressure at the inlet of the impactor. This pressure was kept at \(~0\) atm in all experiments as recommended by the manufacturer of the impactor.

Particles collected upon impaction plates, loaded with aluminum or Teflon substrates, as they traveled through the impactor stages. The particles that collected on the impactor stages were separated into six categories as follows: (1) PM\(_{0.32}\) (stages 8-13), (2) PM\(_1\) or submicron (stages 6-13), (3) PM\(_{2.5}\) (stages 4-13), (4) PM\(_{1.5}\) or fine fragment mode (stages 3-5), (5) PM\(_{10}\) (stages 2-13), and (6) PM\(_{18}\) (stages 1-18). The total ash collected during combustion of the biomasses is represented by the summation of the particles collected on all 13 impactor stages as well as the impactor inlet stage. The nominal particle cut sizes, as provided by the impactor manufacturer, are provided in Table 3. As the particles traveled through the impactor, small
heaps were formed as they accumulated on the substrates. The substrates were weighed prior to and after each experiment, through the use of a Mettler Sartorius Model ME-36S laboratory microbalance, to obtain the particulate yields and particle size distributions from combustion of each biomass in the various environments. The inlet stage contained particles larger than 18 micrometers and was not taken into account for the particulate yields or size distributions. Upon completion of the experiments, the loaded substrates were stored in a petri-slide plastic container for further analysis. Samples were prepared from the stored substrates using segments where particle heaps had accumulated to observe the morphology of the particles via scanning electron microscopy (SEM). In order to prevent charging of the particles and obtain accurate representations of the particles, the samples were carbon-coated during the preparation process. These substrate samples were then attached to metal stubs by means of carbon tapes. In addition, ashes collected on stage 6 (PM$_{0.56-1}$) and stage 9 (PM$_{0.1-0.18}$) were chosen to represent the chemical composition of the PM$_1$ yields, based on prior work$^{23}$. Elemental analysis of these samples was performed prior to the carbon coating of the samples through utilization of the techniques of Scanning Electron Microscope Energy-Dispersive X-ray Spectroscopy (SEM-EDS).

**Table 3: Nominal cut size of the stages in the Nano-Moudi ash impactor.** Cut-off sizes were determined by the instrument supplier based on the density of ammonium sulfate particles whose density is 1.77 g/cm$^3$. The density of ash particles varies and is not necessarily equal to this value.

<table>
<thead>
<tr>
<th>Stage</th>
<th>Inlet</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>Filter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal Cut Size (nm)</td>
<td>18,000</td>
<td>10,000</td>
<td>5,600</td>
<td>3,200</td>
<td>1,800</td>
<td>1,000</td>
<td>560</td>
<td>320</td>
<td>180</td>
<td>100</td>
<td>56</td>
<td>32</td>
<td>18</td>
<td>10</td>
<td>0</td>
</tr>
</tbody>
</table>
Combustion tests were conducted with oxidant gases consisting of either O$_2$/N$_2$ or O$_2$/CO$_2$ mixtures. In N$_2$ environments oxygen mole fractions of 21% (air), 40%, and 60% were utilized. In CO$_2$ environments, oxygen mole fractions of 30%, 40%, and 60% were utilized with the 30% and 40% oxygen mole fractions representing a plausible range of practical oxy-fuel conditions$^{18, 23-26}$. Gas flowrates were metered by Matheson rotameters. The injection rate of the biomass powders in the DTF was approximately 0.01 g/min. The amount of pulverized fuel fed to the DTF during each experiment was calculated by measuring the weights of the fuel contained in the vial at the beginning and end of each run. Yields of ash particles were computed based on the amount of fuel introduced to the furnace. For the corn and olive residues, experiments lasted for 20 minutes. In order to obtain accurate ash yields, experiments utilizing the low-ash content torrefied pine sawdust were conducted for 30 minutes. Triplicate combustion experiments were conducted at each condition. Furthermore, at each condition, the average of the chemical composition data was obtained based on measurements from 5 different locations of the accumulated particles on the loaded substrates.

4.4. Analysis and Results

4.4.1. Ash Yields

Figure 3, depicts the particulate emissions of each of the three biomasses utilized in this study from combustion in N$_2$ and CO$_2$ background gases, at a variety of oxygen mole fractions. Oxygen mole fractions of 21% (Air), 40%, and 60% were utilized for N$_2$ environments while 30%, 40%, and 60% for CO$_2$ environments. In an effort to investigate the effect of the different combustion environments and oxygen mole fractions on particle generation, the yields were
observed in six different categories. These categories include PM$_{0.32}$, PM$_{1.0}$ (the submicron mode), PM$_{2.5}$, PM$_{1-5}$ (fine fragment mode), PM$_{10}$, and PM$_{18}$.

Figure 3: PM$_{0.32}$, PM$_{1}$ (submicron), PM$_{2.5}$, PM$_{1-5}$ (fine fragment mode), PM$_{10}$, and PM$_{18}$ ash emission yields from burning of Olive Residue, Corn Residue, and Torrefied Pine Sawdust under various O$_2$/N$_2$ and O$_2$/CO$_2$ atmospheres. All yields are expressed as mg/g of fuel introduced to the drop-tube furnace (DTF).
As seen in Figure 3, olive residue has by far the most ash particle emissions, followed by corn residue and then by torrefied pine sawdust at a distant third. In addition, the combustion of olive residue and torrefied pine sawdust generated ash yields analogous to their respective ash contents. The combustion of olive residue, which has the highest ash content of 7.6% (wt%), produced total yields from combustion in air of approximately 78 mg/g_{fuel fed}, torrefied pine sawdust, with the lowest ash content of 0.4 (wt%), produced total ash yields in air of approximately 5 mg/g_{fuel fed}. On the contrary, corn residue is comprised of 7.1% (wt %) ash but only produced total ash yields of approximately 14 mg/g_{fuel fed} when combustion occurred in air.

For the combustion of all biomasses in oxy-fuel environments (O_2/CO_2), the submicron ash yields, PM_1, are lower than those in O_2/N_2 combustion environments. The average yields in N_2 environments, over all oxygen mole fractions, for olive residue, corn residue, and torrefied pine sawdust are 22.06, 2.25, and 0.64 mg/g_{fuel fed}, respectively. Changing the background gas to CO_2 reduces these averages to 18.9, 1.46, and 0.41 mg/g_{fuel fed}. Increasing the oxygen mole fraction in N_2 environments caused a slight overall increase, equal to 8.9%, in the PM_1 yields of olive residue. In CO_2 environments, the submicron yields of olive residue increased when the oxygen mole fraction was increased from 30% to 40%. Less definitive trends, however, were observed in the yields of corn residue and torrefied pine sawdust in both N_2 and CO_2 environments when the oxygen mole fraction was increased. For corn residue, a decrease, equivalent to 24%, was observed when the oxygen mole fraction was changed from 40% to 60% in N_2 environments while the yields were nearly constant in CO_2 environments. The combustion of torrefied pine sawdust in both environments remained nearly constant across all oxygen mole fractions for both environments.
The yields of the fine fragment mode, PM$_{1.5}$, make up approximately 20% of the total ash yields. No single trend is observed over the yields of all three biomasses when the background gas is changed from N$_2$ to CO$_2$. In CO$_2$ environments, the generated fine fragment ash yields of olive residue were lower than those produced in O$_2$/N$_2$ combustion environments. However, the PM$_{1.5}$ yields generated from combustion of corn residue and torrefied pine sawdust in CO$_2$ environments were similar to those in N$_2$ environments. As with changing the combustion environment, increasing the oxygen mole fraction affected the PM$_{1.5}$ yields of each biomass differently. Increasing the oxygen mole fraction to 40% in both combustion environments caused the yields of olive residue to increase substantially while the yields remained relatively constant when the mole fraction increased from 40% to 60%. In contrast, when combustion of torrefied pine sawdust was performed in both environments, the PM$_{1.5}$ yields remain nearly constant as the oxygen mole fraction was increased. A minimum yield was observed in the fine fragment ash yields of combustion of corn residue in N$_2$ environments while in CO$_2$ environments the yields increased steadily.

