PARTICULATE EMISSIONS FROM COMBUSTION OF BIOMASS IN CONVENTIONAL COMBUSTION (AIR) AND OXY-COMBUSTION CONDITIONS

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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 O₂ mole fraction was increased from 20% to 60% in N₂ environments while a range of 30% to 60% O₂ mole fractions were used in CO₂ environments to represent plausible dry oxy-fuel combustion conditions. Submicron particulate matter (PM₁) emission yields of all three fuels were typically lower in O₂/CO₂ environments than in O₂/N₂ environments. When the oxygen mole fraction was increased, the PM₁ yields typically increased. The mass fractions of submicron particulate matter (PM₁/PM₁₈) collected from biomass combustion were higher than those of coal combustion. PM₁ constituted approximately 50 wt% of the collected ash particles in PM₁₈ 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 PM₁ 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 PM₁ from the biomasses. In addition, phosphorous and sulfur also existed in high amounts in PM₁ of corn residue. Super-micron particles (PM₁-₁₈) 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.
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# TABLE OF CONTENTS

ABSTRACT ................................................................................................................................ ii

ACKNOWLEDGEMENT ........................................................................................................ iv

TABLE OF CONTENTS ........................................................................................................... v

LIST OF FIGURES ................................................................................................................ vii

LIST OF TABLES ................................................................................................................... viii

1.0 Introduction ................................................................................................................... 1

2.0 Literature Review ........................................................................................................ 7

2.1 Ash Yields and Particle Size Distributions ................................................................. 7

2.2 Chemical Composition of Ash Particles ................................................................. 11

3.0 Experimental Setup and Procedure ....................................................................... 14

3.1 Biomass Background and Characteristics ....................................................... 14

3.2 Ashing Experiments ............................................................................................... 18

3.3 Combustion Experiments and SEM-EDS Analysis ................................................ 18

4.0 Results ................................................................................................................... 23

4.1 Ash Yields ........................................................................................................... 23

4.2 Particle Size Distributions .................................................................................... 26

4.3 Chemical Composition of Submicron Ash Particles ........................................ 28

5.0 Discussion ............................................................................................................. 33

5.1 Ash Yields ........................................................................................................... 33
5.2 Particle Size Distributions ........................................................................................................ 40

5.3 Chemical Composition of Submicron Particles .................................................................. 43

6.0 Conclusions ....................................................................................................................... 47

7.0 Recommendations for Further Work .................................................................................... 49

8.0 Works Cited ......................................................................................................................... 51

9.0 Appendix ........................................................................................................................... 54

9.1 Deposition Indices – Without the Effects of Phosphorous ................................................. 54

9.2 Deposition Indices – With the Effects of Phosphorous ....................................................... 55
LIST OF FIGURES

Figure 1: Schematic of pre- and post-combustion capture and sequester technologies .......................... 3

Figure 2: Typical oxy-fuel combustion plant configuration ................................................................. 4

Figure 3: Cross section view of the experimental set-up consisting of the 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. ................................................................................................................................................................. 19

Figure 4: 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). .................................................................................................................................................................................. 24

Figure 5: 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 .................... 27
LIST OF TABLES

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)\textsuperscript{25} in Spain. The proximate analysis for the corn residue was provided by Giuntoli et. al\textsuperscript{41} while the ultimate analysis was obtained from Alves et. al.\textsuperscript{37}........ 17

Table 2: Photographs of the olive residue, torrefied pine sawdust, and corn residue. The first row shows the particles as received while the second row represents the ground and sieved powders. ....................................................................................................................................................... 18

Table 3: Nominal cut size of the stages of the Nano-Moudi ash impactor stages. 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. ................................................................................................................................................................. 21

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 1hr. ........................................................................................................................................ 29

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 corn residue (CR) biomass in air and a simulated oxy-fuel atmospheres (40%O$_2$-60%CO$_2$)......................................................................................................................... 30

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$_2$).............................................. 32
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.  

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 9: Calculated deposition indices for the three biomasses utilized in this study (Olive Residue, Torrefied Pine Sawdust, and Corn Residue) and the three coals previously studied in this laboratory and the Olive Residue (indicated by *) studied by Masiá et al.  

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. and other web-based sources). All temperatures are in Celsius with the corresponding value in Kelvin is provided in parentheses.  

Table 11: High-speed, high magnification cinematography images of single particles of biomass (Olive Residue and Torrefied Pine Sawdust) in air and 50% O₂ – 50% CO₂.  


1.0 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 energy 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 ~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.

