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TECHNICAL REPORT

Laboratory-Scale Study to Model Wildland-Urban Interface Combustion Emissions

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Executive Summary

Background

Large-scale wildfires that impact populated areas at the wildland urban interface (WUI) are increasing in frequency and magnitude. There are many unknowns associated with the types of chemicals and other pollutants that are emitted during the combustion phase of WUI fires and those that remain in post-fire residues. The complexity of fire fuels in the WUI is at the root of this issue since forest biomass burns along with community structures, vehicles, manufacturing facilities, and everything in the path of the fire. Data indicate that emissions from these fires are likely complex mixtures of chemicals, heavy metals, respirable particles, organic acids, and other hazardous gases.

Inhalation exposure to these combustion products represents a significant challenge to public health; however, their impact on workers, first responders, and the general population cannot be properly determined unless such emissions are well characterized. Novel methods are required to begin filling these data gaps.

To address this issue, Chemical Insights Research Institute (CIRI) of UL Research Institutes teamed with researchers from West Virginia University (WVU) to use a novel combustion generation system to burn mixtures of biomass and synthetic building materials (SBMs) and characterize their emissions. This research was done in WVU's unique Inhalation Facility located in the WVU Center for Inhalation Toxicology (iTOX). The first goal of this project was to produce and combust bulk pellets (pressed sawdust) representing geographic regions of the United States: the Northeast, the Northwest, the Southeast, and the Southwest. The second goal was to incorporate common SBMs into the pressed pellets and combust them. The specific SBMs included oriented strand board (OSB), foam board insulation or foamboard (FB), and vinyl flooring (VF). Emissions from each combustion fuel mixture were then characterized for particle concentration and size distributions, inorganic and organic gases, and metals. Discrete samples were collected for metals, aldehydes, and volatile organic compounds (VOCs) and provided to CIRI for additional analyses.

The complete research report, prepared by WVU, follows this Executive Summary. Authors included: WT Goldsmith, A. Ranpara, and TP Batchelor from the WVU Department of Physiology, Pharmacology & Toxicology, the WVU Center for Inhalation Toxicology; J Wang and R Burns of the WVU Center for Sustainable Biomaterials and Bioenergy, Division of Forestry and Natural Resources; and DF Harper, Center for Renewable Carbon of University of Tennessee. The additional metal and chemical characterization of the combustion emissions by CIRI will be reported separately.

Methodology

Combustion pellets with twenty different formulations of wood and SBMs were created using four regionally representative wood species: Douglas fir, red oak, ponderosa pine, and loblolly pine, and three types of SBMs: oriented strand board (OSB), polystyrene foam insulation or foamboard (FB), and vinyl flooring (VF). There were five different pellet compositions created for each of the four wood species including:

- 100% wood
- 75% wood + 25% OSB
- 97% wood + 3% FB
- 83% wood + 17% VF
- 55% wood + 25% OSB + 3% FB + 17% VF

These pellets were used as fire fuel in the novel laboratory-scale combustion system. Fire-associated aerosol and chemical emission profiles were evaluated by direct sampling of the exhaust gas. Ash residues were collected from the floor of the combustion system after each experimental burn. Aerosol characterizations were conducted with gravimetric techniques, direct reading instruments, and electron microscopy. Combustion-associated gases were continuously measured with photoionization and electrochemical detection. Combustion-associated VOCs were collected in a water trap and evaluated with offline headspace gas chromatography and mass spectrometry (GC/MS).

Results

Aerosol measurements showed that 100% wood and 75% wood + 25% OSB pellet compositions produced the highest number of particles but lower overall particle mass. Pellets consisting of 83% wood + 17% VF and 55% wood + 25% OSB + 3% FB + 17% VF were associated with lower overall particle numbers but increased particle mass emissions. The overall size distribution of the aerosols, regardless of wood species, was dominated by ultrafine particles and there were only subtle size distribution shifts detected among the different pellet formulations.

Evaluation of combustion efficiency through gas analysis indicated 100% wood pellets, 75% wood + 25% OSB, and 97% wood + 3% FP underwent more complete combustion compared to pellets containing 83% wood + 17% VF and 55% wood + 25% OSB + 3% FB + 17% VF.

Headspace GC/MS analysis showed that acetaldehyde, formaldehyde, and hexanal were present across all wood types with the highest values in pellets containing red oak. The addition of OSB in pellets increased the levels of acrolein. Pellets containing FB showed higher levels of acetaldehyde, formaldehyde, and hexanal as well as the presence of aromatic VOCs, such as styrene and ethyl benzene. Formaldehyde levels were elevated two to three times when FB was added in the pellets. Pellets containing VF were associated with increased emissions of halogenated VOCs such as bromochloromethane and benzene, a Group 1 carcinogen. Pellets containing wood and a mixture of all three SBMs emitted all the organic compounds associated with the other pellet formulations in addition to bromofluorobenzene and toluene. Scanning electron microscopy evaluation did not detect metals as part of the emission profile for any pellet formulation.

Conclusions

There are many unknowns related to the chemistry of WUI fire emissions and residues. This study represents an important foundational step based on the application of a novel combustion system and standardized fire fuels to simulate WUI fire emissions. These data will be useful for exposure and risk modeling and will aid in the laboratory evaluation of the potential for differential toxicity based on various formulations of fuel pellets.

1.0 Introduction

The frequency and severity of wildfires represent a significant challenge to public health. Because modern building approaches regularly situate structures adjacent to (and in) wildlands, the frequency of wildland-urban interface (WUI) fires has risen. Novel building materials are consumed in WUI fires, but our understanding of these complex emissions is poor. The purpose of these studies was to develop synthetic wood pellets comprised of common building materials and characterize in high detail the physical and chemical signatures of these combustion emissions.

These studies were performed in two phases. The first phase focused on characterization of woods from four distinct regions of the United States: 1) Northwest: Douglas fir; 2) Northeast: red oak; 3) Southwest: ponderosa pine; 4) Southeast: loblolly pine. Once these raw materials were obtained, sawdust was created and pressed into bulk pellets. These pellets were rigorously characterized to determine: particle concentration and size distribution; gas analyses; and metal evaluation. The second phase introduced synthetic materials to the pellet formulation prior to pellet formation/pressing. The synthetic materials selected are among the most common modern building materials and included: oriented strand board (OSB); foam board insulation (FB); and vinyl flooring (VF). The percentages of pellet mixtures studied in this project are presented in **Table 1**. In total, 20 different pellet compositions were studied.

The schematic of the combustion generator is presented in **Figure 1**. To sample emissions directly from the flue, a custom manifold was machined that allowed all characterization equipment to be simultaneously attached for real-time and off-line sampling. The following measurements were made for every experimental pellet: filter sampling (gravimetric analysis); particle count concentration (condensation particle counter), thermal desorption (TD) tube sampling; speciation of, or total volatile organic chemical (TVOC) analysis; particle collection for transmission electron microscopy (TEM), scanning electron microscopy (SEM), and inductively coupled plasma mass spectrometry (ICP-MS); chemical speciation using gas chromatography-mass spectroscopy (GC/MS), multiple gas analyzers; and particle size distributions: count aerodynamic diameter (high-resolution electrical low-pressure impactor [ELPI+]); count mobility diameter (scanning mobility particle sizer [SMPS]), count aerodynamic diameter (aerodynamic particle sizer [APS]); and mass size distribution (nano micro-orifice uniform deposit impactor [MOUDI]).

Table 1: Pellet composition and percent contributions (by mass) used in these experiments. The first number in the synthetic and mixture columns represents the amount of wood in the pellet.