In both combustion environments, the PM$_1$, PM$_{2.5}$, and PM$_{10}$ ash yields of all biomasses show similar trends to their respective PM$_{18}$, with the ash yields of PM$_1$ and PM$_{2.5}$ equivalent to approximately half and two thirds of the PM$_{18}$, respectively. The PM$_{2.5}$ and PM$_{18}$ particulate yields of the corn and olive residues are typically lower in O$_2$/CO$_2$ environments than those in O$_2$/N$_2$ while the yields of torrefied pine sawdust were similar in both combustion environments. Increasing the oxygen mole fraction in N$_2$ environments, caused an increase in PM$_{2.5}$ yields for olive residue. In CO$_2$ environments, the PM$_{2.5}$ yields also increased when the oxygen mole fraction was changed from 30% to 40%. In both combustion environments, the PM$_{2.5}$ yields of corn residue and torrefied pine sawdust remained nearly constant.
4.4.2. Particle Size Distributions

The particle size distributions (PSDs) of the particulate matter emissions from the combustion of each biomass in each environment are provided in Figure 4.

Figure 4: Particle size distributions (PSDs) of ash emissions from burning of corn residue, olive residue, and torrefied pine sawdust under various $O_2/N_2$ and $O_2/CO_2$ environments.
The PM$_{18}$ size distributions for all three biomasses, in each combustion environment, are multimodal. Olive residue demonstrated two submicron modes, centered at $\sim 0.03$ µm and $\sim 0.6$ µm, and with the exception of the air and 30% O$_2$-70% CO$_2$ combustion environments a super-micron mode, centered at $\sim 6$ µm. The super-micron mode for the aforementioned two environments appears to have occurred above 18 µm. Corn residue also exhibited two submicron modes as well as a super-micron mode. The submicron modes were centered at $\sim 0.03$ µm and $\sim 0.6$ µm while the super-micron mode appears to have occurred above 18 µm. For torrefied pine sawdust a submicron mode is consistently observed at $\sim 0.03$ µm. The fine fragment mode, centered at $\sim 6$ µm, appears to shift to the left in higher temperature combustion environments, where it is centered between $\sim 0.3$ µm to $\sim 0.6$ µm. Trends may not be indicative for this type of biomass, however, as yields from each stage were low. As seen in Figure 4, the particle size distributions of corn and olive residue are consistent between the N$_2$ and CO$_2$ combustion environments. In addition, increasing the oxygen mole fraction also appears to have no clear effect on the particle size distributions of these two biomasses.

4.4.3. Chemical Composition of Ash Particles

The mineral oxide compositions of olive residue, corn residue, and torrefied pine sawdust are provided in Table 4. The mineral oxide compositions of the olive residue and torrefied pine sawdust were provided by INCAR-CSIC while the composition of the corn residue was obtained utilizing SEM-EDS after ashing experiments were conducted in the laboratories herein. Ashing occurred in a muffle furnace operated at $T_g = 900$ °C (1173 K) in air for 1 hr.
Table 4: Ash chemical compositions, given as mass %, of olive residue (OR), Torrefied Pine Sawdust (TOPI), and the ashed corn residue. The chemical analysis of the olive residue and torrefied pine sawdust was provided by INCAR-CSIC (815°C (1088 K) for 1 hr). The chemical analysis of the corn residue ash was obtained from SEM-EDS after ashing experiments conducted in air at 900 °C (1173 K) for 1 hr.

<table>
<thead>
<tr>
<th>Elements mass (%)</th>
<th>Olive Residue</th>
<th>Torrefied Pine Sawdust</th>
<th>Corn Residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂O</td>
<td>14.80</td>
<td>1.30</td>
<td>12.90</td>
</tr>
<tr>
<td>MgO</td>
<td>3.90</td>
<td>10.50</td>
<td>4.95</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>2.20</td>
<td>2.76</td>
<td>1.30</td>
</tr>
<tr>
<td>SiO₂</td>
<td>13.50</td>
<td>22.90</td>
<td>1.81</td>
</tr>
<tr>
<td>P₂O₇</td>
<td>7.17</td>
<td>3.49</td>
<td>27.36</td>
</tr>
<tr>
<td>SO₃</td>
<td>2.50</td>
<td>2.29</td>
<td>22.97</td>
</tr>
<tr>
<td>Cl</td>
<td>12.80</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>K₂O</td>
<td>31.77</td>
<td>16.40</td>
<td>28.70</td>
</tr>
<tr>
<td>CaO</td>
<td>9.30</td>
<td>34.71</td>
<td>0.00</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.89</td>
<td>3.14</td>
<td>0.00</td>
</tr>
<tr>
<td>MnO</td>
<td>0.00</td>
<td>1.60</td>
<td>0.00</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.12</td>
<td>0.27</td>
<td>0.00</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.00</td>
<td>0.04</td>
<td>0.00</td>
</tr>
<tr>
<td>CuO</td>
<td>0.03</td>
<td>0.04</td>
<td>0.00</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.05</td>
<td>0.37</td>
<td>0.00</td>
</tr>
<tr>
<td>SrO</td>
<td>0.04</td>
<td>0.14</td>
<td>0.00</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>0.00</td>
<td>0.04</td>
<td>0.00</td>
</tr>
</tbody>
</table>

The PM₀.1-0.18 (stage 9 ash particles) and the PM₀.56-1 (stage 6 ash particles) were analyzed utilizing the SEM-EDS technique. Mass fractions of the major elements detected in the PM₀.1-0.18 (stage 9 particles) from burning of olive residue and corn residue in air and a typical oxy-fuel environment (40%O₂-60%CO₂) are provided in Table 5, while the mass fractions of PM₀.56-1 of all three biomasses are provided in Table 6. The corresponding oxy-fuel environments for olive residue and torrefied pine sawdust to air were chosen by matching the char temperatures of each
condition, as provided in Table 7. However, as no complete temperature data is available for corn residue, the oxy-fuel environment of 40% O₂-60% CO₂ was chosen.

Potassium (K), chlorine (Cl), and sulfur (S) were the major elements found in PM₀.₁₋₀.₁₈ (stage 9 ash particles) from combustion of olive residue in both air and the oxy-fuel condition (40%O₂-60%CO₂). K had the highest mass fraction of the PM₀.₁₋₀.₁₈ which is in line with the chemical composition of the high temperature ash analysis of this biomass, see Table 4. However, the mass fractions of silicon (Si) and S in PM₀.₁₋₀.₁₈ did not follow the bulk ash chemical composition of the OR; Si was lower and S was higher in PM₀.₁₋₀.₁₈ than the bulk ash. Moreover, K and Cl mass fractions of PM₀.₁₋₀.₁₈ decreased while sodium (Na) and S mass fractions were increased in 40% O₂-60% CO₂ condition compared to those in air, see Table 5. Similarly, major components observed in PM₀.₁₋₀.₁₈ from combustion of corn residue in air and 40% O₂ – 60% CO₂ were K, S, and Cl. In addition, phosphorous (P) was a major component of the PM₀.₁₋₀.₁₈, existing in higher amounts than olive residue. This is expected as corn residue has the highest P content of the three biomasses. However, the amount of P that is detected in PM₀.₁₋₀.₁₈ was not consistent with the wt% analyzed in the bulk ash. As observed with olive residue, the K and Cl mass fractions of PM₀.₁₋₀.₁₈ for corn residue decreased in 40% O₂-60% CO₂ condition compared to those in air, see Table 5. The Na mass fractions also increased.
Table 5: Chemical compositions, given as mass%, of stage 9 (PM$_{0.1-0.18}$) particles emitted from combustion of an olive residue (OR) and Torrefied Pine Sawdust (TOPI) biomass in air and a simulated oxy-fuel atmospheres (30%O$_2$-70%CO$_2$, 40%O$_2$-60%CO$_2$).