Clean coal technologies are a collection of technologies (pre- and post-combustion) that have been developing since the early part of the 20\(^{th}\) century\(^5\) to reduce the environmental footprint of coal-based electricity plants. These include technologies that increase the operational efficiency of a power plant and those that reduce emissions\(^6\). Initially, the development of clean coal technologies focused upon the reduction of traditional pollutant emissions such as sulfur dioxide and nitrogen oxides (precursors to smog and acid rain) as well as particulate matter\(^7\). Despite the use of coal tripling since 1970, a significant drop in these pollutants has occurred through the use of clean coal techniques such as chemically washing minerals and impurities from the coal, flue gas desulfurization units (scrubbers), low nitrogen oxide burners, selective catalytic reduction, electrostatic precipitators, fluidized bed combustion, and integrated gasification combine cycle (IGCC)\(^8,9\). In addition, according to the National Energy Technology
Laboratory, new coal power plants built today emit 90% less sulfur dioxide, nitrogen oxides, mercury, and particulates through the use of these emission reduction technologies\textsuperscript{5, 10}. Due to increasing concerns over environmental impacts over the years, a new generation of clean coal technologies has emerged with the intention of reducing greenhouse gases including carbon dioxide\textsuperscript{7}. As carbon dioxide emissions from power plants are implicated in global warming, Carbon Capture and Storage (CCS) technologies are at the forefront of those being developed. These technologies involve either the pre- or post-combustion capture of carbon dioxide emissions followed by their transportation and storage. The simplest strategy to capture carbon dioxide is through chemical scrubbing of the flue gases post-combustion\textsuperscript{11}. In addition, this strategy requires the least modification to power plants, making it the most suitable for retrofitting of existing power plants. During post-combustion capture, chemical separation processes are performed in an absorbent tower and utilize a solvent to remove carbon dioxide from the flue gas\textsuperscript{11}. The absorbed carbon dioxide is then liberated from the solvent and compressed for transportation and storage. Liberating the carbon dioxide, however, requires thermal energy, reducing the efficiency of the power plant. Depending on the plant type, the absorbent used, and the flue gasses, Ghoniem\textsuperscript{11} estimates that the efficiency of coal plants utilizing post-combustion capture would be reduced by 8-16 percent. Furthermore, he reports that carbon dioxide compression for transport and storage would further reduce efficiency by 2-4%. The pre-combustion capture of carbon dioxide emissions generated from burning coal, involves partial oxidation of the fuel hydrocarbons to syngas, through gasification of the coal\textsuperscript{11, 12}. The syngas then undergoes a gas-water shift reaction to oxidize the carbon monoxide to carbon dioxide and increase the hydrogen content of the stream. The resulting carbon dioxide is then separated, leaving the other portions of fuel gas behind to burn with air in the combustion
chamber of the gas turbine. As with post-combustion capture, the efficiency of power plants utilizing pre-combustion capture will decrease as an air separation unit is required to obtain the oxygen required for partial oxidation of the coal. A schematic of pre- and post-combustion capture strategies are provided in Figure 1.

![Figure 1: Schematic of pre- and post-combustion capture and sequester technologies](image)

In addition to pre- and post combustion capture, Carbon Capture and Storage (CCS) in conjunction with oxy-fuel combustion is another promising clean coal technology that can capture more than 90% of carbon dioxide emissions generated from the use of coal and other fossil fuels in electricity generation\(^1\). 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\(^2\). If the flue gas is dried, then combustion takes place in \(O_2/CO_2\) environments. As with pre- and post-combustion capture technologies, the efficiency of coal-fired power plants utilizing oxy-fuel combustion will decrease. The use of the ASU is estimated to reduce plant efficiency by 5-7% while recirculating the flue gases further decreases
efficiency by approximately 4%. A diagram depicting the typical configuration of an oxy-fuel combustion plant is provided in Figure 2.

![Diagram of Oxy-fuel Combustion Plant](image)

**Figure 2: Typical oxy-fuel combustion plant configuration**

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 CO₂ emitted to the atmosphere, while two medium sized power plants, (~16 MW each) exclusively fired with pulverized orujillo (a waste residue of the olive oil industry), have recently been built in Spain. In addition, bagasse (a by-product of the sugar cane industry) supplied 3% of the Brazilian energy matrix in 2009. 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. In addition, during the same year, the use of biomass accounted for 1.5% of the world’s generated electricity. 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, 20, 21}. The energy used in the growing, harvesting, and transportation processes results in CO\textsubscript{2} 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{20, 21}. 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{13, 20}, 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 CO\textsubscript{2}). 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 2, 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 CO\textsubscript{2} 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{22} 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.
2.0 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{23} and Yuzbasi et. al.\textsuperscript{24} Riaza et al.\textsuperscript{25} 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{26} while Fryda et. al\textsuperscript{20} 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.

