COMPARATIVE ANALYSIS OF THE EMISSION RATES AND PHYSIOCHEMICAL PROPERTIES OF AEROSOLS GENERATED FROM THE COMBUSTION OF SOLID FUELS

by

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(Under the Direction of Rawad Saleh)

ABSTRACT

Thermal pretreatment of biomass fuels, or torrefaction, enhances their energy density, making torrefied biomass a viable sustainable alternative for coal. Because torrefaction reduces the levels of volatile organic compounds, an expected added benefit is reducing aerosol formation in combustion. Here, we compare the emission rates, chemical composition, and light-absorption properties of aerosols emitted from the combustion of pine, torrefied pine, and bituminous coal. Coal emissions were dominated by sulfates, with modest organic content, while pine and torrefied-pine emissions were dominated by organics. Organic-aerosol emissions from all fuels were light-absorbing and categorized as brown carbon. Within the combustion temperature range investigated (400 ºC – 1000 ºC), coal emission rates (11.35±.029 g/MJ) were highest at 800 ºC, while those of pine (25.1±4.02 g/MJ) and torrefied pine (5.6±0.8 g/MJ) were highest at 400 ºC. These results indicate that torrefaction significantly reduces aerosol emissions, making torrefied biomass an attractive fuel for domestic and industrial use.

INDEX WORDS: biomass, combustion, aerosols, solid fuels, energy production, torrefaction, coal, electrospray-ionization spectrometry, ion chromatography, photoacoustic spectroscopy

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DEDICATION

This work is dedicated to my parents, Philip and Karen Perrie for their support through both undergrad and graduate school.

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CHAPTER 1

INTRODUCTION

Coal and biomass are the most widely used solid fuels throughout the world (Anenberg et al., 2013). Globally, they account for over 200 exajoules (EJ) of energy consumed annually (Association, 2020; Edmund Henrich, 2015) out of the 624 EJ of total energy consumption (Edmund Henrich, 2015; Hannah Ritchie, 2020). Both fuels are used in industrial and residential settings. Globally, 3 billion people use coal and biomass for residential heating and cooking (Anenberg et al., 2013; Astakoti, 2019), while coal is one of the most used widely used fuels for power production. It is worth noting that emissions from residential heating are a very important yet understudied contributor to climate change (Mingjie Xie, 2018; Ni, 2021).

Biomass is viewed as one of the viable renewable (carbon-neutral) alternatives to coal, either by replacement or co-firing in power plants (Munir et al., 2009). The European Union had planned to produce 20% of its electricity from renewable sources by 2020, and per the 2010 Renewable Energy Action Plans, biomass demand was expected to be equivalent to 178 metric tons of oil by 2020, with a projected growth of approximately 6.5% annually (L.W.M. Beurskens, 2011). In 2020, the European Union adjusted its old climate plan and set a new target for 55% reduction in greenhouse gas emissions by 2030, with biomass playing a major role in the 32% of energy derived from renewable sources (Commission, 2020). Biomass currently makes up approximately 10% of global annual consumption and is the primary source of domestic energy in developing countries (de Koning et al., 1985; Edmund Henrich, 2015). Biomass is a sustainable fuel that has a net zero-carbon footprint, due to the fact that it only releases the carbon that it takes out of the atmosphere as it is grown (M.V. Gil, 2015; McKendry, 2002; van der Stelt et al., 2011). Therefore, replacing coal with biomass in various combustion applications leads to overall reduction in global CO_2 emissions (Demirbaş, 2003). In addition, biomass has less sulfur than coal, thereby reducing SO_x emissions through co-firing (Demirbaş, 2003; Munir et al., 2010). Additionally, biomass is widely available from multiple sources including agriculture (corn stalks, cotton, cotton bush, surplus food), waste (vine and tree pruning, food waste, forest residue) and harvested trees (Anenberg et al., 2013; Asli Toptas, 2015; Collins Ndibe, 2015; Fisher et al., 2012; McKendry, 2002; Rijal et al., 2020; Zhang et al., 2000).

There are three major limitations associated with using biomass in place of or in conjunction with coal. First, biomass has a significantly lower carbon content compared to coal, thus a lower heating value (energy density). Second, the moisture content of biomass can inhibit efficient combustion (Huangfu et al., 2014; Korus & Szlęk, 2015; Yuntenwi et al., 2008). Third, biomass in its raw form is difficult to transport, store, and feed it into existing gasification systems (Mani et al., 2006; Shahab Sokhansanj, 2009). To overcome these limitations and avoid high levels of PM emissions, biomass undergoes a process called torrefaction (Shao et al., 2019). Torrefaction is a pyrolysis process that is carried out without the presence of oxygen under atmospheric conditions. It is a mild thermal treatment where the fuel is heated between 200°C and 300°C (Yue et al., 2017). During this process, the fibrous structure and the tenacity of the biomass are destroyed (van der Stelt et al., 2011) and oxygen and water are removed from the biomass via carboxylation and dehydration processes (Fisher et al., 2012; Yue et al., 2017), leaving the processed biomass to have a heating value similar to that of coal (Manouchehrinejad & Mani, 2018; Phanphanich & Mani, 2011; van der Stelt et al., 2011; Yue et al., 2017). Recently, torrefied biomass has been explored as an option to complement or replace coal (Asli Toptas, 2015; Collins Ndibe, 2015; M.V. Gil, 2015; Phanphanich & Mani, 2011).

While replacing coal usage with biomass leads to a reduction in greenhouse gas emissions, it is not clear that biomass combustion provides improvements in reducing particulate matter (or aerosol) emissions relative to coal. Carbonaceous aerosols, including organic aerosols (OA) such as black carbon and brown carbon, are of special interest due to their significant, though poorly constrained, effects on the climate (Myhre, 2013; T. C. Bond, 2013). OA is made up of highly complex molecules with diverse chemical structures and optical properties. In addition to climate implications, OA can have health implication in humans. Exposure to aerosols is associated with various adverse health effects including inflammation, pulmonary disease, and genotoxic responses (Apte et al., 2015; Chen et al., 2016; J. Kelz, 2010; Kim et al., 2019; Kim et al., 2015; Sangcheol et al., 2021). Furthermore, aerosol emissions from both coal and biomass combustion are light-absorbing (Islam et al., 2022; Tami C. Bond, 2004) and can induce climate warming by absorbing solar radiation and heating up the atmosphere (Rawad Saleh, 2015; T. C. Bond, 2013). Therefore, quantifying the emissions rates of aerosols emitted from solid fuel combustion (both coal and biomass), and characterizing their physicochemical properties is important for assessing their effect on air quality and the climate system.