<table>
<thead>
<tr>
<th>Elements (%)</th>
<th>Olive Residue PM$_{0.1-0.18}$ (stg 9)</th>
<th>Corn Residue PM$_{0.1-0.18}$ (stg 9)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Air</td>
<td>40%O$_2$-60%CO$_2$</td>
</tr>
<tr>
<td>Na</td>
<td>7.8</td>
<td>8.5</td>
</tr>
<tr>
<td>Mg</td>
<td>0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>Al</td>
<td>3.5</td>
<td>3.2</td>
</tr>
<tr>
<td>Si</td>
<td>0.3</td>
<td>0.8</td>
</tr>
<tr>
<td>P</td>
<td>1.5</td>
<td>1.9</td>
</tr>
<tr>
<td>S</td>
<td>11.7</td>
<td>12.2</td>
</tr>
<tr>
<td>Cl</td>
<td>27.4</td>
<td>23.5</td>
</tr>
<tr>
<td>K</td>
<td>40.2</td>
<td>37.2</td>
</tr>
<tr>
<td>Ca</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Fe</td>
<td>0.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

The chemical composition given as mass fraction of PM$_{0.56-1}$ is similar to PM$_{0.1-0.18}$ for olive residue with the majority consisting of K, Cl, and S. However, P and Na compositions are higher in PM$_{0.56-1}$ which are parallel to the bulk ash, shown in Table 4. The chemical composition of PM$_{0.56-1}$ from burning of torrefied pine sawdust reflected its bulk ash composition with calcium (Ca) and magnesium (Mg) having the highest mass fractions. Mass fractions of all other elements were also in parallel to the bulk ash with the exception of K and Si which were both lower in PM$_{0.56-1}$. For corn residue, K and P were the major elements in PM$_{0.56-1}$ in both environments. In addition, all other elements reflected their bulk ash mass fractions with the exception of P and S. The mass fractions of P and S increased in PM$_{0.56-1}$ compared to PM$_{0.1-0.18}$; however, the mass fractions still do not reflect those found in the bulk ash. No clear trend was observed when the background gas was switched from N$_2$ to CO$_2$ for the three biomasses.
Table 6: Chemical compositions, given as mass%, of stage 6 (PM$_{0.56-1}$) particles emitted from combustion of an olive residue (OR), Torrefied Pine Sawdust (TOPI), and Corn Residue (CR) in air and simulated oxy-fuel atmospheres (30%O$_2$-70%CO$_2$, 40%O$_2$-60%CO$_2$).

<table>
<thead>
<tr>
<th>Elements (%)</th>
<th>Olive Residue PM$_{0.56-1}$ (stg 6)</th>
<th>Torrefied Pine Sawdust PM$_{0.56-1}$ (stg 6)</th>
<th>Corn Residue PM$_{0.56-1}$ (stg 6)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Air 40%O$_2$-60%CO$_2$</td>
<td>Air 30%O$_2$-70%CO$_2$</td>
<td>Air 40%O$_2$-60%CO$_2$</td>
</tr>
<tr>
<td>Na</td>
<td>11.7 10.7</td>
<td>0.6 0.6</td>
<td>12.5 10.1</td>
</tr>
<tr>
<td>Mg</td>
<td>0.9 1.0</td>
<td>9.2 11.4</td>
<td>2.0 3.5</td>
</tr>
<tr>
<td>Al</td>
<td>2.7 2.4</td>
<td>5.9 3.2</td>
<td>2.0 3.1</td>
</tr>
<tr>
<td>Si</td>
<td>0.3 0.6</td>
<td>4.8 2.7</td>
<td>0.9 1.5</td>
</tr>
<tr>
<td>P</td>
<td>5.1 4.6</td>
<td>2.2 2.9</td>
<td>13.8 17.7</td>
</tr>
<tr>
<td>S</td>
<td>10.9 13.4</td>
<td>1.8 1</td>
<td>14.2 8.3</td>
</tr>
<tr>
<td>Cl</td>
<td>18.0 13.2</td>
<td>0 0.5</td>
<td>2.5 2.1</td>
</tr>
<tr>
<td>K</td>
<td>35.5 40.2</td>
<td>2.0 1.8</td>
<td>32.6 26.4</td>
</tr>
<tr>
<td>Ca</td>
<td>0.0 0.0</td>
<td>41.8 51.2</td>
<td>0.0 8.4</td>
</tr>
<tr>
<td>Fe</td>
<td>0.3 0.0</td>
<td>5.1 4.7</td>
<td>0.0 0.0</td>
</tr>
</tbody>
</table>

Table 7: Average deduced temperatures for the chars of torrefied pine sawdust (TOPI), olive residue (OR), and corn residue (CR) burning in air and in different oxy-fuel atmospheres $^{17}$.

<table>
<thead>
<tr>
<th>Fuels Burned</th>
<th>Ambient Gases</th>
<th>Average char combustion temperatures (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olive Residue (OR)</td>
<td>Air</td>
<td>1650</td>
</tr>
<tr>
<td></td>
<td>30% O$_2$-70%CO$_2$</td>
<td>1550</td>
</tr>
<tr>
<td></td>
<td>35% O$_2$-65%CO$_2$</td>
<td>1650</td>
</tr>
<tr>
<td></td>
<td>50% O$_2$-50%CO$_2$</td>
<td>1850</td>
</tr>
<tr>
<td>Torrefied pine sawdust (TOPI)</td>
<td>Air</td>
<td>1750</td>
</tr>
<tr>
<td></td>
<td>30% O$_2$-70%CO$_2$</td>
<td>1730</td>
</tr>
<tr>
<td></td>
<td>35% O$_2$-65%CO$_2$</td>
<td>1800</td>
</tr>
<tr>
<td></td>
<td>50% O$_2$-50%CO$_2$</td>
<td>2000</td>
</tr>
<tr>
<td>Corn Residue (CR)</td>
<td>Air</td>
<td>1420</td>
</tr>
</tbody>
</table>
4.5. Discussion

4.5.1. Ash Yields

In general, yields were lower in O$_2$/CO$_2$ combustion environments than those in O$_2$/N$_2$ environments for submicron ash particles. This can be explained by the reduction mechanism suggested by Quann and Sarofim$^{27}$. According to this mechanism, submicron particles are formed via vaporization followed by condensation which is strongly affected by temperature$^{28-30}$. Therefore, in order to eliminate the temperature affect and observe the differences in the submicron particle yields between air and oxy-fuel environments, the char temperatures observed during combustion must be matched between each environment. For example, combustion of olive residue in a 35% O$_2$ – 65% CO$_2$ environment experienced the same char temperature as in air whereas for torrefied pine sawdust, the air and 30% O$_2$ – 70% CO$_2$ environments experienced similar char temperatures. When the yields from these oxy-fuel environments are compared to those from air, the yields are observed to be lower. Combustion in an oxy-fuel environment for olive residue reduced the yield from ~20.9mg/g$_{fuel}$ fed to 19.2 while for torrefied pine sawdust the yield was reduced from 0.5mg/g$_{fuel}$ fed to 0.3. This is in parallel with Fryda et. al$^{11}$ who observed lower amounts of fine ash deposited on the filter (includes PM$_1$) when the combustion environment was changed from air to oxy-fuel. This is also in parallel to coal combustion experiments conducted in the same laboratory$^{26}$ as well as other studies$^{31-33}$.