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{18} 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{17}, 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{18} reported multimodal particle size distributions (PSD’s) for the combustion of orujillo and its blends, Christensen and Livbjerg\textsuperscript{15} 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\textsuperscript{15}, 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, Johansson et al.\textsuperscript{27} 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.²¹ 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 PM₁₀. The mass fraction of submicron particles accounted for approximately two thirds of the PM₁₀ in an atmosphere of 20% O₂ in N₂. Increasing the oxygen mole fraction to 50% caused the mass fraction of submicron particles (PM₁) to decrease (to ~50 %) while the percentage of super-micron (PM₁-10) particles in PM₁₀ 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 PM₁₀ yields increased. They suggested that at higher oxygen mole fractions larger ash particles were more likely to fragment, forming much more PM₁₀. Wang and his co-workers²¹ 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.\textsuperscript{20} 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\textsubscript{2} – 70\% CO\textsubscript{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.\textsuperscript{20} 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{28}, 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{20} 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 O₂/CO₂ environments than in O₂/N₂ 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.

2.2 Chemical Composition of Ash Particles

In addition to particle size distributions, 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{17,18} and its blends\textsuperscript{18}, Jiménez and Ballester also studied the chemical composition of the resulting particulate emissions\textsuperscript{18} 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 (K₂SO₄) 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 (SO₂), and hydrogen chloride (HCl) existed in the gas phase and were the only stable species. When the temperature decreased, KOH
reacted with the SO$_2$ and through nucleation formed K$_2$SO$_4$ 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{17}. When orujillo was co-fired with coal, KCl disappeared from the particles, substituted by more K$_2$SO$_4$\textsuperscript{18}. 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{17}. The study conducted by Christensen and Livbjerg\textsuperscript{15} 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$_2$SO$_4$ 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{27} 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{21} 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{15, 17, 18}. 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.²⁰ 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. al²⁰ concluded that blending of coals with biomass in both combustion conditions did not change the ash chemistry.
3.0 Experimental Setup and Procedure

3.1 Biomass Background and Characteristics

Biomass may be categorized into different types. These types include residues (such as sewage sludge, agricultural, industrial, and land based and aquatic animal wastes), herbaceous (such as grasses, stalks, and straw), aquatic (such as kelp), woody (such as sawdust), and derivatives (such as paper)\textsuperscript{29, 30}. In this study three different biomasses were burned; two industrial residues, olive residue (OR) and corn residue (CR), and one woody biomass, torrefied pine sawdust (TOPI).

The olive residue burned in this study was obtained from the Instituto Nacional del Carbón (INCAR-CSIC) and was used in a recent study\textsuperscript{25}. Olive residue is a byproduct of the olive oil industry. During olive oil production, olives are ground into a paste and the oil extracted mechanically. Oil is then removed from the remaining paste chemically through the use of solvents, resulting in a dry residue (mostly comprised of the skins and pits of the olives) with a high calorific value. The resulting olive residue, or orujillo, has many advantages as an energy source; it is easy to collect and transport, provides farmers a safe way to dispose of a potential material that could cause pollution\textsuperscript{31}, produces a high temperature when burned\textsuperscript{32}, and is widely available due to the growing olive oil industry. Due to these benefits, it is commonly used today as a low cost renewable fuel for domestic and industrial heating. In addition, olive residue is an attractive fuel for electricity generation. For example, Endesa, Spain’s largest power company built two power plants early in the 21\textsuperscript{st} century that exclusively fire 105,000 tons of orujillo per year to produce 16 MW of electricity\textsuperscript{33}. As a result, with every hectare of olive grove generating approximately two tones of olive residue\textsuperscript{31} and with approximately 190 million olive trees, Spain (the world’s leader in olive oil production) alone has enough orujillo to generate 500 MW of
electricity from 30 power plants\textsuperscript{33}. The olive residue used herein (and in recent studies\textsuperscript{25}) is used in fuel blends with coal and pet coke at ELCOGAS, S.A, an IGCC power station located in Ciudad Real, Spain.