The combustion of both coal and biomass has been shown to produce high levels of aerosol emissions, especially in low-efficiency domestic burning in developing countries (Islam et al., 2022; Mingjie Xie, 2018; Simões Amaral et al., 2016; Yazdani et al., 2021), but also in industrial processes (Demirbaş, 2003; Ma et al., 2016; Zhang et al., 2008). For example, one study on coal combustion reported aerosol emission rates ranging between 188 and 767 g/MJ (grams of emissions per mega-Joule energy produced) for conditions typical for domestic burning compared to 5-8 g/MJ for combustion conditions typical for industrial combustion (Zhang et al., 2008). Reports on aerosol emission rates from biomass combustion are also highly variable. Shen et al. (2014) found biomass emissions to range from 29 to 823 mg-$PM_{2.5}$/mega-Joule. Amaral et al. (2016) presented values for agriculture biomass burning ranging from 147 to 758.8 mg-$PM_{2.5}$/mega-Joule, and forest biomass burning ranging from .104 to 1.262 g-$PM_{2.5}$/mega-Joule. Particulate emissions for torrefied biomass have been found to be more consistent but highly dependent on the torrefaction temperature and residence time. For example, Shao et al. (2019) found ranges of particulate emissions for torrefied corn stalks to be 107.7, 110.2, and 115.4 mg-PM_1/mega-Joule (particles with an aerodynamic diameter less than 1 micron) for torrefaction temperatures of 220, 260, and 300 ºC respectively, with a residence time of 30 minutes for each sample. Maxwell et al. (2020) found PM1 emissions to range between 108 mg-PM_1/mega-Joule for spruce torrefied at 260 ºC for 30 minutes, and 222.7 mg-PM_1/mega-Joule for willow torrefied at 250 ºC for 90 minutes.

In addition to differences in fuel chemical make-up, an important reason in the large variability in emission rates is the differences in combustion conditions across the different studies. For example, even for the same fuel, the combustion process, thus emissions rates, would be different for pulverized (powdered) (Collins Ndibe, 2015; Wang, 2013; Zhang et al., 2000) than briquettes (Dai et al., 2019; Mitchell et al., 2016; Zhang et al., 2000), and / or lumps (Mitchell et al., 2016). This makes it challenging to assess the effect of fuel type on aerosol emission rates and physicochemical properties. Of special interest but currently missing knowledge is the effect of the reduced content of VOCs in torrefied biomass compared to its untreated counterpart (Shao et al., 2019) on aerosol emissions and physicochemical properties. In this study, we compare the emission rates, chemical composition, and light-absorption properties of aerosols emitted from the combustion of pine, torrefied pine, and bituminous coal. To investigate the effect of fuel type on differences in aerosol emissions, we performed controlled-combustion experiments that ensured consistent combustion conditions across fuels, thus leaving fuel type as the only variable. The experiment were performed at a fixed air-to-fuel ratio, and at temperatures ranging between 400 °C and 1000 °C to capture conditions relevant for both domestic and industrial combustion. Online and offline characterization of aerosol emissions were used to quantify differences in emission rates as well as physicochemical properties across fuels and combustion temperatures.

CHAPTER 2

METHODS

Overview

We performed controlled-combustion experiments to compare the aerosol emissions from 3 solid fuels: (1) pine, (2) torrefied pine, and (3) bituminous coal. Since the major focus of this study is to investigate the effect of fuel type on emissions, the experiments were designed to maintain the same combustion conditions across fuels. We employed a suite of online and offline techniques to characterize the aerosol emissions. A schematic of the experimental setup is shown in Figure 1, and detailed description of the experimental design, validation, and execution is provided in the subsequent sections of the this chapter.

2.1 Fuel preparation

One of the challenges associated with combustion experiments involving solid fuels is the difficulty in maintaining steady and uniform combustion when performing the experiments using chunks of fuel. This configuration creates large differences in combustion temperature and air-to-fuel ratio (A/F), that lead to highly variable emissions within experiments (i.e. temporally) and across experiments. In order to obtain uniform and steady combustion experiments, we combusted fuel particles with sizes ranging between 90 and 120 µm used in similar experiments by Chen et al. (2012), Gao and Wu (2011), and Matsuoka et al. (2003). Utilizing this small fuel particle size ensures that the fuel and air are well-mixed during the combustion process, thus ensuring uniform combustion.

To that end, the fuels were processed in Dr. Sudhagar Mani's laboratory at the University of Georgia (UGA) Both biomass samples were received as pine chips from a local saw mill operation (Phanphanich & Mani, 2011).

The torrefied pine was prepared at Dr. Main's laboratory. The torrefaction process took place in a batch torrefaction reactor that was placed in an externally heated electric furnace. A nitrogen flow of 2 Liters per minute was introduced to the batch reactor as a carrier gas to prevent oxidation. The sample was then heated 10 ºC per minute under atmospheric pressure to 275 ºC for 20 minutes (Manouchehrinejad & Mani, 2018; Phanphanich & Mani, 2011).

After torrefaction, the raw pine chips and the torrefied biomass chips were ground using a heavy-duty knife mill (Retsch SM 2000, Germany). The resulting pulverized fuel was then sifted using two sieves in series in order to isolate particles between 90 and 120 microns.