For all biomasses, approximately half of the collected PM$_{18}$ mass is found in the submicron mode which is consistent with the literature$^{6,12,34}$ in which submicron particles were predominant in the total ash. However, this is different than coal studies in which half of the collected PM$_{18}$ mass was found to tend towards the fine fragment mode (FFM)$^{26}$ and 20% (wt%)
was found to exist in the submicron mode. In the current study, only 20% (wt%) of the total ash particles were found in the fine fragment mode. This shift in particle modes can be explained by the high alkali content of the biomasses. On average, the alkali content of the biomasses used in this study were approximately ten times higher than the content found in the coals previously used in this laboratory\textsuperscript{26}. The coals, however, contained approximately ten times the amount of refractory metal oxides than the biomasses. Alkalis, such as potassium and sodium, have lower vaporization temperatures than refractory metal oxides and as a result are more likely to vaporize and condense as the flue gas is cooled resulting in high submicron particle yields\textsuperscript{6, 8, 9, 12}. Although the ratios of PM\textsubscript{1}/PM\textsubscript{18} generated by the combustion of the biomasses are higher than those of coal, the submicron yields generated by the combustion of olive residue and torrefied pine sawdust were not in line with those of the coals burned in a previous study\textsuperscript{26}. Combustion of olive residue in both background gases generated submicron yields approximately seven times higher than the average generated submicron yields of coal while those of torrefied pine sawdust were approximately seven times lower. Corn residue generated submicron yields closest to those of coal. The differences between the yields may be attributed to the differences in the fuel compositions. Olive and corn residue contain lower ash contents than that of coal but higher amounts of alkalis that tend to form smaller particles while torrefied pine sawdust contains an ash content that is ~30 times lower than those of coal resulting in lower submicron yields.

In the present study, the ash yields produced by combustion of each biomass were different; olive residue with the highest yields and torrefied pine sawdust with the lowest, indicating the type of biomass affects the yields. In general, this is consistent with the ash content of the parent fuels as olive residue has the highest ash content and torrefied pine sawdust the lowest. Corn residue, however, has a similar ash content to olive residue, 7.1% (wt) and 7.6%
(wt) respectively (see Table 1, Table 8), but exhibits much lower ash yields collected by the impactor. In order to explain the yields, the ash content of each biomass was verified through ashing experiments. The results from each ashing experiment along with the ash content provided by the proximate analysis and obtained by the impactor results are provided in Table 8.

**Table 8: Ash content of fuels obtained by proximate analysis, ashing experiments in horizontal furnace, and the impactor results. The results are provided in wt %. Ash contents obtained from ashing experiments and the impactor were obtained from burning of the biomasses in air.**

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Ash Content (wt %)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Proximate Analysis</td>
<td>Ashing Experiments</td>
<td>Collected by Impactor</td>
</tr>
<tr>
<td>Olive Residue</td>
<td>7.6</td>
<td>5.8</td>
<td>8</td>
</tr>
<tr>
<td>TOPI</td>
<td>0.4</td>
<td>0.4</td>
<td>0.5</td>
</tr>
<tr>
<td>Corn Residue</td>
<td>7.1</td>
<td>6.3</td>
<td>1.4</td>
</tr>
</tbody>
</table>

According to Table 8, the impactor results are in agreement with the proximate analysis and ashing experiments for olive residue and torrefied pine sawdust. Although the ashing experiments conducted for corn residue reflected the proximate analysis, those collected by the impactor were not in line with the parent fuel’s ash content, indicating for this biomass the collection efficiency by the impactor was rather low. In addition, when the combustion environment was changed from air to an oxy-fuel environment (40% O₂ - 60% CO₂), the percentage of ash collected by the impactor was reduced (to approximately ~0.7%). This in line with Fryda et. al\textsuperscript{11} who observed that the tendencies of the coal and biomass blends to deposit were higher in oxy-fuel environments. The low collection efficiency, resulting in lower ash yields, from combustion of corn residue may be due to the differences in the elemental
composition of the biomasses. According to Masiá et. al\textsuperscript{35}, the elemental composition of biomass and waste fuels vary depending on the origin of the fuels. As seen in Table 1, corn residue contains the highest sulfur content (6.7 wt\%) of the three biomasses. According to Baxter\textsuperscript{20}, sulfur in the flue gas reacts with some alkali species (such as sodium and potassium) which may then condense and cause deposits on the combustion surfaces. In addition, according to Masiá et. al\textsuperscript{35}, when chlorine is not present, alkalis play a less important role in deposit formation. Little chlorine is observed to exist in the corn residue burned in this study and as a result, the alkalis are more likely to react with the sulfur contained in the fuel. The high sulfur and low chlorine contents of the corn residue could increase its tendency to create deposits that then build up on the furnace surfaces. As a result this would lead to lower than expected ash yields collected by the impactor. In addition, sulfur is directly related to slagging as indicated by the slagging index. Common deposition indices were calculated for the three biomasses and the values are provided in Table 9 along with those for the olive residue utilized by Masiá et. al\textsuperscript{35}. 
Table 9: Calculated deposition indices for the three biomasses utilized in this study (Olive Residue, Torrefied Pine Sawdust, and Corn Residue), the Olive Residue studied by Masia et. al\textsuperscript{35}, and the three coals previously studied in this laboratory.

<table>
<thead>
<tr>
<th>Deposition Indices</th>
<th>Olive Residue</th>
<th>Torrefied Pine Sawdust</th>
<th>Corn Residue</th>
<th>Olive Residue*</th>
<th>PSOC 1451 Bituminous</th>
<th>DECS 26 Sub-bituminous</th>
<th>PSOC 1443 Lignite</th>
<th>Inclinations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slagging Index ($R_s$)</td>
<td>0.8</td>
<td>0</td>
<td>100.3</td>
<td>0.5</td>
<td>0.3</td>
<td>0.3</td>
<td>0.2</td>
<td>$R_s &lt; 0.6$ - low slagging</td>
</tr>
<tr>
<td>Fouling Index ($F_u$)</td>
<td>182</td>
<td>45</td>
<td>623</td>
<td>83</td>
<td>0.5</td>
<td>1.6</td>
<td>0.3</td>
<td>$F_u \leq 0.6$ – low fouling</td>
</tr>
<tr>
<td>Slagging Index w/ Phosphorus ($R_{s+P}$)</td>
<td>0.9</td>
<td>0</td>
<td>159.2</td>
<td>0.6</td>
<td>0.3</td>
<td>0.3</td>
<td>0.2</td>
<td>$S_R &gt; 72$ – low slagging</td>
</tr>
<tr>
<td>Fouling Index w/ Phosphorus ($F_{u+P}$)</td>
<td>203</td>
<td>48</td>
<td>989</td>
<td>91</td>
<td>0.5</td>
<td>1.6</td>
<td>0.3</td>
<td>$S_R &gt; 72$ – medium slagging</td>
</tr>
<tr>
<td>Slag Viscosity Index ($S_R$)</td>
<td>29</td>
<td>129.4</td>
<td>4.4</td>
<td>51.7</td>
<td>2068.4</td>
<td>1440.9</td>
<td>5206.5</td>
<td>$S_R \leq 65$ – high slagging</td>
</tr>
</tbody>
</table>