Wood Species (WOOD) (100%)	Oriented strand board (OSB) (% WOOD / OSB)	Polystyrene foam board (FB) (% WOOD / FB)	Vinyl flooring (VF) (% WOOD / VF)	Mixture (% WOOD / OSB / FB / VF)
Red oak	75/25	97/3	83/17	55/25/3/17
Douglas fir	75/25	97/3	83/17	55/25/3/17
Ponderosa pine	75/25	97/3	83/17	55/25/3/17
Loblolly pine	75/25	97/3	83/17	55/25/3/17

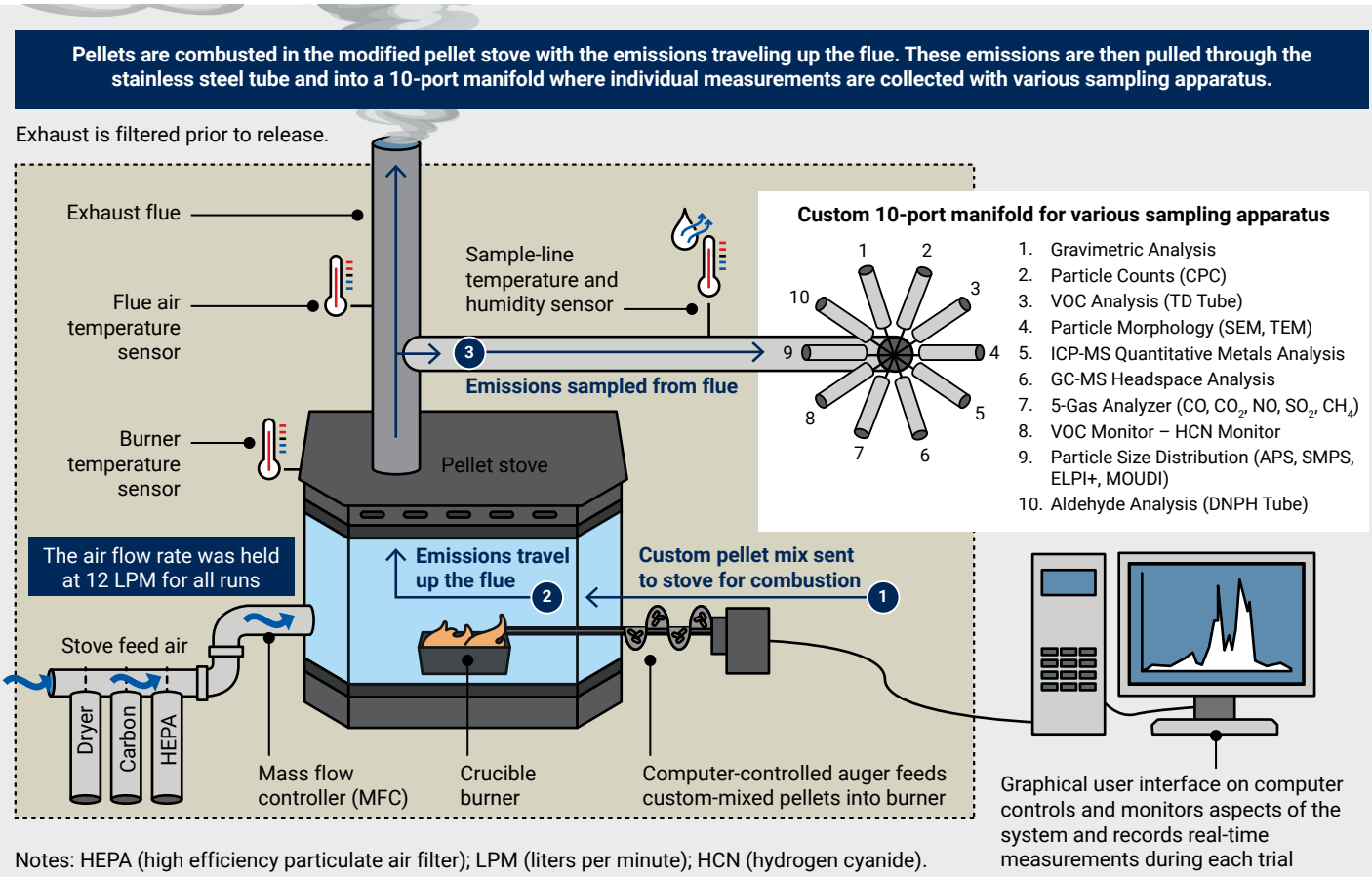

Figure 1: Combustion Generator schematic in the West Virginia University (WVU) Center for Inhalation Toxicology (iTOX).

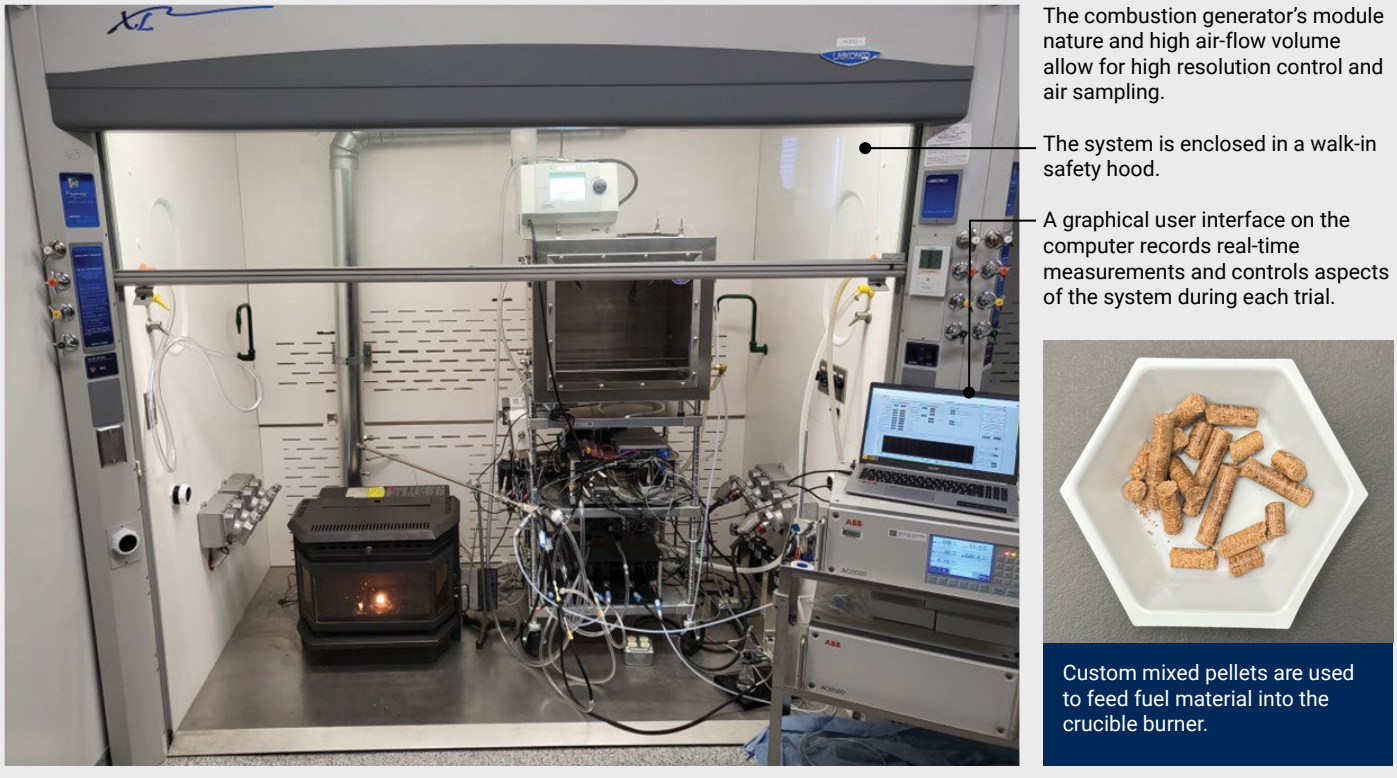

Figure 2: Picture of the Combustion Generator located in a walk-in hood in the Inhalation Facility of the WVU Center for Inhalation Toxicology (iTOX).