2.2 Combustion experiments

In order to obtain high-quality online measurements that can allow for comparison across experiments, it is imperative for the emissions to be consistent over a long-enough period of time. Our group has previously designed a steady-flow combustion system that achieves highly stable emissions using liquid fuels (Atwi et al., 2021; Cheng et al., 2021; Cheng et al., 2019; Saleh et al., 2018; Yu et al., 2021). The design involved introducing the fuels in vapor form into a combustion chamber using a controlled flow of air into a bubbler containing the fuel. The air flow, saturated with fuel vapor, would then be introduced into the combustion chamber. To employ a similar approach for the solid fuels, we needed a system that produces a steady flow of solid fuel particles into the combustion chamber. To that end, we built a particle feeder system based on the design of Molinder and Wiinikka (2015). The particle feeder system consists of a vertically mounted glass hopper for the fuel particles attached to a syringe pump pusher block (BrainTree Scientific Inc. Model BS-300). A ¼" diameter stainless steel tube leads from the center of the fuel hopper down into the combustion chamber. The syringe pump pushes the fuel hopper up at a set speed, allowing the fuel particles to fall down the stainless-steel tube and into the combustion chamber along with carrier air introduced at the top of the fuel hopper. In this configuration, the pumping speed of the syringe pump can be adjusted to determine mass flow rate of the fuel into the combustion chamber. Two 12-volt vibration motors were attached to the fuel hopper to agitate the fuel and prevent sticking on the walls of the hopper. Prior to the combustion experiments, we obtained a calibration curve relating fuel mass flowrate to pumping speed of syringe pump. This process involved setting the pumping speed to different values, collecting fuel over a period of two minutes, and weighing the collected fuel.

The combustion chamber is a custom designed quartz-glass chamber and was heated using a temperature-controlled heater (Thermcraft). The temperature inside the combustion chamber was controlled using a proportional-integral-derivative (PID) controller and a thermocouple (Omega Engineering Inc., Norwalk, CT, USA). The combustion experiments were performed at 4 set temperatures: 400, 600, 800, and 1000 °C. These temperatures encompass ranges encountered in both domestic and industrial settings (Fisher et al., 2012; Joo et al., 2018; Jun Li, 2013; L. Van De Steene, 1999; Q. Li et al., 2016; Matsuoka et al., 2003; Mingjie Xie, 2018; Peng et al., 2022).

We maintained the carbon-based A/F to 25 for all experiments, which is within the range of values reported in previous studies (Collins Ndibe, 2015; Li et al., 2019; M.V. Gil, 2015; Wang, 2013). For torrefied biomass and coal, A/F of 25 was used, as both fuels have similar carbon contents (Yue et al., 2017). The pine was maintained at A/F of 18.5 due to its lower carbon content (Manouchehrinejad & Mani, 2018). The carrier air flow was maintained at 1 liter per minute (LPM), controlled by a mass flow controller (Dakota Instruments, USA), and the set A/F was obtained by setting the pumping speed of the syringe pump based on the value found during calibration tests.

Though the particle feeder system described above allows performing the combustion experiments at steady-flow conditions, there were fluctuations in the aerosols emissions due to the fact that the particle flow was not perfectly continuous. To minimize these fluctuations, the emissions were sent through a 55-gallon drum (see Figure 1) which acted as a flow capacitor. Dilution air was added to the chamber to control emission concentrations for the online measurements, described in Section 2.3.

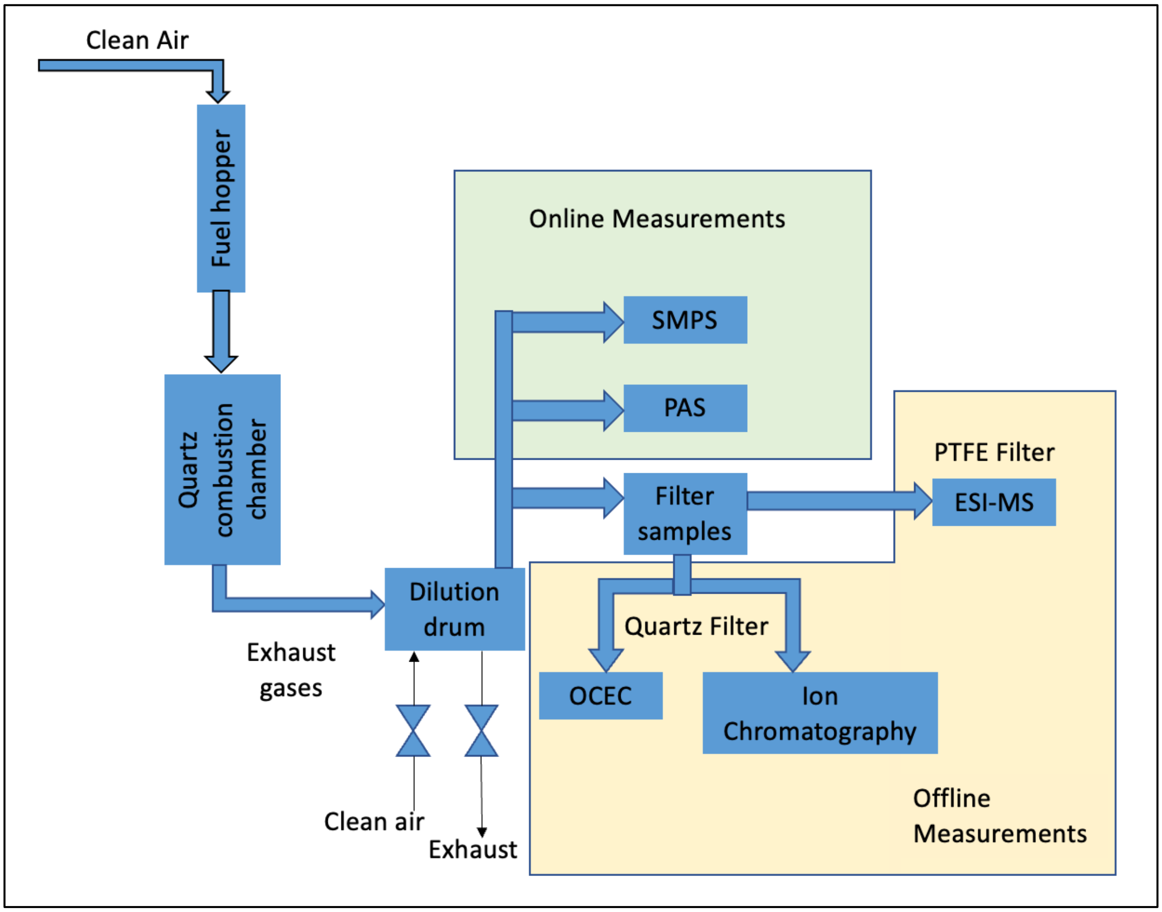

Figure 1:Block Diagram of Experimental Setup

2.3 Online measurements: Emission rates and light-absorption properties

We measured the aerosol size distributions at a 90-second resolution using a scanning mobility particle sizer (SMPS, TSI). The SMPS consists of a Differential Mobility Analyzer (DMA, TSI, Model 3081A00), an Advanced Aerosol Neutralizer (TSI, Model 3088), and a Condensation Particle Counter (CPC, TSI, Model 3772). The SMPS size distributions were integrated to obtain the total aerosol mass concentration. For consistent comparison across fuels, aerosol emission factors were calculated as milligram aerosol per mega-joule energy produced as shown in Equation 1:

$$EF = C_{aerosol} \cdot A_f \cdot HV \cdot D \,/ F_f$$

Equation 1: Emission Factor

Where, EF is the emission factor [mg/MJ], $C_{aerosol}$ is the aerosol mass concentration obtained from SMPS measurements [µg/m^3], A_f is the carrier air flow rate [1 lpm], F_f is the fuel mass flowrate [kg/min], HV is the fuel heating value (27.72 MJ/kg for coal, 18.46 for pine, and 22.86 for torrefied biomass (Phanphanich & Mani, 2011)), and D is the dilution ratio.

The aerosol light-absorption coefficients were measured at a 1-second resolution at 3 wavelengths that cover the visible spectrum (422 nm, 532 nm, and 782 nm) using a multi-pass Photoacoustic Spectrophotometry (Multi PAS III, Geoffrey Smith's group, University of Georgia)(Fischer & Smith, 2018). Measurements at 532 nm and 422 nm were used in the analysis described below.

We calculated the mass absorption cross-section (MAC [m^2/g]) as:

$$MAC(\lambda) = \; b_{abs}/C_{aerosol}$$

Equation 2: Mass absorption cross-section

In this equation, b_{abs} is the absorption coefficient measured using the Multi-PAS III, and $C_{aerosol}$ is the aerosol mass concentration calculated by integrating the SMPS size distribution of the particles using an average particle density of 1.2 g/cm^3 for organic molecules (C. Li et al., 2016; Sumlin et al., 2018). MAC is a practical measure of how efficient the particles are at absorbing light. For light-absorbing aerosol, MAC exhibits a power-law dependence on wavelength in the visible spectrum (D.A. Lack, 2010; Haolin Sun, 2007). This wavelength dependence is usually quantified using the absorption Ångström exponent (AAE), which is calculated as:

$$AAE = \frac{log(\frac{MAC_{532}}{MAC_{422}})}{log(\frac{422}{532})}$$

Equation 3: Ångström Exponent

Where MAC_{532} and MAC_{422} are the MAC values at 532 nm and 422 nm, respectively. AAE values close to 1 indicate that the particles are efficient at absorbing light at all wavelengths, which is usually associated with black carbon (BC). AAE values larger than 1 indicate that the particles are more efficient at absorbing in the short-visible than the long-visible wavelengths, which is characteristic of brown carbon (BrC) (Saleh, 2020).

2.4 Offline measurements: Chemical speciation

The aerosol emissions were collected on a quartz (PALL Life Sciences, 47 mm) and polytetrafluoroethylene (PTFE) filter (SterliTech Corporation, 47 mm) for offline analysis. We targeted a particle loading for approximately 300 µg on each filter. The sampling time ranged from 1 to 4 hours depending on the aerosol concentration in each experiment.

Filters were then placed in petri dishes and covered with aluminum foil in a freezer until analysis took place. For analysis, the PTFE filters were used for filter ultra-high-resolution electrospray ionization mass spectroscopy (ESI-MS). The mass spectra for each sample was obtained using a Brüker SolariX XR 12T Fourier-transform ion cyclotron resonance (FTICR) using both positive and negative ionization modes in order to capture the maximum number of compounds. The ESI-MS sample was prepared by placing half of the PTFE filter in a 10 ml methanol solution and extracting using procedures described by Cheng et al. (2021). The sample was then analyzed by the

Proteomics and Mass Spectrometry Facility at UGA. The output file was input in the open-source software mMass (mmass.org). Background peaks present in a blank methanol solution were excluded from the samples. Identified peaks were then analyzed in Formularity (Tolić et al., 2017), a program that automatically assigns chemical formulas based on user-specified parameters.

For the Quartz filters, a 1.5 cm^2 punch was taken from them for organic carbon/elemental carbon (OC/EC) analysis using an OCEC Analyzer (Sunset Laboratories, USA). The OCEC uses a combination of thermal and optical analysis to quantify the amount of organic carbon (OC) and elemental carbon (EC) present in the sample. The instrument was run using the NIOSH 870 protocol.

The remainder of the Quartz filter was analyzed for inorganic ions. Ions of interest were K^+, Cl^-, SO_4^{2-}, NH_4^+, NO_3^-, and Na^+ (Dai et al., 2019; Yinxiao Zhang, 2018). We extracted each sample filter in 20 mL of ultra-pure water and sonicated for 10 minutes, and 8 mL of the solution was analyzed using ion chromatography (IC) analysis using a Dionex Integrion High-Pressure Ion Chromatography Instrument (Thermo-Fischer, USA) in Dr. Amanda Frossard's laboratory at UGA.

A calibration curve for IC analysis was created from standards of each ion. Standards were prepared in ultra-purified water and analyzed. Prior to running IC with experimental samples, test samples of a solution of $(NH_4)_2SO_4$, NaCl, KCl, and NH_4NO_3 was prepared and pipetted onto a blank Quartz filters. The solution was made up of 0.5 liters of ultra-pure water and 0.03 g of each solute. 1 mL of solution was pipetted onto a blank Quartz filter. The filter was then extracted and analyzed using the same procedure as above. As shown in Table 1, this accuracy of the analysis was better than 11%.