* Obtained from Masiá et. al\textsuperscript{32}

It is important to note that these indices and corresponding inclinations were developed for coals and great care should be taken when interpreting them for biomasses, as they are chemically different from coal\textsuperscript{36}. The slagging index, $R_s$, was determined by multiplying the sulfur content of each fuel by the ratio of basic compounds (low melting temperature) to acidic (high melting temperature) compounds. As seen in Table 10, the slagging index for corn residue is extremely high indicating that combustion of this biomass will most likely lead to deposits...
upon the combustion surfaces. On the contrary, olive residue and torrefied pine sawdust have medium and low slagging inclinations, respectively, which is consistent with the low sulfur content and high collection efficiency of the impactor observed in this study. In addition, the indices reported in Table 10 for olive residue and torrefied pine sawdust are in line with those reported by Masiá et. al\textsuperscript{35} for a variety of biomasses. The minor differences between the slagging indices of the olive residues used herein and in their work can be accounted for the higher sodium oxide (Na\textsubscript{2}O) content in the ash of the olive residue utilized in this study. On the contrary, the indices reported for the corn residue are much higher than the values reported by Masiá et. al\textsuperscript{35}. The sulfur trioxide (SO\textsubscript{3}) and sodium oxide content of the corn residue utilized in this study is much higher than any of the biomasses used in the aforementioned study. These increased amounts directly increase the deposition indices. Another reason for the low collection efficiency of the impactor for the corn residue ash particles may be attributed to the low melting temperature of the corn residue ash. During the ashing experiments it was observed that the corn residue ash started to melt while that of olive residue and torrefied pine sawdust did not, indicative of a lower melting temperature of the ash for this fuel. This could be a result of the high phosphorous pentoxide (P\textsubscript{2}O\textsubscript{5}) content found in the corn residue ash, as seen in Table 4. High contents of phosphorous pentoxide, which has a low melting point as seen in Table 10, have been observed to enhance the development of low melting phases in the fly ash\textsuperscript{35, 37}. 
Table 10: Melting and vaporization temperatures of some common oxides as well as sub-oxides and metals (reduced oxides) found in their ashes (from Ref.38 and other web-based sources). All temperatures are in Celsius with the corresponding value in Kelvin is provided in parentheses.

<table>
<thead>
<tr>
<th>Elements</th>
<th>T_{melting} (°C)</th>
<th>T_{vaporization} (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>44.2 (317)</td>
<td>280 (553)</td>
</tr>
<tr>
<td>P_2O_5</td>
<td>340 (613)</td>
<td>360 (633)</td>
</tr>
<tr>
<td>K</td>
<td>63.7 (337)</td>
<td>774 (1047)</td>
</tr>
<tr>
<td>K_2O</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>S</td>
<td>115 (388)</td>
<td>444.6 (718)</td>
</tr>
<tr>
<td>SO_3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Na</td>
<td>97.7 (371)</td>
<td>883 (1156)</td>
</tr>
<tr>
<td>Na_2O</td>
<td>1132 (1405)</td>
<td>1950 (2223)</td>
</tr>
<tr>
<td>Mg</td>
<td>650 (923)</td>
<td>1107 (1380)</td>
</tr>
<tr>
<td>MgO</td>
<td>2852 (3125)</td>
<td>3600 (3872)</td>
</tr>
<tr>
<td>CaO</td>
<td>2613 (2886)</td>
<td>2850 (3123)</td>
</tr>
<tr>
<td>Ca</td>
<td>839 (1112)</td>
<td>1484 (1757)</td>
</tr>
<tr>
<td>SiO_2</td>
<td>1600-1725 (1873-1998)</td>
<td>2230 (2503)</td>
</tr>
<tr>
<td>SiO</td>
<td>1702 (2048)</td>
<td>1880 (2153)</td>
</tr>
<tr>
<td>Al_2O_3</td>
<td>2072 (2345)</td>
<td>2977 (3250)</td>
</tr>
<tr>
<td>AlO</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe_2O_3</td>
<td>1565 (1838)</td>
<td>-</td>
</tr>
<tr>
<td>FeO</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

As a result, ash particles could melt during combustion and deposit on furnace surfaces, causing lower ash yields for this fuel and a lower collection efficiency of the impactor. In addition, when phosphorous pentoxide is taken into account as a basic compound in the slagging index, the slagging tendency, represented by R_{S+P} of corn residue increases by ~60%. On the contrary, the slagging tendency of olive residue and torrefied pine sawdust increase slightly due to their lower phosphorous pentoxide content.

As the oxygen mole fraction increases, the temperature of combustion also increases. This increase in temperature is reflected in the yields of PM_1 by an increasing trend. This is not observed, however, for the PM_1 yields of corn residue. For this biomass, as oxygen concentration
is increased from 21% to 60% in N\textsubscript{2} environments, submicron yields decreased while all others increased. This is in agreement with Wang et. al\textsuperscript{12} who reported that as oxygen mole fraction increased from 20% to 50%, PM\textsubscript{1}/PM\textsubscript{10} decreased from an average of ~70% (wt\%) to ~50% (wt\%), respectively while the PM\textsubscript{1+}/PM\textsubscript{10} increased. This ratio decreases from ~60\% to ~50\% when the oxygen mole fraction is changed from 21\% to 60\% for the corn residue utilized in this study. Wang et. al\textsuperscript{12} reported that the increase of oxygen mole fraction may enhance mineral matter vaporization, especially in biomass. However, according to this study, molten large ash particles were observed to capture very fine particulate matter from combustion at higher oxygen mole fractions resulting in higher combustion temperatures. This is consistent with Gani et. al\textsuperscript{39}.

As previously stated, the ash of corn residue contains high contents of phosphorous pentoxide, lowering the ash particle’s melting temperature. As oxygen mole fractions increase, the melting of the corn residue’s ash is enhanced, capturing smaller particles as combustion occurs. The increase in yields of olive residue between 30\% and 40\% in CO\textsubscript{2} environments may be a result of the char temperature. Between these oxygen mole fractions, the char temperature increases substantially with increasing oxygen. When the oxygen mole fraction is further changed from 40\% to 60\%, however, small changes in the ash yields are observed which corresponds to small changes in the char temperature.

4.5.2. Particle Size Distributions

A submicron peak is observed at ~0.03 \mu m for all three biomasses. In addition, a subsequent submicron peak is observed for the corn and olive residues at ~0.6 \mu m. For coal studies conducted within the same laboratory, mode peaks were observed at ~0.2 and ~5 \mu m\textsuperscript{26}. This difference is due to the high alkali content of the biomasses. The alkalis in biomasses are more
likely to vaporize and condense than the refractory metal oxides found in coal, tending to form more submicron particles, shifting the mean particle mode diameters to the left\(^9\).