2.0 Materials and Methods

To simulate the combined combustion of different wood species and synthetic building materials (SBMs), such as that seen in a WUI fire, a novel combustion generator was developed. This generator utilized a wood pellet stove that was modified to allow measurement and control of temperatures and fuel feed rates. A diagram of the system is shown in **Figure 1** and a picture of the system is shown in **Figure 2**. Various pellet types were constructed from mixtures of wood and SBMs (**Table 1**) then combusted in the stove. The effluents from each fire were pulled into various sampling apparatus (**Table 2**) to characterize the aerosols and chemicals emitted during the combustion process from each of the pellet mixtures.

Table 2: Sampling instrumentation and protocols utilized to measure emissions from simulated wildland-urban interface fires.

Variable Type	Sampling Instrument	Manufacturer's Information	Metric (Unit) of Measurement	Sampling Flow Rate (LPM)	Data Log Period
Aerosols	SMPS 3381	TSI Inc., Shoreview, MN	Particle size distribution (#/cc)	0.3	30 minute sample
	APS 3321	TSI Inc., Shoreview, MN	Particle size distribution (#/cc)	5	30 minute sample
	ELPI+	Dekati Ltd., Finland	Particle size distribution (#/cc)	10	30 minute sample
	MOUDI 115R	Thermo Electron Corporation, Franklin, MA	Particle size distribution (mg/m^3)	10	30 minute sample
	CPC 3075	TSI Inc., Shoreview, MN	Particle concentration (#/cc)	0.3	Sample / 2 sec, 30 minutes total
	Gravimetric Sampling (37 mm PTFE Filter)	SKC, Eighty Four, PA	Mass Concentration (mg/m^3)	1	30 minute sample
	TEM	JEM 1400 (JEOL Ltd., Peabody, MA) on 200 mesh copper grid	Particle morphology	1	45 second sample
	FE-SEM with EDS	S4800 (Hitachi Ltd., Tokyo, Japan) with the Bruker 25 mm filter polycarbonate membrane	Particle morphology and qualitative heavy metal analysis	1	45 second sample
Chemicals	TVOC 2	Ion Science LTD., United Kingdom	Total volatile organic chemical concentration (PPM)	0.5	Sample / 2 sec, 30 minutes total
	AO2000 Combustion Gas Analyzer	ABB Ltd., Zurich, Switzerland	CO, CO_2, SO_2, NO (PPM)	1	Sample / 2 sec, 30 minutes total
	GC/MS	Agilent Technologies, Inc., Santa Clara, CA	Chemical identification and speciation including VOCs, VCCs, and PAHs	1	2 – combined 30 minute samples across 2 trials, 60 minutes total

2.1 COMBUSTION PELLET DEVELOPMENT

Collaborators from West Virginia University (WVU) Center for Sustainable Biomaterials & Bioenergy and from the Center for Renewable Carbon at the University of Tennessee were instrumental in the development and construction of the novel pellets used in this study. Since this was a pilot project to examine the efficacy of using novel pellets made from SBMs, one of this research's aims was to produce a maximal measurable amount of chemicals from each SBM. This assisted us with determining which chemicals were produced from each individual SBM and each SBM mixture. At the same time this needed to be balanced with the ability to create a stable rigid pellet (rigidity decreased as the percent of wood in the pellet decreased) and also not to overload/clog our sampling devices with too-high levels of aerosols and gases.

Wood species were chosen from each of the four regions of the United States: Northwest – Douglas fir (DF), Northeast – red oak (RO), Southwest – ponderosa pine (PP), and Southeast – loblolly pine (LL). Sawdust from each of the four wood types was donated by our contacts located in the different regions. The three SBMs chosen for this study were oriented strand board (OSB), foam board insulation (FB), and vinyl flooring (VF). Initial testing to determine optimal emission output amounts for each of the SBMs revealed the pellet percentages to be 25% for OSB, 3% for FB and 17% for VF. Pellets were created for each wood type (100% wood species), for each wood type with each synthetic (75% wood – 25% OSB, 97% wood – 3% FB, 83% wood – 17% VF) and for each wood type with all SBMs (55% wood – 25% OSB – 3% FB – 17% VF) for a total of 20 different pellet types.

Wood was collected as sawdust and the bulk SBMs were grinded into suitable particle sizes (fine powder) for creating pellets. The sawdust and SBM mixtures were dried and then water was sprayed onto the mixture to achieve an optimal moisture content for creating pellets (~12% wood moisture equivalent). This powder mixture was then fed into a pellet maker, and the finished pellets were then collected and sealed for later use.

2.2 NOVEL COMBUSTION GENERATOR

The combustion generator was centered around a modified wood pellet stove. The pellet stove originally was equipped with an auger to deliver pellets and a fan with a damper to provide air to feed the combustion. All electronic controls that were native to the stove were bypassed and replaced with our modified custom controls.

A relay was added to the auger that allowed power to the auger to be pulsed on and off, meaning a user defined duty cycle rate could be applied to the auger power to control the feed rate of the pellets. Prior to each pellet use, the specific pellet type was run through the auger at different rates and the total weight of pellets dropped during a 20-minute period was measured. In this way, a calibration factor for each pellet type was calculated that permitted the pellet drop rate to be defined in terms of g/min. For this study, to compare each pellet type in terms of equal mass burned, the rate was held at 6 g/min throughout all runs.

With the damper fully open the typical air flow rate feeding the stove was ~12 liters per minute (LPM.) To minimize the effects of variations in room air conditions, a mass flow controller (MFC) was used to pump air into the stove at a user-defined rate. Compressed house air was dried then HEPA and carbon filtered before being fed into the MFC. For this pilot study the air flow rate was held at 12 LPM for all runs. The fan was also left in place and activated when the stove was on since we found this distributed the air in a more uniform manner around the burner where the pellets were dropped.

A peristaltic pump (P720, Instech Laboratories, Inc., Plymouth, PA) was installed to deliver accelerants such as gasoline or jet fuel to determine their effects on the emissions. A stainless steel (SS) line was fed into the stove and terminated directly over the burner so that the accelerant could be dripped into the burner during runs at user-defined rates. While the capability was developed, accelerants were not used in the present study.

An electric igniter in the stove initially heated pellets until a flame occurred and after combustion began the emissions travelled up the stove flue. An SS elbow was inserted into the middle of the flue (facing the emissions stream) and piped out of the flue through an SS pipe and into a custom SS 10-port manifold where individual sampling devices were attached. Thermocouples were inserted directly above the burner, directly beside the elbow in the flue and a temperature-humidity probe was also inserted right before the manifold so that temperature could be measured at the burn site, at

the pull-site from the flue, and at the sampling point in the manifold. The sampling equipment used for this study are explained in the Aerosol Characterization and Chemical Characterization sections and also described in **Table 2**.

A graphical user interface (GUI) was coded in the LabVIEW environment to monitor, graph, record and control system variables. A screenshot of the main GUI tab is shown in **Figure 3**. System and sampling air flow rates were set in the GUI along with pellet drop rates. Dilution air for sampling apparatus could also be modified with the GUI using the corresponding dilution factor being displayed. Instrument zeroes and calibration factors could be set in the GUI during device calibrations. Real-time system variable values were displayed and graphed to observe data trends. Various alarms were also implemented to alert the user to instrument communication issues or if any variables of interest were outside of expected ranges.

2.3 AEROSOL CHARACTERIZATION

The size, morphology, and composition of aerosols influence deposition rates in different areas of the respiratory tract and may lead to adverse health effects in exposed populations. Environmental conditions surrounding fires such as temperature, fuel sources, and completeness of combustion also contribute to aerosol formation. The aerosols emitted from the combustion of wood and SBM pellets in this study were characterized in multiple ways.