Table 1:Results of test of accuracy of the extraction procedure for ion analysis

Ion	Set concentration	Retrieved concentration	% Difference
Na^+	0.49	0.5048	2.82%
Cl^-	1.35	1.2578	7%
K^+	0.66	0.5844	11%
NH_4^+	0.62	0.6727	7.95%
SO_4^{2-}	0.91	0.8348	8.2%
NO_3^-	0.97	0.8934	7.58%

2.5 Validation of combustion system stability

As described in the Section 2.2, the design employed in this study allows for steady flow combustion of solid fuels. However, as expected, the flow is not as steady as with liquid or gaseous flow, which would lead to fluctuations in the emissions. A 55 gallon drum was employed in order to minimize emission fluctuations by acting as a capacitor. The drum provides a residence time of 5-12 minutes depending on the amount of dilution air used, which was dependent upon the emission concentration. This configuration enabled us to maintain relatively stable aerosol emissions over a period long enough to perform high-quality real-time measurements (Section 2.3) and collect filter samples for offline analysis (Section 2.4). The stability of the system is illustrated in Figure 2. Figure 2a shows a time series of the number distribution obtained from SMPS measurements, confirming that both the size and number concentration remained relatively stable over the course of the experiments (1 hour). The stability of the emissions is further illustrated in Figure 2b, which overlays the time series of the aerosol mass concentrations (C_{aerosol} obtained from integrating the SMPS size distribution) and the absorption coefficients at 532 nm ($b_{\mathrm{abs,532}}$), measured using the Multi-PAS III. Overall, C_{aerosol} for this experiment was 787 ± 20 (average ± standard deviation [μg/m^3]), $b_{\mathrm{abs,532}}$ was 19.5 ± 4.52, and $b_{\mathrm{abs,422}}$ was 116.15 ± 14.8.

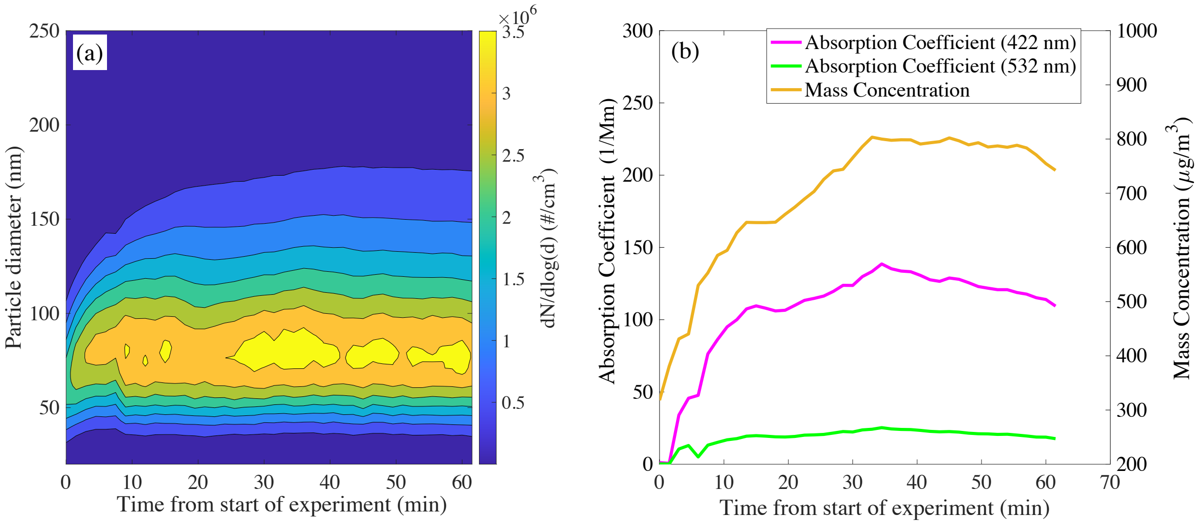

Figure 2: Time series of emissions from a coal combustion experiment that illustrates the stability of the combustion system. (a) SMPS number distribution. (b) Aerosol mass concentrations (Caerosol) from SMPS measurements and absorption coefficients at 532 nm (b_{abs532}) and at 422 nm (b_{abs422})

CHAPTER 3

RESULTS

3.1. Aerosol emission factors

Figure 3 depicts the aerosol emission factors, calculated as described in Section 2.3 as a function of combustion temperature for pine, torrefied pine, and coal. Both pine and torrefied pine exhibited an inverse relation between aerosol emissions and combustion temperature. This trend indicates that the combustion efficiency of these fuels increased with increasing temperature, thus reducing the emissions of partially combusted/oxidized species, including aerosols. An important practical implication of this finding is that utilizing these biomass fuels in industrial applications (where the combustion temperatures are relatively high) is expected to produce relatively low aerosol emissions. On the other hand, biomass-burning in domestic settings, where starting and burnout temperatures are relatively low, leads to significant aerosol emissions.

Importantly, the torrefied pine emissions are significantly lower than the pine emissions at all temperatures. This finding suggests that the removal of VOCs in the torrefaction process plays an important role in limiting aerosol formation in combustion. Coal displayed a different trend, with emission factors peaking around 800ºC. Previous work by Joo et al. (2018) studied coal combustion at four temperatures and found the highest levels of $PM_{2.5}$ emissions occurred at 700 ºC, similar to our results. This trend can potentially be explained by differences in organic and inorganic aerosol formation in coal combustion. Similar to the biomass fuels, the carbon content of the coal is expected to be more efficiently combusted with increasing temperature, thus decreasing the emissions of partially oxidized carbon (including in aerosol form) with increasing temperature. However, coal has a relatively high sulfur content, which is also oxidized in the combustion process to produce different form of sulfur-containing compounds, including inorganic sulfates in aerosol form (this is further explored in Section 3.2). It is plausible that the formation of sulfate aerosols becomes more efficient with increasing temperature (up to ~800 °C), thus resulting in the observed trend.