Wang et al.\(^{12}\) suggested that when the oxygen mole fraction increases, large particles tend to fragment to form much finer particles, smaller than 10 µm. In addition, high-speed, high magnification cinematography obtained from another study conducted in this laboratory on combustion observations of biomasses indicated that increasing the oxygen mole fraction from 21% to 50% increased peripheral fragmentation of the char, as seen in Table 11. In the study herein, the increased fragmentation was observed as a shift in the fine fragment mode from above 18 µm to below 10 µm. This may be attributed to changes in the experienced char temperatures, which is affected by fuel type and the oxygen mole fraction in the environment. Torrefied pine sawdust experienced the highest char temperatures as listed in Table 7. For temperatures above 1800 K, a mode is centered between ~0.3 and ~0.6 µm, as seen in Figure 4. As the char temperature decreases (1750 – 1800 K) this mode shifts to the right and becomes a super-micron mode centered at ~6 µm. For the burning of olive residue in combustion environments with similar char temperatures, the location of the super-micron mode is the same. When olive residue is burned in combustion environments with lower char temperatures (1550 – 1650 K), however, the super-micron mode shifts to above 18 µm. This is similar to the ash size distributions of corn residue which burns at the lowest char temperatures. The submicron modes for all environments are similar and unaffected by the char temperatures, since the predominant compounds in this mode vaporize at low temperatures.
Table 11: High-speed, high magnification cinematography images of single particles of biomass (Olive Residue and Torrefied Pine Sawdust) in air and 50% O$_2$ – 50% CO$_2$.$^{17}$

<table>
<thead>
<tr>
<th></th>
<th>Air</th>
<th>50% O$_2$ – 50% CO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olive Residue</td>
<td><img src="image1" alt="Image" /></td>
<td><img src="image2" alt="Image" /></td>
</tr>
<tr>
<td>Torrefied Pine Sawdust</td>
<td><img src="image3" alt="Image" /></td>
<td><img src="image4" alt="Image" /></td>
</tr>
</tbody>
</table>

In this study, a bimodal size distribution, with peaks at ~0.03 and ~0.6 µm, was observed in PM$_{18}$ for the combustion of olive residue in air. Another mode exists above this range. This is in agreement with a study conducted in 2005 by Jiménez and Ballester$^9$ who also observed a bimodal distribution in PM$_{10}$ of orujillo when combusted in air. However, they observed mode peaks at ~0.2 and ~3 µm. This may be due to differences in the elemental compositions between the two biomasses. The orujillo utilized by Jiménez and Ballester$^9$ has higher aluminum and silicon contents in the bulk ash than those in the bulk ash of the olive residue burned herein. These elements have high vaporization points and tend to form larger ash particles due to fragmentation. In addition, by co-firing orujillo with coal, Jiménez and Ballester$^9$ observed that the mean particle diameter of the submicron mode peak was consistent with that when orujillo was fired alone. This indicates that when biomass is co-fired with coal, the high alkali content of the biomass dominates the formation of submicron particles. The PM$_{10}$ size distribution of the torrefied pine sawdust burned in air this study is biomodal with peaks at ~0.03 µm and ~6 µm.
This bimodal distribution is in accordance with the study conducted by Pagels et. al\textsuperscript{34} who also burned a woody biomass (moist forest residue). However, the mean particle mode diameters observed by Pagels et. al\textsuperscript{34} were ~0.2 and ~2 µm. This may be due to the differences between the fuels fed particle size.

4.5.3 Chemical Composition of Biomass Particulates

According to Jiménez and Ballester\textsuperscript{8}, the submicron particles emitted by orujillo combustion in air, are essentially composed of K\textsubscript{2}SO\textsubscript{4} (potassium sulfate) and KCl (potassium chloride) in almost the same amount, on a mass basis. This results in a mass ratio of sulfur to chlorine of ~0.3. The results of combustion of the olive residue utilized in the present study in air are in line with those of Jiménez and Ballester\textsuperscript{8} as the majority of PM\textsubscript{1.1-18} was comprised of potassium, chlorine, and sulfur. The resulting sulfur to chlorine mass ratio is ~0.4. In this study, the mass fractions of Si and S in PM\textsubscript{0.1-0.18} were not in agreement with the composition of the bulk ash of the olive residue. Si was lower while S was higher than those in the bulk ash. This could be attributed to the high vaporization temperature of the Si as mentioned in the study of Kazanc and Levendis\textsuperscript{26}. When the background gas was changed from N\textsubscript{2} to CO\textsubscript{2} for the combustion of olive residue, the mass fraction of K and Cl decreased in PM\textsubscript{0.1-0.18} while those of Na and Si increased slightly. This may be attributed to the temperature difference between the two environments; with the char temperature of the 40% O\textsubscript{2} – 60% CO\textsubscript{2} environment being slightly higher (~50 degrees C higher as interpolated from Table 7) than that of air. Higher vaporization temperatures of Si and Na compared to the K and Cl may have caused this difference as they are more temperature dependant in the range of combustion temperatures. The PM\textsubscript{0.56-1} ash particles of the olive residue in both environments have similar to the bulk ash
composition. This is in accordance with Jiménez and Ballester\textsuperscript{8, 9} who reported that the coarse particles essentially retain the original fuel characteristics indicating differences between the formation mechanisms for fine and coarse particles.

The mass fractions of the PM\textsubscript{56-1} particles resulting from the combustion of torrefied pine sawdust in both air and oxy-fuel environments are in line with those of the bulk ash. Silicon and potassium, however, exist in lower mass fractions in these particles. This is due to the vaporization temperature of these elements. Silicon has a high vaporization point and is more likely to fragment during combustion, forming coarser particles while potassium has a low vaporization point, causing more fine particles to form.

The PM\textsubscript{0.1-0.18} particles resulting from combustion of corn residue in air and 40\% O\textsubscript{2} – 60\% CO\textsubscript{2} consist mostly of K, Cl, and S, indicating these particles are likely formed by vaporization followed by condensation of these low vaporization point elements. Like olive residue, the particles deposited on stage 6 reflect the bulk ash of the fuel. Exceptions to this are phosphorous and sulfur which are not in line with the expected amounts. Both elements were lower than their expected amounts. Corn residue contains the highest contents of both phosphorous and sulfur when compared to the other biomasses burned in this study. However, when the sulfur mass fractions of the particles collected on stage 6 and 9 from the combustion of olive residue and corn residue are compared, the mass fractions are similar. This may indicate that sulfation of particles occurs, leading to deposition of particles on the combustion surfaces as previously discussed. In addition, the mass fraction of phosphorous is higher in the particles of stage 6 than those of stage 9, as expected. The discrepancy between the mass fractions of these fine particles and bulk ash may be attributed to the low melting temperature of phosphorous. As
previously stated, the low melting temperature of phosphorous causes it to melt during the combustion process, also contributing to deposition on the furnace walls.

For combustion of the three biomasses, changing the background gas from N\textsubscript{2} to CO\textsubscript{2} had no clear effect on the chemical composition of the PM\textsubscript{56-1}. This is in line with the results obtained by Fryda et. al\textsuperscript{11} as well as the results of the chemical composition of the PM\textsubscript{56-1} emissions produced by the three coals studied in this laboratory\textsuperscript{23}. In addition, the latter study observed a decrease of Si and Al in the PM\textsubscript{1-18} emissions while no clear trend was observed in the PM\textsubscript{1-18} emissions of biomass when the background gas was changed from N\textsubscript{2} to CO\textsubscript{2}. The difference between these studies can be attributed to the differences between the fuel compositions. Coals contain higher amounts of Al\textsubscript{2}O\textsubscript{3} and SiO\textsubscript{2} than the biomasses utilized in this study while the biomasses contain higher amounts of alkalis. The PM\textsubscript{1-18} emissions are assumed to form by vaporization and condensation. The Al\textsubscript{2}O\textsubscript{3} and SiO\textsubscript{2} found in coal have high vaporization points and are more likely to undergo reduction mechanisms to form more volatile respective suboxides. When the background gas is changed from N\textsubscript{2} to CO\textsubscript{2}, these suboxides are less likely to form. On the contrary, the alkalis of biomass have low vaporization points and directly vaporize, regardless of the combustion environment.