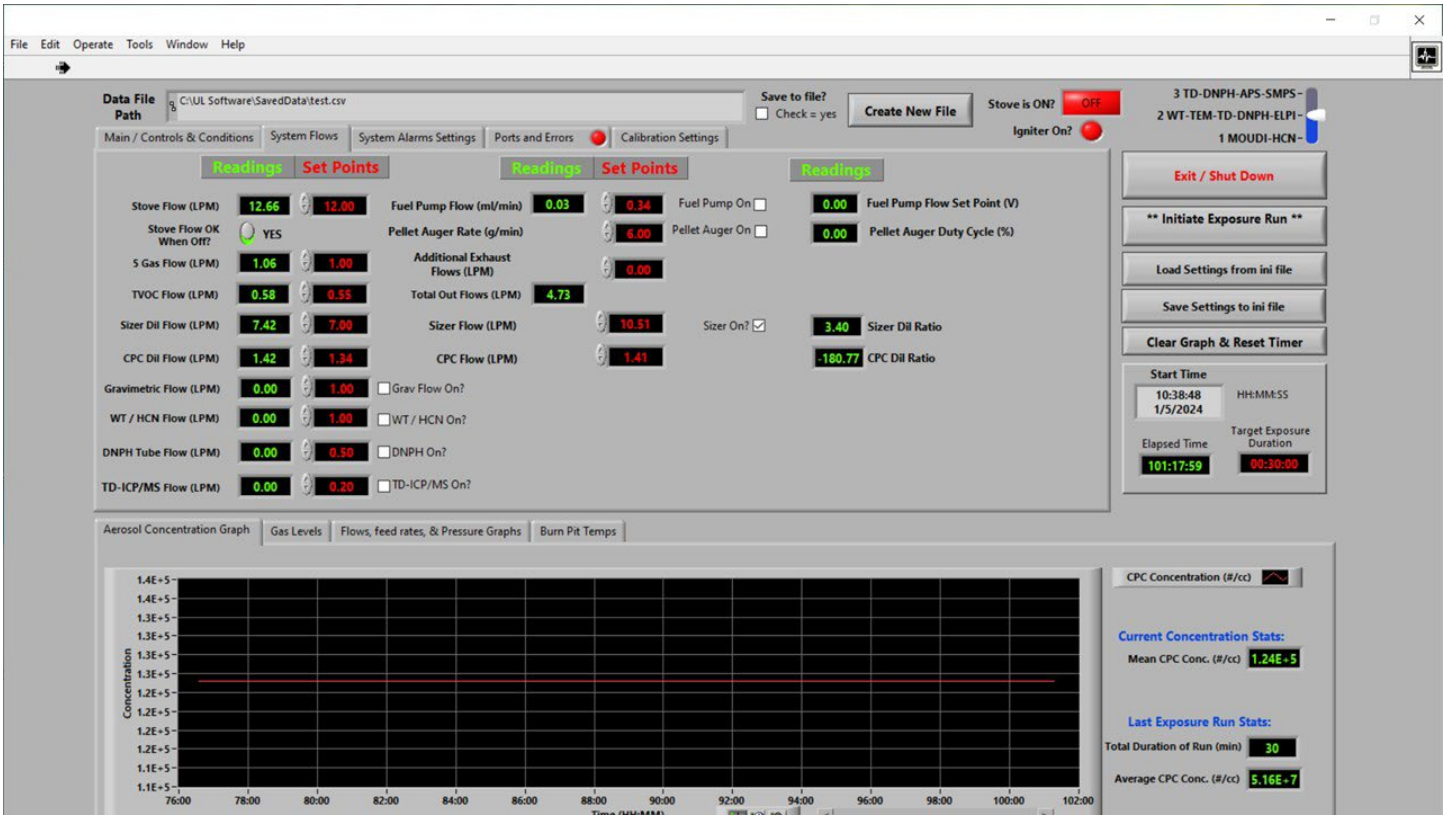

Figure 3: Screenshot of the custom software developed to provide a graphical user interface and to display, control and record environmental variables during combustion experiments.

Average total aerosol mass concentrations were measured gravimetrically. Emissions were pulled through a sample port on the manifold onto closed-faced 37 mm PTFE filters with a 0.45 µm pore size (SKC Inc., Eight Four, PA). The sample air flow rate was controlled with an MFC and the run's flow rate varied depending on how much total aerosol was being produced for a particular pellet. We attempted to collect as much sample as possible to increase our resolution, but limited the flow rate to ensure that filters did not become overloaded with particles with corresponding MFC flow issues. The air flow rate range for sample collection ranged from 0.3–1.0 LPM (depending on the expected aerosol mass concentration) and each sample was collected for the full 30 minutes of a run.

In a similar fashion, samples were also pulled onto preassembled Air filter Cassettes (37 mm, 3 PTFE, 0.45 µm with support pad, Electron Microscopy Science, Hatfield, PA) for quantitative heavy metal analysis of the aerosols using ICP/MS technique. These samples were collected for five minutes each and typically occurred for minutes 25-30 of a run. The sample flow rate was pulled from the manifold with an MFC at a rate of 0.2 LPM. The ICP/MS analysis was conducted by CIRI researchers and the results are not included in this version of the report.

The particle morphology of the aerosols was evaluated with electron microscopy (S-4800, Hitachi, Tokyo, Japan). Aerosols were collected on a 200 mesh copper grid (Electron Microscopy Science, Hatfield, PA), and onto a 25 mm diameter, 0.2 µm pore size track-etched polycarbonate filters (Sterlitech Corporation, VA) by drawing air from the manifold through an MFC at 1 LPM for 45 sec. After collection, filters were prepared for transmission and scanning electron microscopy (TEM and SEM, respectively). The SEM samples were also analyzed with energy dispersion spectroscopy (EDS) with X-ray for qualitative heavy metal detection.

Real-time particle count concentrations were measured throughout each trial with a condensation particle counter (CPC 3075, TSI Inc., St. Paul, MN). Particle size distributions were measured for each pellet type with multiple instruments (one trial for each instrument). A high-resolution electrical low-pressure impactor (ELPI+, Dekati, Tampere, Finland) counted particles throughout the entire size range of interest (6 nm – 10 µm). A combination of a scanning particle mobility sizer (SMPS 3938, TSI Inc., St. Paul, MN, range 13 nm – 743 nm) and an aerodynamic particle sizer (APS 3321 TSI Inc., St. Paul, MN, range 370 nm – 20 µm) was also utilized to determine the count size distribution over a similar range. The aerosol mass size distribution was measured with a nano micro-orifice uniform deposit impactor (MOUDI 115R, MSP Corp, Shoreview, MN). Since there were a high number of particles present during combustion, air dilution was used, as needed, for each of these instruments to prevent exceeding their maximum levels of detection. Log-normal fits of the particle size distributions were calculated and reported as count median diameter (CMD: ELPI+, SMPS/APS combination) or mass median aerodynamic diameter (MMAD: MOUDI) with geometric standard deviation (GSD). The CMDs, MMADs, and GSDs were calculated in two separate ways: 1) a log-probit method (Graphical) that de-emphasized particles on the far ends of the distribution in order to better focus on the position of the main mode of the aerosol produced, and 2) a statistical method (Statistical) that took into account the entirety of the measurements to better identify the spread of the distribution in case there were multiple modes.

2.4 CHEMICAL CHARACTERIZATION

Real-time measurements of gases were performed with three instruments. Total volatile organics were continuously measured during each trial with an isobutylene calibrated photo-ionization detector (TVOC-2, ION Science Ltd, Stafford, TX). Hydrogen cyanide (HCN) was measured with a universal gas detector supplied with an HCN sensor and calibration cap (99030, PureAire, Lake Zurich, IL). The TVOC 2 and HCN monitor were attached in series and one MFC pulled air from the manifold for both devices. Combustion gases (CO, NO, SO_2, CO_2, and CH_4) were recorded in real time for each trial with a 5-gas analyzer (AO2000, ABB Ltd., Zurich, Switzerland) attached to a separate MFC.