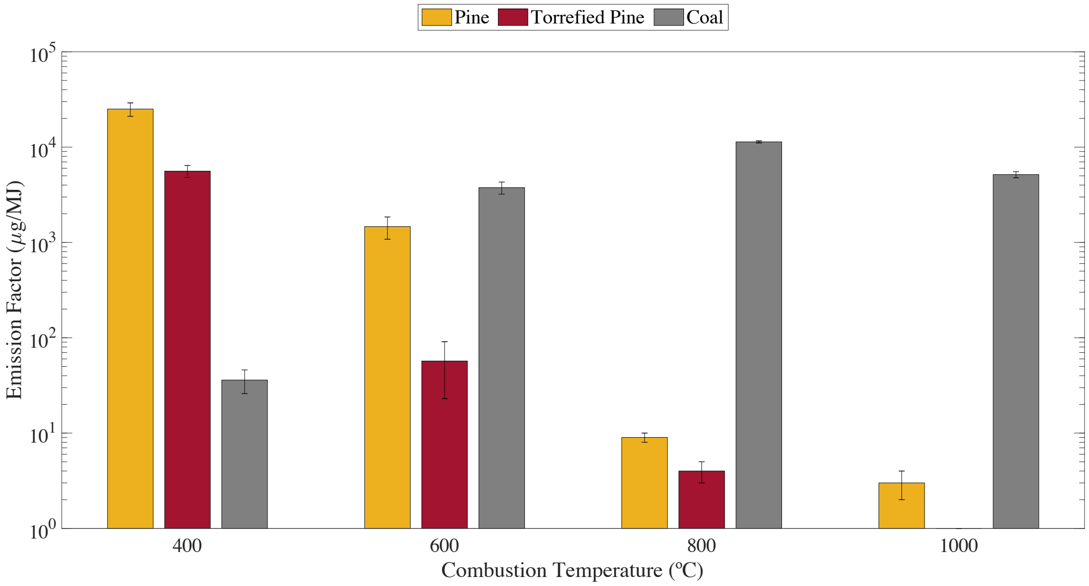

Figure 3: Aerosol emission factors as a function of combustion temperature for pine, torrefied pine, and coal. The value of each bar is the average of all SMPS measurements over the whole experiment and the error bar represents one standard deviation. There were no measurable aerosol emissions at 1000 °C for torrefied pine.

Torrefied pine combustion produced significantly lower aerosol emission than coal combustion at all combustion temperatures larger than 400 °C. These findings indicates that torrefied biomass can be an attractive alternative to coal for energy production and residential heating not only due to reducing greenhouse gas emissions, but also aerosol pollution.

3.2. Chemical speciation

We collected filter samples, as described in Section 2.4, for offline chemical speciation for the combustion temperature that produced the highest levels of aerosol emissions for each fuel. This temperature was 400 ºC for pine and torrefied pine, and 800 ºC for coal (Figure 3).

Table 2 presents a summary of the fractions of organic carbon (OC), elemental carbon (EC), and inorganic ions in the aerosol. The carbonaceous aerosol fraction was almost entirely OC for both pine and torrefied pine, with very small contribution from EC. This is expected because the low combustion temperature of 400 ºC is not high enough to produce EC (Chen & Bond, 2010; Saleh et al., 2018). On the other hand, coal combustion at 800 ºC produced a non-negligible amount of EC, with EC/OC = 0.22. For all fuels, the inorganic portion of the emissions are most likely composed of molecules such as metals (for coal), sulfates, nitrates, and ammonium (Dai et al., 2019; Yazdani et al., 2021). Among the inorganic ions analyzed in this study, only sulfate (SO_4^{-2}) was detected in significant proportion in coal emissions. While we did not perform chemical analysis on the fuel samples in this research, bituminous coal is known to have high sulfur content (up to 6%) (Vasireddy et al., 2011), and is therefore expected to produce high levels of SO_4^{-2}. In our experiments SO_4^{-2} alone constituted 50.57% of the aerosol mass, which is consistent with the relatively high SO_4^{-2} levels observed in primary coal emissions in previous studies (Dai et al., 2019; Joo et al., 2018; Yinxiao Zhang, 2018). As shown in Table 2, inorganic ions did not have any significant contribution to aerosol emissions from pine and torrefied pine combustion.

Table 2:Fractions of organic carbon (OC), elemental carbon (EC), and inorganic ions in the aerosol emissions at combustion temperature that produced the highest levels of aerosol emissions for each fuel.

	Pine (400 ºC)	Torrefied pine (400 ºC)	Coal (800 ºC)
OC	98.84% ± 5.2%	99.16% ± 5.52%	38.6% ± 2.5%
EC	0.85% ± 0.39%	0.83% ± 0.61%	8.49% ± 1.0%
Total inorganic ions	0.31% ± 20.46%	0.19% ± 20.46%	52.9% ± 20.46%
Na^+	0.18% ± 0.62%	0.00% ± 0.62%	1.59% ± 0.62%
Cl^-	0.13% ± 0.45%	0.18% ± 0.45%	0.13% ± 0.45%
K^+	0.00% ± 0.78%	0.00% ± 0.78%	0.33% ± 0.78%
NH_4^-	0.00% ± 17.65%	0.00% ± 17.65%	0.00% ± 17.65%
SO_4^{2-}	0.00% ± 0.35%	0.00% ± 0.35%	50.7% ± 0.35%

NO_3^+	0.003% ± 0.61%	0.014% ± 0.61%	0.1% ± 0.61%

The chemical composition of the organic aerosol fraction was further explored using ESI-MS. The sample preparation and analysis procedure is described in Section 2.4. The numbers of distinct organic compounds identified by ESI-MS were 73 for pine (at combustion temperature of 400 ºC), 32 for torrefied pine (at combustion temperature of 400 ºC), and 68 for coal (at combustion temperature of 800 ºC). The difference in the amount of identified compounds is partly reflective of chemical diversity of the fuels. The torrefaction process removes a fraction of the organic compounds present in the biomass, thus the torrefied pine is less complex than the pine. Coal, on the other hand, features a highly diverse mixture of complex organic compounds (Agency, 1993; Dai et al., 2019; Yazdani et al., 2021).

Figure 4 shows Van Krevelen plots (O:C vs H:C) for all three fuels, which provide a general description of the elemental composition of the organic aerosol emissions. It is noteworthy that the average O:C values were 0.19 for pine, 0.14 for torrefied pine, and 0.11 for coal. The relatively high O:C in pine emissions is reflective of the prevalence of oxygenated organic compounds in the biomass fuel. A fraction of these oxygenated compounds is removed in the torrefaction process (Chen et al., 2018; Fisher et al., 2012; van der Stelt et al., 2011) which results in the lower O:C in the torrefied pine emissions. Coal contains the least amount of oxygenated compounds among the 3 fuels (Angelika Więckol-Ryk, 2017; Ilham, 2022) with aromatic hydrocarbons constituting a significant fraction of its organic content (Lin et al., 2020). Therefore, as expected, O:C of coal emissions (0.11) was the lowest among the 3 fuels.