The torrefied pine sawdust was also obtained from INCAR-CSIC, with the parent pellet sample being obtained from Pellets Asturias S.L., a pellets industry situated in Austria, Spain. Wood pellets are produced in pellet mills and plants from dry, untreated industrial wood waste with sawdust being the main component. After the raw material is received, it is dried and ground into a uniform size to ensure good quality of the pellet. The material is then forced through a press, under high pressure and temperature, to form cylindrical wood pellets. The pellets are then cooled to allow the natural bonding agents of the wood (the wood’s lignin and resin) to set. The use of wood pellets as an alternative fuel in North America began in the 1970’s as a response to the energy crisis. They were used mainly as a heat source by the industrial, commercial, and institutional sectors and later became popular for residential heating through the use of pellet stoves. In 2010, approximately 13.5 million tones of wood pellets were consumed as a fuel source with the primary purpose of reducing carbon dioxide emissions\textsuperscript{34}. In addition to environmental benefits, pellets have a high energy density, are easy to use, and have numerous economic benefits\textsuperscript{35}. The use of chemical and thermal preconditioning technologies have the ability to increase the variety of materials that may be used to produce pellets\textsuperscript{34}, as well as increase the quality of biomass fuels\textsuperscript{36}. One such example is torrefaction, which involves heating the biomass at a moderate temperature under inert atmospheres. During this process, the density, specific heating value, and uniformity of the biomass increases. The torrefied biomass also acquires a hydrophobic nature, causing no moisture to be acquired during storage of the product\textsuperscript{36}. Currently, a variety of different torrefaction technologies are being developed by a
number of initiatives\textsuperscript{34}. In the study herein, the torrefaction of the pine sawdust was performed at INCAR-CSIC in order to ease its delivery to the furnace. 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 with solubles (DDGS), was provided by a North American ethanol-producing company and used in a recent study\textsuperscript{37}. DDGS are a co-product of dry-milled ethanol production. During this production process, hammer mills grind the corn grains to reduce the particle size and in return maximize ethanol yields. The ground corn grains are then cooked, fermented, and distilled to produce ethanol. The remaining water and solids, known as whole stillage, are then converted into wet distillers’, distillers’ dried grains, condensed distillers, and dried distillers’ grains with solubles through the use of a centrifuge and drying techniques\textsuperscript{38}. During the dry-milled production process, one metric ton of corn produces approximately 378 liters of ethanol and 309 kg of DDGS\textsuperscript{39}. The resultant DDGS is primarily used as a low cost livestock feed due to its high energy, protein, and phosphorous content\textsuperscript{38}. Due to a growing demand and positive benefits in animal feeds, United States’ exports of DDGS have grown from 1 million tons in 2006 to more than 8 million tons in 2011\textsuperscript{40}. As a result, DDGS accounts for the second largest source of income for an ethanol plant, accounting for 10-20 % of the total income of United States ethanol plants\textsuperscript{39}. DDGS is largely available, with more than 200 ethanol plants located in the United States each with the capacity to produce 30 million tons of DDGS\textsuperscript{40}. In addition to its high abundance, its low moisture content and high energy content also make DDGS an attractive energy source.
The chemical compositions and properties of the olive residue, torrefied pine sawdust, and corn residue are listed in Table 1. Photos of the as received and the sieved biomass samples used herein, are provided in Table 2. 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.

<table>
<thead>
<tr>
<th>Biomass Type</th>
<th>OR</th>
<th>TOPI</th>
<th>CR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Olive Residue</td>
<td>Torrefied Pine Sawdust</td>
<td>Corn Residue</td>
</tr>
<tr>
<td>Proximate Analysis (wt %, db)</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>Ultimate Analysis (wt%, daf)</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>
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<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

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) in Spain. The proximate analysis for the corn residue was provided by Giuntoli et. al while the ultimate analysis was obtained from Alves et. al.
3.2 Ashing Experiments

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.

3.3 Combustion Experiments and SEM-EDS Analysis

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 3. 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 3: Cross section view of the experimental set-up consisting of the 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 \( N_2 \) 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 (dilution ratio of \( \sim 0.4 \)) 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 \( \sim 0 \) 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) \( \text{PM}_{0.32} \) (stages 8-13), (2) \( \text{PM}_1 \) or submicron (stages 6-13), (3) \( \text{PM}_{2.5} \) (stages 4-13), (4) \( \text{PM}_{1.5} \) or fine fragment mode (stages 3-5), (5) \( \text{PM}_{10} \) (stages 2-13), and (6) \( \text{PM}_{18} \) (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 chemical composition of the PM$_{1}$ yields. Based on a prior work$^{42}$, ashes collected on stage 6 (PM$_{0.56-1}$) and stage 9 (PM$_{0.1-0.18}$) were chosen as a representation of the PM$_{1}$. Substrate samples were attached to metal stubs by means of carbon tapes and the elemental analysis of these samples was then performed through utilization of the techniques of Scanning Electron Microscope Energy-Dispersive X-ray Spectroscopy (SEM-EDS).

<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>d&lt;10</td>
</tr>
</tbody>
</table>

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

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$^{26,42-45}$. 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.
4.0 Results

4.1 Ash Yields

Figure 4 depicts the particulate emissions of each of the three biomasses utilized in this study from combustion in N₂ and CO₂ background gases, at a variety of oxygen mole fractions. Oxygen mole fractions of 21% (Air), 40%, and 60% were utilized for N₂ environments while 30%, 40%, and 60% for CO₂ 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 PM₀.₃₂, PM₁.₀ (the submicron mode), PM₂.₅, PM₁.₅ (fine fragment mode), PM₁₀, and PM₁₈.
As seen in Figure 4, 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.
sawdust, with the lowest ash content of 0.4 (wt%), produced total ash yields in air of approximately 5 mg/g\textsubscript{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\textsubscript{fuel} fed when combustion occurred in air.