To provide more detailed chemical speciation, gas chromatography mass spectrometry (GC/MS) was performed. The combustion emissions were drawn at 1 LPM from the flue for 60 minutes (trial 2nd and 3rd) and sampled in a flask containing 50 mL of pure water (≥17 milli Ω) and evaluated separately for specific VOCs (>60) and VCCs (>10) of interest. After water trap collection, chemical speciation was performed off-line with a headspace autosampler (Model# 7697A) coupled with gas chromatography (GC, Model #8890) and mass spectrometer (MS, Model# 7000) from Agilent Technologies Inc., Santa Clara, CA.

Air samples were pulled into thermal desorption (TD) tubes for GC/MS assessments for VOCs. Air samples were also pulled into dinitrophenylhydrazine (DNPH) tubes for aldehyde assessments via liquid chromatography/mass spectrometry. These samples were collected for five minutes each and typically occurred for minutes 25-30 of a run. The sample flow rate was pulled from the manifold with an MFC at a rate of 0.2 and 0.5 LPM for TD and DNPH tubes, respectively. These analyses were conducted by CIRI researchers and the results are not included in this version of the report.

2.5 FLOOR ASH COLLECTION

Aerosols that did not travel up the flue, and instead landed on the floor of the stove (floor ash), were collected in custom-shaped aluminum foil trays for analysis and further studies. These aerosols could be considered similar to the ash found after WUI fires encountered by first responders, follow up inspections and the general public. To collect these ashes, aluminum foil was placed on the bottom of the stove before each trial. After the trial was complete and the stove had cooled, the ashes collected on the foil were transferred to a 50 ml centrifuge tube for later use and analysis.

2.6 WOOD AND BUILDING SYNTHETICS TESTING

To test the efficacy of our pellet production and the utility of the novel combustion generator, 20 different pellet types were created and tested. For each pellet type, a calibration curve was calculated by varying the pellet drop duty cycle and measuring the weight of the pellets dropped over a unit time so that, during trials, pellets could be dropped at a rate of 6 g/min.

Twenty different pellet types were tested during this study (**Table 1**). Three trials were conducted for each pellet type to collect all the measurements of interest, including replicates, where possible. If, during a given trial, measurements were considered corrupt or incomplete, additional trials were conducted. For each trial, a suitable number of pellets were dropped into the burner to start the fire. After the igniter lit the fire, the pellet auger was activated. Once the flue was warm and the flue temperature had equilibrated, a trial was conducted for 30 minutes. Typically, the data from the real-time instrumentation was collected during each of the three trials (temperatures, humidity, particle counts, total VOCs, HCN, combustion gases). In addition, gravimetric analysis of the mass concentration of the aerosols was also conducted for each trial. Each of the particle size instruments was used for one trial apiece (first trial- MOUDI, second- ELPI+, third- SMPS/APS combo). Separate measurements with the metal ICP/MS filters along with TD and DNPH tubes were conducted in trials 2 and 3. Water-trap sampling for CGMS analysis was conducted across trials 2 and 3 (one measurement for the sampling from both trials to increase our level of detection). SEM/TEM filter samples were collected at the end of trial 3.

To ensure that any residuals left from previous runs in the stove or flue were negligible, two different tests were performed. A “cold” trial was conducted where no heating or combustion occurred, yet clean air was still pumped through the stove at a rate of 12 LPM. A “hot” trial was also conducted where no combustion occurred. Instead, the clean air was passed by two high wattage cylindrical electrical heaters (CSS-508885/120V, Omega Engineering Inc., Norwalk, CT), placed in the burner area of the generator, that were capable of producing a similar amount of heat as during the typical combustion trials. As with the “cold" trial, the fan was active for the “hot" trial. Particle concentration, size distributions, and chemical analysis were performed during these trials to assess whether aerosols or volatile chemicals were released from the oven or stack due to the disturbance or re-volatilization of any residue from previous experiments.

3.0 Results and Discussion

3.1 COMBUSTION PELLET DEVELOPMENT

Pellet formation proved challenging, but after much trial and error, each of the proposed 20 pellet types proposed in **Table 1** were successfully formulated and combusted. The moisture level of the sawdust, particle size of the SBMs, and the percentage of pellet that was composed of wood or OSB (natural binders in the wood products) were all important for creating pellets with rigidity that could withstand handling and transport in the stove’s auger. Different densities in the pellets resulted in separate pellet auger duty cycle percentages for each pellet (**Table 2**). This change in auger speed for each pellet resulted in a constant feed rate of 6 g/min, irrespective of pellet type.

3.2 NOVEL COMBUSTION GENERATOR

The WVU combustion generator was modified in various ways for this project. Instead of conducting air samples from the exposure chamber, a custom manifold with 10 ports was designed to allow multiple instruments/methodologies to sample simultaneously. In addition, the sampling was conducted near the base of the flue with no air dilution (unless purposely added for an individual sample to prevent overload). A new MFC was added to feed the stove and combustion. Previously, a fan pulled in room air to feed the combustion, but for this project tighter control over the cleanliness of the input air and humidity was required. Additional MFCs were also added for the sampling apparatus and methodologies that did not have internal pumps. This was done to tightly control the sampling airflows and to keep the airflows consistent during trials despite high aerosol amounts that could add resistance and affect pump performance, in some cases.
The software was also heavily modified to reflect the needs of this project. Automatic routines were added that turned samplers on and off at the needed times depending on timing and whether the system had reached equilibrium.

3.3 ENVIRONMENTAL CONDITIONS

The environmental conditions for each pellet type are shown in **Table 3**. In general, the combustion efficiency and temperatures near the site of the combustion and in the flue were higher for wood only and wood plus OSB pellets. These levels decreased in pellets that contained VF.

3.4 AEROSOL CHARACTERIZATION

The results for the aerosol measurements for each pellet type are shown in **Table 4**. Typically, the wood only and wood plus OSB pellets produced higher numbers of particles, but, interestingly, lower total mass concentration values. This seemed due to shifts in the particle size distribution curves as noted by lower CMD and MMAD values. Conversely, the wood plus VF and MIX pellets emitted less particles, but higher mass amounts due to size distribution shifts reflected by higher CMDs and MMADs. In general, the wood plus FB emission measurements fell between the wood/wood plus OSB and wood plus VF/MIX amounts. Morphological features for the aerosols were examined with TEM and SEM for each of the pellet types. Representative TEM images for each of the four wood only species is shown in **Figure 4**. Similar representative images are shown for Douglas fir and SBM mixtures in **Figure 5**.

3.5 CHEMICAL CHARACTERIZATION

The results for the chemical characterization for each pellet type are shown in **Table 5**. Typically, the CO values were smaller, and the CO_2 values were higher for wood only, wood plus OSB and wood plus FB for the combusted pellets indicating more complete combustion when compared to the wood plus VF and MIX pellets. The TVOC measurements tended to increase with the addition of SBMs and was higher, in all species of wood, for the MIX pellets. For the individual VOCs measured with GC/MS, acetaldehyde, formaldehyde, and hexanaldehyde were present in all the wood species with the highest values seen for RO. The wood plus OSB pellets increased the levels of acrolein. The wood plus FB pellets showed increased values for acetaldehyde, ethyl benzene, formaldehyde, hexanaldehyde, and styrene. The wood plus VF pellets showed the highest levels of bromochloromethane. The emissions from the MIX pellets tended to show all the VOCs measured with the individual SBMs and also introduced detectable levels of bromofluorobenzene and toluene. SEM coupled with EDS did not reveal evidence of metal constituents in sampled aerosols for any of the emissions studied. It should be noted that the CH_4 values from the combustion gas analyzer were extremely variable and the HCN monitor also produced no usable data. Since the validity of both measurements is in question, we did not include those values in this report.