Figure 5 shows the relative abundance of different classes of organic compounds identified by ESI-MS for aerosol emissions from the 3 fuels. Notably, CHO compounds constitute the majority of pine emissions (72%) but only 50% of torrefied pine emissions, which is in-line with the discussion above regarding the reduction in oxygenated compounds by the torrefaction process. CHN compounds meanwhile, were not present in the pine sample but made up 27% of the torrefied pine emissions.

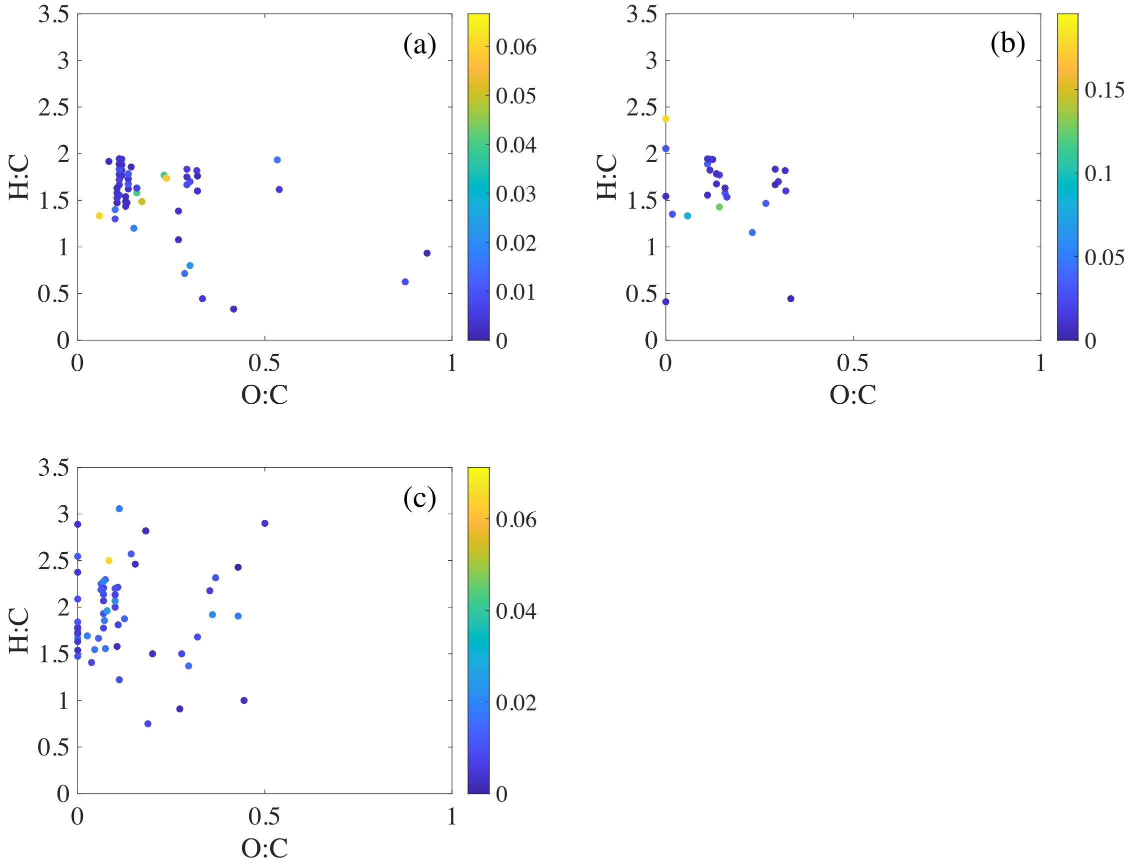

Figure 4: Van Krevelen plots obtained from ESI-MS analysis for aerosol emissions from the combustion of (a) pine at 400 °C, (b) torrefied pine at 400 °C, and coal at 800 °C. Marker color indicates relative abundance of each compound.

Coal emissions, on the other hand, contained no CHO compounds, but had 51% CHONS, indicating high abundance of sulfur-containing organic compounds. In fact, organic sulfur was found in over half the identified compounds for coal (total), which reflects the high sulfur content of bituminous coal and is in-line with the high levels of inorganic sulfates in coal emissions (Table 2).

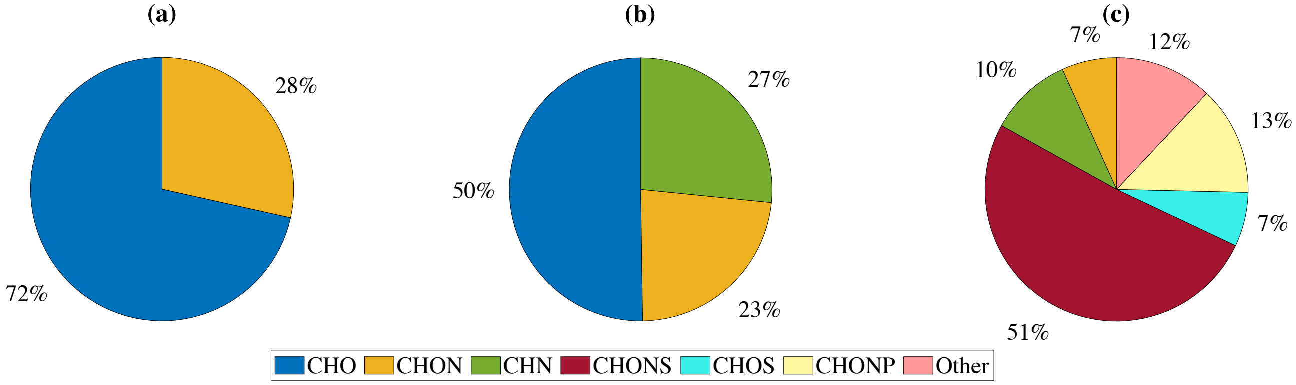

Figure 5:Classes of organic compounds identified by ESI-MS in aerosol emissions from combustion of (a) pine, (b) torrefied pine, and (c) coal

3.3. Light-absorption properties

The mass absorption cross-sections (MAC) and absorption Ångström exponents (AAE) of the carbonaceous fraction of the aerosol emissions from the 3 fuels are shown in Table 3. The MAC and AAE values were calculated from individual SMPS and Multi-PAS III data points (Section 2.4) and averaged over the whole experiment. For pine and torrefied pine, the aerosol mass concentration obtained from integrating the SMPS size distribution was assumed to be equal to the organic aerosol mass in the MAC calculations (see Section 2.4). This is justified because OC was the dominant species in the emissions of these fuels (Table 2). However, a substantial fraction of coal emissions were inorganic, mostly SO_4^{-2}. Therefore, the MAC calculations for coal emissions involved apportioning the integrated SMPS mass concentration into carbonaceous and inorganic, and using the carbonaceous aerosol mass in the calculations.