For the combustion of all biomasses in oxy-fuel environments (O\textsubscript{2}/CO\textsubscript{2}), the submicron ash yields, PM\textsubscript{1}, are lower than those in O\textsubscript{2}/N\textsubscript{2} combustion environments. The average yields in N\textsubscript{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\textsubscript{fuel} fed, respectively. Changing the background gas to CO\textsubscript{2} reduces these averages to 18.9, 1.46, and 0.41 mg/g\textsubscript{fuel} fed. Increasing the oxygen mole fraction in N\textsubscript{2} environments caused a slight overall increase, equal to 8.9%, in the PM\textsubscript{1} yields of olive residue. In CO\textsubscript{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\textsubscript{2} and CO\textsubscript{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\textsubscript{2} environments while the yields were nearly constant in CO\textsubscript{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\textsubscript{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\textsubscript{2} to CO\textsubscript{2}. In CO\textsubscript{2} environments, the generated fine fragment ash yields of olive residue were lower than those produced in O\textsubscript{2}/N\textsubscript{2} combustion environments. However, the PM\textsubscript{1-5} yields generated from combustion of corn residue and torrefied pine sawdust in CO\textsubscript{2} environments were similar to those in N\textsubscript{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.

4.2 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 5.
The PM$_{18}$ size distributions for all three biomasses, in each combustion environment, are multimodal. Olive residue demonstrated two submicron modes, centered at ~0.03 µm and ~0.6
µm, and a super-micron mode. With the exception of the low oxygen mole fraction combustion environments (air and 30% O₂-70% CO₂), the super-micron mode was centered at ~6 µm. For the aforementioned two environments, this mode 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 ~0.03 µm and ~0.6 µm while the super-micron mode appears to have occurred above 18 µm. In addition, increasing the oxygen mole fraction appears to have no clear effect on the particle size distributions of the corn residue. For torrefied pine sawdust a submicron mode is consistently observed at ~0.03 µm. The fine fragment mode, centered at ~6 µm, appears to shift to the left in higher temperature combustion environments, where it is centered between ~0.3 µm to ~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 5, the particle size distributions of corn and olive residue are consistent between the N₂ and CO₂ combustion environments.

4.3 Chemical Composition of Submicron 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>
<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>P₂O₅</td>
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</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>
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<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>
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<tr>
<td>MnO</td>
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<td>1.60</td>
<td>0.00</td>
</tr>
<tr>
<td>TiO₂</td>
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<td>0.27</td>
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</tr>
<tr>
<td>Cr₂O₃</td>
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</tr>
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<td>CuO</td>
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<td>0.04</td>
<td>0.00</td>
</tr>
<tr>
<td>ZnO</td>
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<tr>
<td>SrO</td>
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<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>

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.

The PM$_{0.1-0.18}$ (stage 9 ash particles) and the PM$_{0.56-1}$ (stage 6 ash particles) were analyzed utilizing the SEM-EDS technique. Mass fractions of the major elements detected in the PM$_{0.1-0.18}$ (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 PM$_{0.56-1}$ 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 PM$_{0.1-0.18}$ (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>
<thead>
<tr>
<th>Element</th>
<th>Olive Residue PM₀.1-0.18 (stg 9)</th>
<th>Corn Residue PM₀.1-0.18 (stg 9)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Air</td>
<td>40%O₂-60%CO₂</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>
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<td>S</td>
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<td>K</td>
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<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>

Table 5: Chemical compositions, given as mass%, of stage 9 (PM₀.1-0.18) particles emitted from combustion of an olive residue (OR) and corn residue (CR) biomass in air and a simulated oxy-fuel atmospheres (40%O₂-60%CO₂).
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>
<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</td>
<td>40% (\text{O}_2)-60% (\text{CO}_2)</td>
<td>Air</td>
</tr>
<tr>
<td>Na</td>
<td>11.7</td>
<td>10.7</td>
<td>0.6</td>
</tr>
<tr>
<td>Mg</td>
<td>0.9</td>
<td>1.0</td>
<td>9.2</td>
</tr>
<tr>
<td>Al</td>
<td>2.7</td>
<td>2.4</td>
<td>5.9</td>
</tr>
<tr>
<td>Si</td>
<td>0.3</td>
<td>0.6</td>
<td>4.8</td>
</tr>
<tr>
<td>P</td>
<td>5.1</td>
<td>4.6</td>
<td>2.2</td>
</tr>
<tr>
<td>S</td>
<td>10.9</td>
<td>13.4</td>
<td>1.8</td>
</tr>
<tr>
<td>Cl</td>
<td>18.0</td>
<td>13.2</td>
<td>0</td>
</tr>
<tr>
<td>K</td>
<td>35.5</td>
<td>40.2</td>
<td>2.0</td>
</tr>
<tr>
<td>Ca</td>
<td>0.0</td>
<td>0.0</td>
<td>41.8</td>
</tr>
<tr>
<td>Fe</td>
<td>0.3</td>
<td>0.0</td>
<td>5.1</td>
</tr>
</tbody>
</table>