Table 3: Environmental conditions during combustion of the pellets used to simulate wildland-urban interface fires. Wood species RO – red oak, LL – loblolly pine, PP – ponderosa pine, DF – Douglas fir. For the synthetic building materials mixed with the balance wood species: OSB – oriented strand board (25%), FB – foam board insulation (3%), VF – vinyl flooring (17%), 3 – all three synthetics with same percentages as mentioned previously. For columns where more than one measurement was conducted, the values are expressed in terms of average ± standard error.

Pellet Type	Pellet Auger Duty Cycle (%)	Combustion Efficiency (%)	Stove Temperature (°C)	Flue Temperature (°C)	Manifold Temperature (°C)	Manifold Relative Humidity (%)
RO	23.0	98.1 ± 0.5	297.7 ± 29.2	112.3 ± 8.7	23.5 ± 2.6	48.2 ± 3.7
RO+OSB	19.0	97.8 ± 0.2	326.3 ± 15.6	106.8 ± 2.3	23.5 ± 2.5	48.2 ± 9.2
RO+FB	18.9	96.2 ± 0.6	261.5 ± 8.5	99.1 ± 1.5	23.6 ± 2.6	49.9 ± 8.9
RO+VF	24.6	95.3 ± 0.9	248.4 ± 9.4	93.0 ± 2.1	25.6 ± 1.4	29.0 ± 4.7
RO+3	22.4	95.2 ± 0.2	229.2 ± 4.8	87.0 ± 1.0	23.7 ± 0.9	58.4 ± 3.3
LL	20.3	96.2 ± 0.9	258.8 ± 22.9	110.0 ± 5.1	21.6 ± 0.9	54.5 ± 2.1
LL+OSB	18.6	96.7 ± 0.7	256.6 ± 18.2	100.7 ± 4.2	22.1 ± 2.3	82.7 ± 11.8
LL+FB	18.8	98.1 ± 0.1	316.3 ± 10.5	106.3 ± 2.9	24.3 ± 1.3	48.4 ± 3.3
LL+VF	19.6	94.6 ± 0.7	203.9 ± 15.1	80.1 ± 3.1	19.0 ± 1.1	84.6 ± 3.7
LL+3	22.8	95.9 ± 1.0	280.6 ± 20.4	94.8 ± 0.4	23.6 ± 1.3	61.3 ± 3.7
PP	24.0	97.9 ± 0.1	345.7 ± 16.0	114.9 ± 3.5	23.1 ± 2.5	61.0 ± 12.0
PP+OSB	18.8	97.5 ± 0.1	296.4 ± 7.6	104.9 ± 1.6	23.6 ± 2.7	56.1 ± 9.0
PP+FB	30.5	97.1 ± 0.4	264.8 ± 11.9	99.0 ± 2.4	25.1 ± 2.0	37.9 ± 5.0
PP+VF	28.2	93.2 ± 2.6	247.4 ± 31.1	88.8 ± 2.2	23.2 ± 1.1	57.9 ± 0.8
PP+3	22.6	94.0 ± 3.1	242.8 ± 42.3	86.4 ± 7.7	22.6 ± 0.4	58.7 ± 3.6
DF	16.5	95.2 ± 0.7	226.4 ± 8.4	87.8 ± 3.9	21.5 ± 0.8	38.8 ± 13.4
DF+OSB	16.4	96.8 ± 0.5	293.1 ± 23.5	106.9 ± 2.2	23.1 ± 2.9	51.6 ± 8.2
DF+FB	21.8	96.6 ± 0.2	281.7 ± 8.3	99.5 ± 0.9	22.8 ± 1.9	66.1 ± 9.4
DF+VF	21.1	92.3 ± 2.6	188.4 ± 20.5	80.7 ± 5.4	22.8 ± 1.0	40.1 ± 4.3
DF+3	24.0	91.6 ± 4.5	211.2 ± 31.9	82.8 ± 7.2	22.8 ± 0.6	51.3 ± 4.7

Table 4: Aerosol characteristics of the emissions for each pellet type during combustion to simulate wildland-urban interface fires.

Wood species: RO – red oak, LL – loblolly pine, PP – ponderosa pine, DF – Douglas fir. For the synthetic building materials mixed with the balance wood species: OSB – oriented strand board (25%), FB – foam board insulation (3%), VF – vinyl flooring (17%), 3 – all three synthetics with same percentages as mentioned previously. Particle and mass concentrations are expressed in terms of average ± standard error. For the mass median aerodynamic diameter (MMAD) and count median diameter (CMD) columns the numbers are expressed as the median ± the geometric standard deviation (GSD). The Graphical method for calculating the medians is from a log-probit fit of the log-normal curve that minimizes the effects of outliers while the Statistical method contains all values.

Pellet Type	Particle Concentration (#/cc)	Mass Concentration (mg/m^3)	MMAD (nm) Graphical	MMAD (nm) Statistical	CMD (nm) ELPI Graphical	CMD (nm) ELPI Statistical	CMD (nm) SMPS/APS Graphical	CMD (nm) SMPS/APS Statistical
RO	3.2e+08 ± 1.2e+08	19.0 ± 8.6	165.0 ± 1.8	251.0 ± 4.0	44.9 ± 1.6	47.2 ± 1.6	93.1 ± 1.4	92.7 ± 1.4
RO+OSB	1.2e+08 ± 4.7e+07	16.8 ± 1.5	153.0 ± 1.6	190.0 ± 3.1	45.7 ± 1.6	47.5 ± 1.6	74.5 ± 1.4	73.9 ± 1.4
RO+FB	4.8e+07 ± 1.7e+07	39.4 ± 7.4	170.0 ± 1.5	216.0 ± 3.0	47.4 ± 1.6	51.7 ± 1.7	87.8 ± 1.4	88.2 ± 1.4
RO+VF	1.6e+08 ± 7.1e+07	41.1 ± 1.2	165.0 ± 1.5	198.0 ± 2.5	69.4 ± 1.8	74.6 ± 1.7	98.7 ± 1.4	98.6 ± 1.4
RO+3	6.6e+07 ± 1.8e+07	51.6 ± 10.8	204.0 ± 1.7	244.0 ± 2.7	70.4 ± 1.7	75.2 ± 1.8	107.0 ± 1.5	109.0 ± 1.5
LL	9.8e+07 ± 1.9e+07	48.3 ± 9.1	166.0 ± 1.8	157.0 ± 2.1	54.0 ± 1.8	61.2 ± 1.7	91.1 ± 1.4	89.5 ± 1.4
LL+OSB	1.2e+08 ± 3.6e+07	25.8 ± 1.5	166.0 ± 1.6	216.0 ± 3.4	45.5 ± 1.5	48.2 ± 1.6	90.5 ± 1.4	90.3 ± 1.4
LL+FB	6.4e+07 ± 5.4e+06	50.5 ± 14.3	180.0 ± 3.0	303.0 ± 4.8	45.1 ± 1.5	46.3 ± 1.6	65.6 ± 1.4	66.2 ± 1.5
LL+VF	2.1e+07 ± 1.2e+07	45.8 ± 7.8	236.0 ± 1.6	247.0 ± 2.2	52.9 ± 1.7	57.9 ± 1.7	115.0 ± 1.5	115.0 ± 1.5
LL+3	7.3e+07 ± 6.9e+06	48.7 ± 19.2	194.0 ± 1.8	226.0 ± 2.1	70.0 ± 1.8	74.7 ± 1.8	101.0 ± 1.4	101.0 ± 1.5
PP	9.7e+07 ± 2.2e+07	16.8 ± 1.2	173.0 ± 2.4	276.0 ± 4.2	47.7 ± 1.6	50.8 ± 1.6	78.4 ± 1.4	77.3 ± 1.4
PP+OSB	7.5e+07 ± 2.2e+07	19.3 ± 3.3	184.0 ± 1.5	234.0 ± 3.2	46.5 ± 1.6	49.5 ± 1.6	83.7 ± 1.4	83.2 ± 1.4
PP+FB	4.8e+07 ± 2e+07	27.6 ± 5.1	168.0 ± 3.1	289.0 ± 4.8	51.0 ± 1.6	56.0 ± 1.7	74.2 ± 1.4	75.0 ± 1.4
PP+VF	2.4e+07 ± 4.4e+06	108.2 ± 26.9	240.0 ± 2.8	322.0 ± 3.8	66.9 ± 1.9	73.5 ± 1.9	126.0 ± 1.5	127.0 ± 1.5
PP+3	1.9e+07 ± 1.4e+06	88.2 ± 15.9	261.0 ± 2.4	388.0 ± 4.1	70.3 ± 1.9	76.7 ± 1.9	144.0 ± 1.5	143.0 ± 1.5
DF	1e+08 ± 3.7e+07	24.4 ± 1.9	140.0 ± 1.5	148.0 ± 2.2	36.5 ± 1.5	36.8 ± 1.5	94.5 ± 1.5	95.9 ± 1.5
DF+OSB	1.5e+08 ± 6.2e+07	17.2 ± 4.1	159.0 ± 1.7	214.0 ± 3.5	44.6 ± 1.5	46.9 ± 1.6	80.1 ± 1.4	79.2 ± 1.4
DF+FB	5.8e+07 ± 3e+07	19.1 ± 2.1	159.0 ± 1.6	180.0 ± 2.7	42.2 ± 1.6	43.3 ± 1.7	75.2 ± 1.5	76.5 ± 1.5
DF+VF	7.5e+07 ± 3.4e+07	119.2 ± 8.3	294.0 ± 2.2	440.0 ± 3.7	57.4 ± 2.0	64.8 ± 2.0	125.0 ± 1.6	125.0 ± 1.6
DF+3	5e+07 ± 2.1e+07	111.7 ± 31.9	259.0 ± 1.8	289.0 ± 2.4	53.5 ± 2.0	61.2 ± 1.9	132.0 ± 1.4	132.0 ± 1.5