If fired in boilers, both conventional and oxy-fuel, the three biomasses studied will cause a reduction in the plant outputs due to their higher tendency to deposit on combustion surfaces. This may be attributed to their high alkali content and high amounts of submicron particle yields. As previously mentioned, the alkali constituents in biomass are \~10 times those of coal while the refractory metals are one tenth. The increased alkali content of the biomass is reflected in the slagging and fouling indices, reported in Table 9, as higher values. The higher refractory metal
oxide and lower alkali contents of the coals are reflected in the deposition indices by lower values. The slagging index of olive residue is three times higher while that of corn residue is 400 times higher than the slagging indices reported for the coals previously studied in this laboratory. The torrefied pine sawdust has a lower slagging index than that of coal due to its lower sulfur content. In addition, the fouling indices of all three biomasses are between 5 times (torrefied pine sawdust) and 780 times (corn residue) higher than those of the coals. When phosphorous is considered, the slagging and fouling indices increase substantially while those of coals remain relatively unchanged, suggesting that the higher phosphorous content of the biomasses will further increase the deposition tendencies of these fuels. The increased mass fractions of submicron particles generated from the combustion of these three biomasses will further affect the deposition tendency since these particles are not easily captured by environmental cleanup devices and contain more alkalis than the corresponding coal particles. As a result, in oxy-fuel combustion facilities these particles may be reintroduced to the furnace when the flue gas is recirculated and deposit on boiler walls, reducing the system output. In addition, the ash contents of the three biomasses contain on average more sulfur and chlorine than those of the coals utilized in a previous study in this laboratory\textsuperscript{23} and those studied by Buhre et. al\textsuperscript{28}. These higher contents will increase their tendency to corrode boiler surfaces, further affecting the system output.

4.6. Conclusions

In this study, three pulverized solid biomasses (olive residue, corn residue, and torrefied pine sawdust) were burned in a laboratory drop-tube furnace. Combustion took place in various O\textsubscript{2}/N\textsubscript{2} and O\textsubscript{2}/CO\textsubscript{2} environments. Particle emissions were collected on 13 stages of a Model 125A
Nano-Moudi-II impactor. Particulate matter yields and size distributions were obtained by weighing the aluminum substrates before and after experiments from each stage, according to their cut sizes. Moreover, the chemical composition of the ash particles were captured with a scanning electron microscopy coupled with an electron dispersive spectroscopy (SEM-EDS) system. Results show the following:

- Olive residue resulted in by far the largest mass fractions of collected ash particles, while torrefied pine sawdust had the lowest. The yields of these two biomasses were analogous with the ash contents (wt %) of the parent fuels. The yields of corn residue, however, were lower than expected when compared to the parent fuel’s ash content. No explanations needed in the conclusions. The mass fractions of submicron particles for all biomasses constituted approximately 50% (wt %) of the PM$_{18}$, and were higher than those generated by coal combustion experiments conducted in the same laboratory. Typically, the submicron ash particle yields from the combustion of all three biomasses were lower in oxy-fuel conditions (30% and 40% O$_2$ with CO$_2$) than in air. Similarly, when the background gas shifted from N$_2$ to CO$_2$ at the same oxygen mole fraction, yields were typically lower.
- As the oxygen mole fraction increases, the PM$_1$ yields of the three biomasses typically increase.
- The PM$_{18}$ size distributions for all three biomasses are multimodal in each combustion environment, with a similar submicron mean particle diameter at ~0.03 µm. An additional submicron peak was observed at ~0.6 µm for olive residue and corn residue in
all combustion environments and for higher oxygen mole fractions of torrefied pine sawdust in both environments.

- As char temperatures experienced during the combustion of the three biomasses increased, the mean particle diameter of the super-micron mode shifted to smaller diameters.

- Changing the background gas had little effect on the chemical composition of submicron particles generated from biomass combustion. These particles contained high amounts of alkalis (potassium, calcium, and sodium) and chlorine, while corresponding coal particles contained high amounts of refractory metals. Phosphorous and sulfur also existed in high amounts in the submicron particles of corn residue.

- Chemical compositions of super-micron particles (PM$_{1.18}$) from combustion of all three biomasses reflected the bulk ash composition of the parent fuels. No clear trend was observed within the mass yields or chemical compositions when the background gas was changed or when the oxygen mole fraction was increased.

- The high amounts of alkalis found in the three biomasses and their corresponding submicron particles will increase the ash deposition tendencies of these fuels in boilers when compared to coal while higher chlorine contents will cause corrosion of boiler surfaces. This will reduce the boiler output indicating steps should be taken to manage the generated submicron particles.

**Acknowledgment**

The authors acknowledge financial assistance from the NSF award CBET-0755431. Technical assistance by Mr. William Fowle, Mr. Reza Khatami, and Mr. Juan Riaza is also acknowledged.
4.7. References


CHAPTER 5
5. Conclusions

The gaseous and particulate emissions from combustion of various coals and biomasses in a drop-tube furnace were observed in this study in various O$_2$/N$_2$ and O$_2$/CO$_2$ environments. The gaseous effluent of the drop tube furnace was channeled to continuous-flow analyzers to measure emissions of NO$_x$ (Thermo Electron Model 10 Chemiluminescent NO-NO$_2$-NO$_x$ analyzer), SO$_2$ (Rosemount Analytical UV SO$_2$ analyzer), and CO (Horiba VIA-510 analyzer). The outputs of the analyzers were recorded by using Lab View software.

For the particulate emission study, a thirteen stage Nano-Moudi cascade impactor (Model125A Non-Rotating by Applied Physics) was coupled to the furnace outlet through a water-cooled probe. 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 which allowed the furnace effluent to be thermally quenched, chemically inerted, and diluted in order to minimize further gas-phase and condensed-phase reactions. Particles were collected upon impaction plates, loaded with aluminum substrates, as they traveled through the impactor stages. 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. Samples were prepared out of the stored aluminum substrates to observe the morphology of the PM$_{1}$ and PM$_{1.5}$ with a Scanning Electron Microscope (SEM) as well as the chemical composition of the PM$_{1}$ with Scanning Electron Microscope coupled with Energy Dispersive Spectroscopy (SEM-EDS). Experimentally obtained chemical compositions of submicron particles (PM$_{1}$) were then compared to the chemical composition of submicron particles with calculations based on Quann and Sarofim’s$^1$ model. A numerical coal combustion
model\textsuperscript{2} was also used to obtain real-time CO and CO\textsubscript{2} concentrations. Results were interpreted based on observations of the combustion behavior and on the deduced particle temperatures of the same fuels burned in this laboratory under similar conditions.

Conclusions of this work are presented in three categories; the effect of 5.1) replacing background N\textsubscript{2} gas with CO\textsubscript{2}, 5.2) ranks, types, and elemental composition, and 5.3) oxygen mole fraction on both gaseous and particulate emissions.

5.1. The effect of replacing background N\textsubscript{2} gas with CO\textsubscript{2} on both gaseous and particulate emissions.

- In the case of coals burned in this study, NO\textsubscript{x} emissions in O\textsubscript{2}/CO\textsubscript{2} environments were lower by 19-43\% than those in O\textsubscript{2}/N\textsubscript{2} environments, at the same O\textsubscript{2} mole fractions (22-39\% for bagasse and blends). However, when combustion in air was compared to combustion at different O\textsubscript{2}/CO\textsubscript{2} combinations, NO\textsubscript{x} reductions (averaged among all four coals) were calculated to be in the range of 9-43\% (9-33\% for bagasse and blends).
- SO\textsubscript{2} emissions remained largely unaffected by the replacement of the N\textsubscript{2} diluent gas with CO\textsubscript{2} from burning of the coals.
- The CO emissions of the fuels were negligible in all cases, except in 20\% O\textsubscript{2}, where they were measurable; they were higher in the CO\textsubscript{2} environment than in the N\textsubscript{2} environment.
- Submicron (PM\textsubscript{1}) and fine fragment mode (PM\textsubscript{1.5}) particle emission yields in O\textsubscript{2}/CO\textsubscript{2} environments were lower than those in O\textsubscript{2}/N\textsubscript{2} environments, at the same O\textsubscript{2} mole fractions for all three coals (bituminous, sub-bituminous, and lignite) and three biomasses (olive residue, corn residue, and torrefied pine sawdust) tested herein.
In either background gases, multi-modal ash particle size distributions were observed for both coals and biomasses.