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% \(\text{O}_2\)-70% \(\text{CO}_2\), 40% \(\text{O}_2\)-60% \(\text{CO}_2\)).

<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></td>
<td>1650</td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>1650</td>
</tr>
<tr>
<td></td>
<td>30% (\text{O}_2)-70% (\text{CO}_2)</td>
<td>1550</td>
</tr>
<tr>
<td></td>
<td>35% (\text{O}_2)-65% (\text{CO}_2)</td>
<td>1650</td>
</tr>
<tr>
<td></td>
<td>50% (\text{O}_2)-50% (\text{CO}_2)</td>
<td>1850</td>
</tr>
<tr>
<td>Torrefied pine sawdust (TOPI)</td>
<td></td>
<td>1750</td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>1750</td>
</tr>
<tr>
<td></td>
<td>30% (\text{O}_2)-70% (\text{CO}_2)</td>
<td>1730</td>
</tr>
<tr>
<td></td>
<td>35% (\text{O}_2)-65% (\text{CO}_2)</td>
<td>1800</td>
</tr>
<tr>
<td></td>
<td>50% (\text{O}_2)-50% (\text{CO}_2)</td>
<td>2000</td>
</tr>
<tr>
<td>Corn Residue (CR)</td>
<td></td>
<td>1420</td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>1420</td>
</tr>
<tr>
<td></td>
<td>35% (\text{O}_2)-65% (\text{CO}_2)</td>
<td>Unavailable</td>
</tr>
<tr>
<td></td>
<td>50% (\text{O}_2)-50% (\text{CO}_2)</td>
<td>Unavailable</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\(^2\).
5.0 Discussion

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\textsuperscript{46}. According to this mechanism, submicron particles are formed via vaporization followed by condensation which is strongly affected by temperature\textsuperscript{47-49}. 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 \~20.9 mg/g$_{fuel,fed}$ to 19.2 while for torrefied pine sawdust the yield was reduced from 0.5 mg/g$_{fuel,fed}$ to 0.3. This is in parallel with Fryda et. al\textsuperscript{20} 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\textsuperscript{45} as well as other studies\textsuperscript{50-52}.

For all biomasses, approximately half of the collected PM$_{18}$ mass is found in the submicron mode which is consistent with the literature\textsuperscript{15, 21, 53} 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)\textsuperscript{45} 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{45}. 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{15, 17, 18, 21}. 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{45}. 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 \textasciitilde 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>
<thead>
<tr>
<th>Biomass</th>
<th>Ash Content (wt %)</th>
<th>Proximate Analysis</th>
<th>Ashing Experiments</th>
<th>Collected By Impactor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olive Residue</td>
<td>7.6</td>
<td>5.8</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>TOPI</td>
<td>0.4</td>
<td>0.4</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Corn Residue</td>
<td>7.1</td>
<td>6.3</td>
<td>1.4</td>
<td></td>
</tr>
</tbody>
</table>

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.

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 is in line with Fryda et. al⁴ 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. al⁵, 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 Baxter²⁸, 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{54}, 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{54}. 


<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>$72 \geq S_R &gt; 65$ – 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>$S_R &lt; 65$ – high slagging</td>
</tr>
</tbody>
</table>

* Obtained from Masiá et. al32

Table 9: Calculated deposition indices for the three biomasses utilized in this study (Olive Residue, Torrefied Pine Sawdust, and Corn Residue) and the three coals previously studied in this laboratory and the Olive Residue (indicated by *) studied by Masiá et. al34.
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{55}. 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 9, 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 9 for olive residue and torrefied pine sawdust are in line with those reported by Masiá et. al\textsuperscript{54} 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$_2$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{54}. The sulfur trioxide (SO$_3$) 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$_2$O$_5$) 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{54,56}.