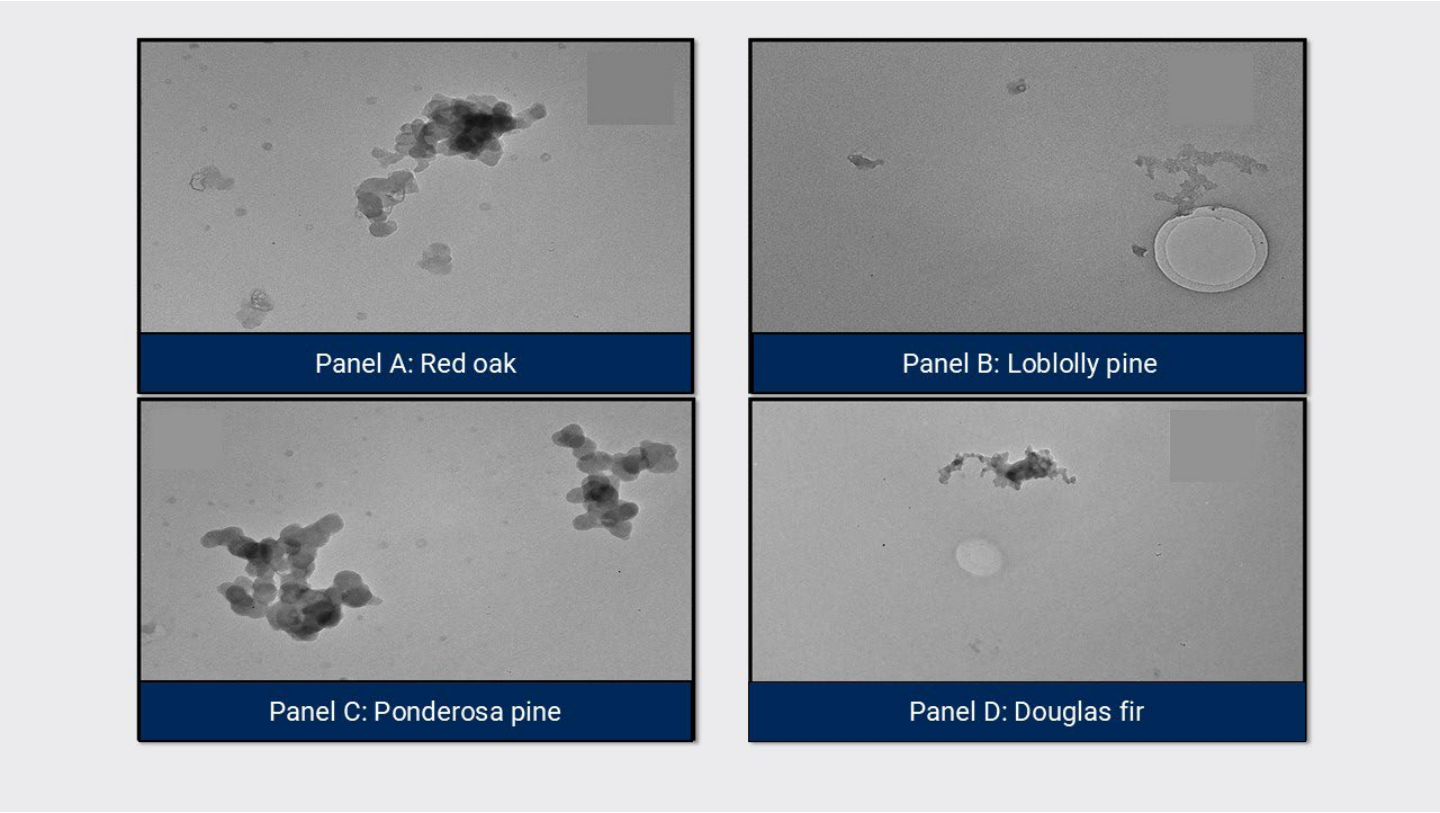

Figure 4: Transmission electron microscopy (TEM) of particles emitted when combusting wood only pellets.