In both air and simulated oxy-combustion (40%O₂-60%CO₂) conditions, spherical particles were mostly observed in the submicron ash mode whereas a mix of irregularly-shaped particles and spherical particles were observed in the PM₁₅ (FFM) from burning of the coals.

The yields of the major elements (Si, Al, Fe, Ca, K, Na, and S) in ultrafine ash particles (PM₀.₃₂) from burning of all three coals were typically lower under oxy-coal conditions than those under conventional air combustion.

PM₀.₅₆₋₁ (stage 6) of the three coals in this study was mainly composed of Si and Al (and Ca for sub-bituminous), regardless of the combustion conditions.

PM₀.₁₋₀.₁₈ particles of all coals were highly-enriched in S regardless of the combustion conditions.

The chemical composition of the PM₀.₅₆₋₁ sub-category was similar in CO₂, and in N₂ background gases.

The composition of the ultrafine PM₀₁₋₀.₁₈ sub-category was affected by replacing N₂ with CO₂, and mass fractions of Si, Ca Al, decreased whereas Na, K and S increased.

This difference in composition and sensitivity to background gas between PM₀.₁₋₀.₁₈ and PM₀.₅₆₋₁ indicates that different mechanisms are responsible for the formation of these particles.
5.2. The effects of fuel ranks, types, and elemental composition on both gaseous and particulate emissions.

- \( \text{NO}_x \) emissions from the various fuels burned did not clearly reflect their nitrogen content (0.2-1.4%), except when large differences were present.
- Conversion of the fuel-nitrogen to \( \text{NO}_x \) was in the range of 20-50% in all cases.
- The \( \text{SO}_2 \) emissions were found to be dependent on the sulfur and calcium contents of the fuels.
- Conversion of the sulfur in the fuel to \( \text{SO}_2 \) spanned the entire possible range, from a few percent to 100% in the cases examined herein.
- Coal rank and ash content of the parent fuel did not have any significant impact on the submicron ash emission yields. All three coals had comparable submicron ash yields (~2 mg/g\(_{\text{fuel-fed}}\)).
- In the case of biomasses, olive residue resulted in by far the largest submicron ash yields with an average of 20.5 mg/g\(_{\text{fuel fed}}\), while torrefied pine sawdust, with an average of 0.5 mg/g\(_{\text{fuel fed}}\), had the lowest submicron yields. The yields of these two biomasses were analogous with the ash contents of the parent fuel. The submicron yields (average of 2.0 mg/g\(_{\text{fuel fed}}\)) of corn residue, however, were lower than expected when compared to the parent fuels ash content.
- Corn residue has similar ash content (wt%) to olive residue, however, it has the highest phosphorous and sulfur content possibly leading to a higher deposition tendency in the furnace. This explains the lower than expected yields.
For all biomasses, the majority (approximately 50 wt%) of the emitted ash particles were found to be submicron particles. This is attributed to the high alkali content of the biomasses.

The degree of fragmentation that the coals experienced during combustion increased their respective PM$_{1.5}$ yields (lignite>sub-bituminous>>bituminous).

The elemental composition of both PM$_{0.1-0.18}$ and PM$_{0.56-1}$ showed a strong correlation with the composition of the ash content (HTA) of the respective coals.

For olive residue, potassium, chlorine, and sulfur were the major constituents of both PM$_{0.56-1}$ (stage 6 particles) and PM$_{0.1-0.18}$ (stage 9 particles) in both air and in a typical oxy-fuel environment. Phosphorous and sodium exist in higher mole fractions in PM$_{0.56-1}$ particles and are more analogous to the bulk ash.

Potassium was the major element observed in particles from both PM$_{0.56-1}$ and PM$_{0.1-0.18}$ for corn residue in both air and in a typical oxy-fuel environment. PM$_{0.1-0.18}$ particles contained more chlorine than PM$_{0.56-1}$ while more phosphorous was observed in PM$_{0.56-1}$ than in PM$_{0.1-0.18}$. Phosphorous and sulfur did not reflect the mass fractions of the bulk ash due to the increased deposition tendency of this biomass.

The mass fractions of elements within the PM$_{0.56-1}$ particles of torrefied pine sawdust resembled those of the bulk ash with calcium and magnesium existing in the highest amounts.

5.3 The effects of oxygen mole fraction on both gaseous and particulate emissions.

NO$_x$ emissions increased with increasing oxygen mole fraction until ~50% O$_2$ was reached; thereafter, they monotonically decreased with increasing O$_2$. At 100% O$_2$, NO$_x$
emissions became comparable to those in air. This trend was observed regardless of the fuel mass flow rate or the equivalence ratio.

- Increasing the oxygen mole fraction increased the submicron emission yields for all coals and biomasses; this increase was more significant in N₂ environments than in CO₂ environments for all coal types tested. Moreover, the submicron ash yields of lower rank coals (lignite and sub-bituminous) were more affected by the oxygen mole fraction than those of the bituminous coal (PSOC 1451).

- The chemical composition of the ultrafine PM_{0.01-0.18} sub-category was affected when the O₂ mole fraction increased in either N₂ or CO₂; the mass fractions of Si, Ca and Al increased at the expense mostly of Na, K and S but, also, in most cases of Fe and Mg.
References


CHAPTER 6
6. Suggestions for Future Work

It may not be practical to replace coal with biomass in existing coal-fired furnaces as biomasses' energy content is lower to those of typical coals. However, its co-firing with coal reduces net carbon dioxide emissions. Therefore, the effect of blending coals with biomasses on gaseous emission yields (NOx, SO2, and CO) was studied herein. However, the particulate emission yields were not studied from co-firing of coal with biomass and were deemed beneficial. High alkali metal biomasses; olive residue, corn residue, and pine sawdust may be blended by low sulfur coals; lignite and sub-bituminous coals used in this study to see the effect of lower vaporization alkali metals (Na, K, etc) in biomass on higher vaporization refractory metals (Si, Al, etc.) in coal matrix. PM1 emission yields from coal were almost unaffected by the coal type; however, biomass PM1 emission yields were greatly affected by the biomass type. Further investigation can be conducted to detect if there is a synergistic effect of blending these two very different composition fuels.

The lower ash collection efficiency of corn residue by the impactor suggested possible deposition of particles on furnace and cooling probe surfaces. The higher deposition indices calculated based on its higher phosphorus and sulfur content supported this assumption. Deposition of the biomasses and coals collected on the cooling probe needs to be experimentally investigated from burning coals that have low deposition tendencies and biomasses that have high deposition tendencies.

A detailed char combustion model was used in this study to obtain temporal and spatial CO and CO2 mole fractions in char particle during the combustion. In addition to this model, a kinetic model can be utilized to determine the mole fraction of the mineral sub-oxide represented
by $\text{MO}_{n-1}(v)$ in Reaction 1. To obtain the kinetic constants that are needed for the aforementioned kinetic model, thermo gravimetric analysis can be done by simulating Reaction 1.

\[ \text{MO}_n(s) + \text{CO} = \text{MO}_{n-1}(v) + \text{CO}_2 \]