<table>
<thead>
<tr>
<th>Elements</th>
<th>T\textsubscript{melting} (°C)</th>
<th>T\textsubscript{vaporization} (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>44.2 (317)</td>
<td>280 (553)</td>
</tr>
<tr>
<td>P\textsubscript{2}O\textsubscript{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\textsubscript{2}O</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>S</td>
<td>115 (388)</td>
<td>444.6 (718)</td>
</tr>
<tr>
<td>S\textsubscript{O} \textsubscript{3}</td>
<td>16.9 (290)</td>
<td>45 (318)</td>
</tr>
<tr>
<td>Na</td>
<td>97.7 (371)</td>
<td>883 (1156)</td>
</tr>
<tr>
<td>Na\textsubscript{2}O</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\textsubscript{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\textsubscript{2}O\textsubscript{3}</td>
<td>2072 (2345)</td>
<td>2977 (3250)</td>
</tr>
<tr>
<td>AlO</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Fe\textsubscript{2}O\textsubscript{3}</td>
<td>1565 (1838)</td>
<td>-</td>
</tr>
<tr>
<td>FeO</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

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.\textsuperscript{57} and other web-based sources). All temperatures are in Celsius with the corresponding value in Kelvin is provided in parentheses.

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\textsubscript{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\textsubscript{1} by an increasing trend. This is not observed, however, for the PM\textsubscript{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{21} who reported that as oxygen mole fraction increased from 20\% to 50\%, PM\textsubscript{1}/PM\textsubscript{10} decreased from an average of \(\sim70\%\) (wt\%) to \(\sim50\%\) (wt\%), respectively while the PM\textsubscript{1+}/PM\textsubscript{10} increased. This ratio decreases from \(\sim60\%\) to \(\sim50\%\) when the oxygen mole fraction is changed from 21\% to 60\% for the corn residue utilized in this study. Wang et. al\textsuperscript{21} 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{58}.

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.

5.2 Particle Size Distributions

A submicron peak is observed at \(\sim0.03\ \mu\text{m}\) for all three biomasses. In addition, a subsequent submicron peak is observed for the corn and olive residues at \(\sim0.6\ \mu\text{m}\). For coal studies conducted within the same laboratory, mode peaks were observed at \(\sim0.2\) and \(\sim5\ \mu\text{m}\)\textsuperscript{45}. 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\textsuperscript{18}. 

40
Wang et al\textsuperscript{21} 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 5. 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.
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$^{18}$ 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$^{18}$ 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$^{18}$ 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$^{53}$ who also burned a woody biomass (moist forest residue). However, the mean particle mode diameters
observed by Pagels et. al\textsuperscript{53} were ~0.2 and ~2 µm. This may be due to the differences between the fuels fed particle size.

\textbf{5.3 Chemical Composition of Submicron Particles}

According to Jiménez and Ballester\textsuperscript{17}, 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{17} 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{45}. 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{17, 18} 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{0.56-1} 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{0.56-1}. This is in line with the results
obtained by Fryda et al. as well as the results of the chemical composition of the PM\textsubscript{1.1-1.8} emissions produced by the three coals studied in this laboratory. In addition, the latter study observed a decrease of Si and Al in the PM\textsubscript{1.1-1.8} emissions while no clear trend was observed in the PM\textsubscript{1.1-1.8} 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{1.1-1.8} 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 lab \(^{42}\) and those studied by Buhre et. al \(^{47}\). These higher contents will increase their tendency to corrode boiler surfaces, further affecting the system output.
6.0 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 O₂/N₂ and O₂/CO₂ 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 was obtained 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. The mass fractions of submicron particles for all biomasses constituted approximately 50% (wt %) of the PM₁₈, 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% O₂ with CO₂) than in air. Similarly, when the background gas shifted from N₂ to CO₂ at the same oxygen mole fraction, yields were typically lower.

- As the oxygen mole fraction increases, the PM₁ yields of the three biomasses typically increase.

- The PM₁₈ 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 values.
- 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.
7.0 Recommendations for Further Work

Though other conversion technologies have been applied, the most popular use of biomass to generate electricity is its direct combustion in dedicated boilers. In addition, biomass is commonly co-fired with coal due to its many technical, economical, and environmental advantages. For example, co-firing of biomass with coal helps reduce the total emissions (including NO\textsubscript{x} and SO\textsubscript{x}) per unit energy produced, minimizes waste, reduces fuel costs, and reduces soil and water pollution\textsuperscript{29}. In addition, co-firing of biomass with coal in existing coal-fired plants provides a less costly way to generate power as co-firing requires minor modifications to plants as opposed to the construction of dedicated biomass-fired power plants\textsuperscript{25}. In addition to conventional combustion, the co-firing of biomass with coal may be utilized in oxy-fuel combustion plants, making the emissions generated from combustion in these environments of technical interest. The gaseous emission yields of biomass and coal blends in conventional and oxy-fuel combustion environments have already previously been studied in this laboratory\textsuperscript{26}. However, the particulate emissions generated from the combustion of biomass and coal blends in oxy-fuel environments have yet to be studied in this laboratory. Biomass fuels contain high amounts of alkali metals that have low vaporization temperatures. During combustion of these fuels, alkali metals tend to vaporize and condense forming submicron particles. On the contrary, coal contains high amounts of refractory metals that have higher vaporization temperatures. Due to these higher temperatures, the ash particles generated by coal combustion are more likely to form by fragmentation, resulting in coarser particles. When these two fuels with very different compositions are blended, a collaborative effect may occur which could possibly affect the resulting submicron ash yields.
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. Submicron particles are health hazardous and have adverse environmental effects. Due the difficulty of environmental clean-up devices to collect submicron particles, ways to decrease the large mass fractions of submicron particles generated by burning of biomasses should be investigated. One such example, is the addition of extra amounts of sulfur dioxide to the post-combustion gas from burning of biomasses, as studied by Jiménez and Ballester$^{59}$.