Aerosol emissions from all 3 fuels were light-absorbing. Based on their MAC and AAE values, they are categorized as weakly absorbing brown carbon (W-BrC) following the classification of Saleh (2020). It should be noted that the aerosol emissions likely contained inorganic ions that were not targeted in our IC analysis. This could be especially significant for coal, which has relatively high inorganic content compared to the biomass fuels. Therefore, the carbonaceous fractions are likely overestimated and the corresponding MAC values are underestimated, especially for coal. Nevertheless, the light-absorption properties obtained here are in agreement with previous studies that investigated biomass and coal emissions (Michael R. Olson, 2015; Mingjie Xie, 2018; Park & Yu, 2016). Figure 6 shows the light absorption properties of each fuel plotted on top of the brown carbon classes. The constraints of the classes are estimations and all fuels display similar light absorption properties.

Table 3:Mass absorption cross-sections at 422 nm and 532 nm and the corresponding absorption Ångström exponents (mean ± standard deviation) of the carbonaceous aerosol emissions from the combustion of the 3 fuels.

Fuel	**MAC_{422} [m^2/g]**	**MAC_{532} [m^2/g]**	**AAE**
Pine (400 °C)	0.63 ± 0.11	0.072 ± 0.016	8.92 ± 0.23
Torrefied Pine (400 °C)	1.22 ± 0.27	0.19 ± 0.04	7.36 ± 0.22
Coal (800 °C)	0.16 ± 0.01	0.063 ± 0.003	7.43 ± 0.08

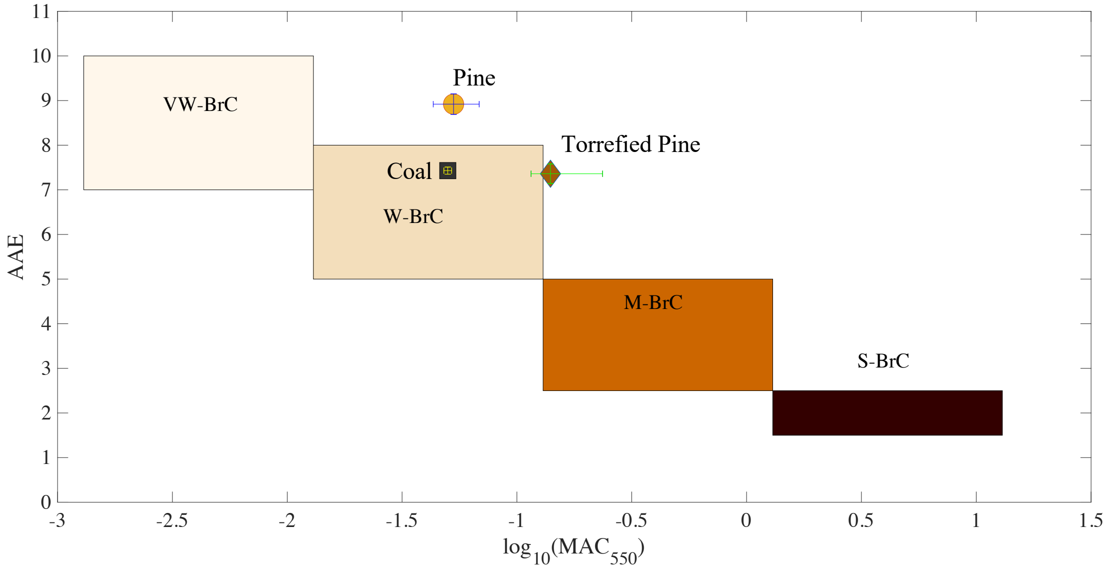

Figure 6: MAC550 plotted against Ångström exponent on top of brown carbon classes for the three samples analyzed. All three fuels generated aerosols classified as W-BrC, weakly absorbing brown carbon.

CHAPTER 4

CONCLUSION

Conclusion

By performing controlled-combustion experiments using a fuel-particle feeding system that approximates steady flow, we were able to perform a comparison of emission factors and physiochemical properties of aerosols from three different fuels. This is the first study to do a head-to-head comparison of biomass, torrefied biomass, and coal under the same combustion conditions. By keeping conditions the same across all experiments, we were able to isolate the effect each fuel type had on their respective emissions. The results of this study show that aerosol emissions from torrefied pine were significantly lower than from raw pine. This indicates that the torrefaction process, the major purpose of which is to increase the energy density of biomass fuels, has the important added benefit of reducing particulate pollution emissions.

By reducing the fraction of VOCs, including oxygenated compounds in the fuel, our results also indicate that torrefaction leads to changing the chemical composition of the aerosol emissions, specifically lowering the contribution of oxygenated organic compounds. These differences in chemical composition have implications both to atmospheric evolution and inhalation toxicity, which are important to investigate in future studies.

While coal emissions were relatively low at low combustion temperatures, they increased significantly at high temperature partly due to the large increase in sulfate emissions. At 800 °C, coal emission factors were 3 orders of magnitude higher than the biomass emissions. The high sulfur content in coal was manifested both as both high content of inorganic sulfate and organic sulfur in the aerosol emissions.

A carbon-neutral fuel with energy density similar to coal and, as found in this study, low aerosol emissions, torrefied biomass is an excellent complement or replacement to coal in industrial and energy production applications. For lower temperatures typical for residential heating and utilization, torrefied biomass is also a better alternative to raw, unprocessed biomass.

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