In the study herein, a low collection efficiency by the impactor of the corn residue ash particles was observed, suggesting possible deposition of these particles on furnace surfaces and this was confirmed through the high calculated deposition indices. In addition, the high alkali and phosphorous contents of biomasses have found to increase the deposition tendencies of biomass while higher amounts of chlorine increase corrosion. Further experiments should be conducted to investigate the tendencies of these biomasses to deposit within the furnace. In addition, ways to mitigate the deposition tendencies of biomass should further be developed, such as water-leaching and fractionation$^{60}$. 


8.0 Works Cited

9.0 Appendix

The slagging, fouling, and slag viscosity indices, common deposition indices, were calculated in order to examine the tendency of the biomass ashes to form deposits. As a comparison, the corresponding indices were also calculated for the ashes of the three coals burned in previously in this laboratory. As phosphorous may enhance deposition tendencies of the ash, the slagging and fouling indices were calculated with and without the inclusion of phosphorous in order to examine its effect.

9.1 Deposition Indices – Without the Effects of Phosphorous

In order to calculate the slagging and fouling indices, the ratio of basic compounds (denoted by B) to acidic compounds (denoted by A) within the bulk ash must first be calculated. This ratio is calculated by dividing the weight percentage of compounds within the bulk ash that have low melting temperatures to those of compounds with high melting temperatures. The calculation of this ratio is shown in Equation 1.

$$\frac{B}{A} = \frac{Fe_2O_3+CaO+MgO+Na_2O+K_2O}{SiO_2+Al_2O_3+TiO_2}$$

Equation (1)

The slagging index is then calculated by multiplying the aforementioned ratio by the weight percent of sulfur present in the dry fuel, as shown in Equation 2,

$$R_S = R_{(b/a)} \times S^d$$

Equation (2)

where $R_S$ and $S^d$ represent the slagging index and sulfur percentage, respectively. The summation of the weight percentages of sodium oxide ($Na_2O$) and potassium oxide ($K_2O$) present in the bulk ash is multiplied by the base-to-acid ratio to calculate the fouling index, as show in Equation 3,

$$F_u = R_{(b/a)} \times (Na_2O + K_2O)$$

Equation (3)

where $F_u$ represents the fouling index.
The slag viscosity index, \( S_R \), is obtained from the weight percentages of silica (\( \text{SiO}_2 \)), iron oxide (\( \text{Fe}_2\text{O}_3 \)), calcium oxide (\( \text{CaO} \)), and magnesium oxide (\( \text{MgO} \)) in the bulk ash as shown in Equation 4.

\[
S_R = \left( \frac{\text{SiO}_2}{\text{SiO}_2 + \text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO}} \right) \times 100
\]  

Equation (4)

9.2 Deposition Indices – With the Effects of Phosphorous

In order to examine the effects phosphorous on the deposition tendencies, the base-to-acid ratio must be recalculated to include the weight percentage of phosphorous pentoxide (\( \text{P}_2\text{O}_5 \)) within the bulk ash. Due to its low melting temperature, phosphorous pentoxide is considered as a base and added to the numerator of Equation 1. The calculation of the new ratio, denoted as \( R_{(b/a)+p} \), is shown in equation 5.

\[
R_{(b/a)+p} = \frac{B}{A} = \frac{\text{Fe}_2\text{O}_3 + \text{CaO} + \text{MgO} + \text{Na}_2\text{O} + \text{K}_2\text{O} + \text{P}_2\text{O}_5}{\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{TiO}_2}
\]  

Equation (5)

Using the new base-to-acid ratio from Equation 5 and substituting into Equations 3 and 4, yields the new slagging and fouling indices as follows:

\[
R_{S+P} = R_{(b/a)+p} \times S^d
\]  

Equation (6)

\[
F_{u+P} = R_{(b/a)+p} \times (\text{Na}_2\text{O} + \text{K}_2\text{O})
\]  

Equation (7)