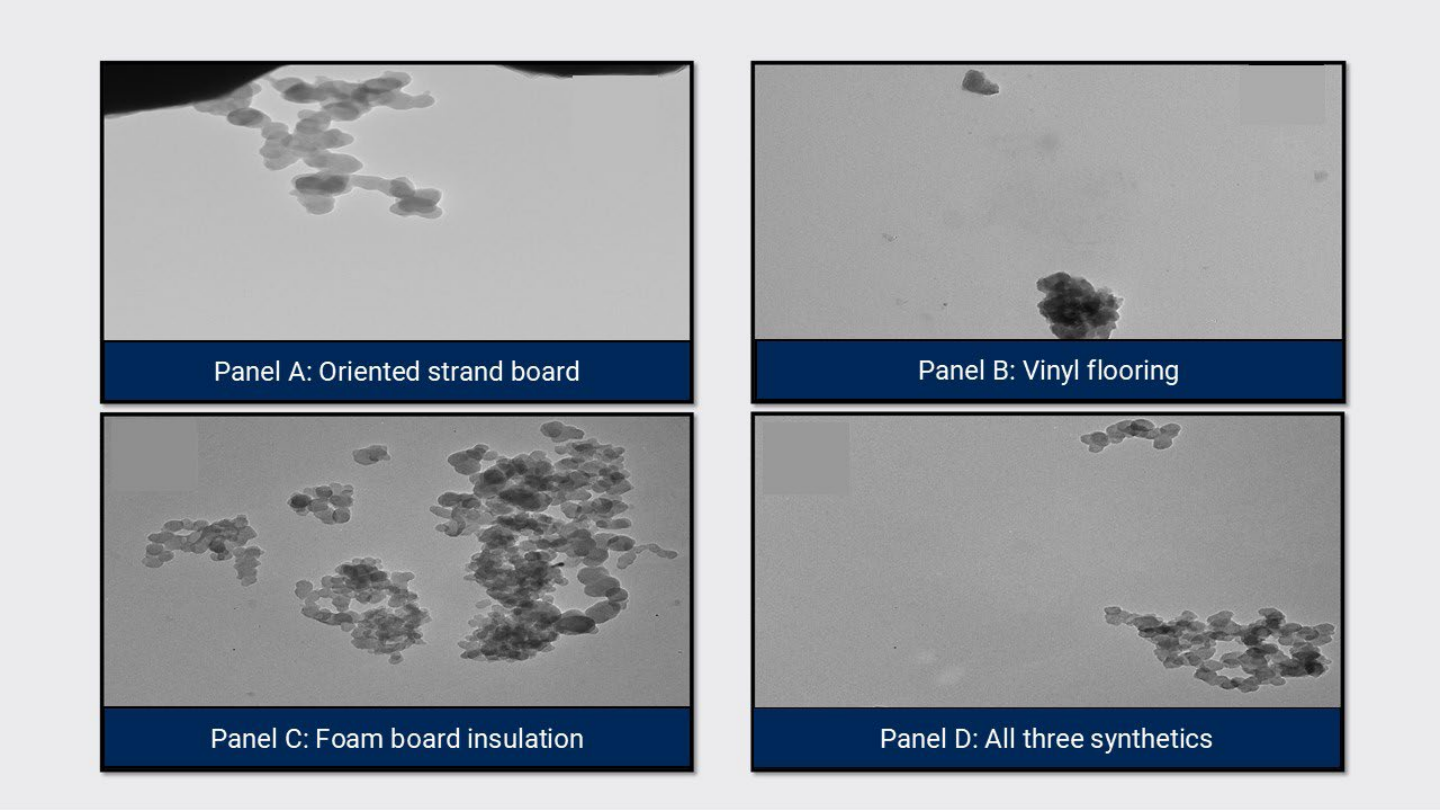

Figure 5: TEM of particles emitted when combusting Douglas fir pellets mixed with synthetic building materials.

Table 5: Chemical characterization of the pellet emissions during combustion to simulate wildland-urban interface fires.

Wood species RO – red oak, LL – loblolly pine, PP – ponderosa pine, DF – Douglas fir. For the synthetic building materials mixed with the balance wood species: OSB – oriented strand board (25%), FB – foam board insulation (3%), VF – vinyl flooring (17%), 3 – all three synthetics with same percentages as mentioned previously. For columns where more than one measurement was conducted, the values are expressed in terms of average ± standard error.

Pellet Type	CO (PPM)	NO (PPM)	CO_2 (PPM)	SO_2 (PPM)	VOC (PPM)	Acetaldehyde (µg/m³)	Acrolein (µg/m³)	Benzene (µg/m³)	Bromochloromethane (µg/m³)	Bromoflurobenzene (µg/m³)	Ethyl Benzene (µg/m³)	Formaldehyde (µg/m³)	Hexanaldehyde (µg/m³)	Styrene (µg/m³)	Toluene (µg/m³)
RO	169.1 ± 18.6	1.7 ± 0.8	10928.9 ± 1537.4	0	4.1 ± 0.5	373	BDL	BDL	BDL	BDL	BDL	1229	574	BDL	BDL
RO+OSB	165.7 ± 10.1	0.6 ± 0.2	8360.4 ± 525.5	0.7 ± 0.5	4.4 ± 0.2	169	923	BDL	BDL	BDL	BDL	405	BDL	BDL	BDL
RO+FB	252.6 ± 18.0	0.2 ± 0.1	8148.5 ± 322.2	2.7 ± 0.4	9.9 ± 2.3	2021	508	BDL	BDL	BDL	510	2077	705	241	BDL
RO+VF	240.7 ± 36.2	0.3 ± 0.2	5788.0 ± 317.1	0.0 ± 0.0	6.0 ± 2.2	447	112	89	163	BDL	113	681	156	29	BDL
RO+3	267.4 ± 22.1	0.4 ± 0.3	6087.8 ± 152.5	2.0 ± 0.3	12.0 ± 2.2	360	419	37	48	63	275	2192	292	67	46
LL	253.0 ± 26.5	0.0 ± 0.0	8048.4 ± 1120.9	4.3 ± 0.2	4.3 ± 1.0	118	211	BDL	BDL	BDL	BDL	568	359	BDL	BDL
LL+OSB	231.8 ± 36.8	0.2 ± 0.1	8137.2 ± 793.3	6.3 ± 0.4	2.5 ± 0.3	502	817	BDL	BDL	BDL	BDL	498	BDL	BDL	BDL
LL+FB	143.1 ± 2.0	0	8526.2 ± 463.9	0.0 ± 0.0	3.6 ± 0.1	802	304	BDL	BDL	BDL	319	1222	280	202	BDL
LL+VF	282.7 ± 18.1	0.6 ± 0.5	5658.4 ± 494.9	2.5 ± 0.7	4.1 ± 0.1	349	88	BDL	BDL	BDL	88	532	122	23	BDL
LL+3	230.1 ± 30.1	0.1 ± 0.0	7053.6 ± 627.2	3.7 ± 0.2	8.1 ± 1.8	456	298	127	34	45	60	648	208	47	37
PP	191.8 ± 6.6	0.2 ± 0.1	10066.7 ± 440.0	0.5 ± 0.3	3.5 ± 0.3	161	BDL	BDL	BDL	BDL	BDL	502	362	BDL	BDL
PP+OSB	201.7 ± 6.4	0.0 ± 0.0	9138.1 ± 292.6	0.3 ± 0.1	3.6 ± 0.2	116	BDL	203	BDL	BDL	BDL	477	BDL	BDL	BDL
PP+FB	197.0 ± 15.2	0.0 ± 0.0	7555.3 ± 412.0	0	8.2 ± 1.6	1983	499	BDL	BDL	BDL	403	3020	692	236	BDL
PP+VF	396.3 ± 94.3	0.2 ± 0.2	6529.1 ± 944.5	8.3 ± 2.2	10.0 ± 2.6	675	170	45	246	BDL	170	1027	235	52	BDL
PP+3	289.7 ± 63.9	0.5 ± 0.2	6373.8 ± 1487.9	4.2 ± 1.7	11.0 ± 2.8	355	414	37	48	62	183	1177	288	66	45
DF	273.8 ± 30.3	0.1 ± 0.1	6593.0 ± 180.0	1.0 ± 1.0	3.9 ± 0.4	102	BDL	BDL	BDL	BDL	BDL	318	317	BDL	BDL
DF+OSB	238.8 ± 9.1	0	8646.3 ± 807.9	0	3.5 ± 0.1	119	412	BDL	BDL	BDL	BDL	285	BDL	BDL	BDL
DF+FB	199.5 ± 7.9	0.0 ± 0.0	7229.9 ± 223.2	2.9 ± 0.4	3.8 ± 0.3	863	217	BDL	BDL	BDL	219	1314	301	103	BDL
DF+VF	408.6 ± 47.0	0.0 ± 0.0	6055.9 ± 1251.3	5.7 ± 2.2	13.0 ± 2.3	863	217	68	315	BDL	218	1301	301	26	BDL
DF+3	347.1 ± 90.7	0	5014.6 ± 1258.8	6.3 ± 1.6	13.3 ± 5.3	452	527	147	61	79	206	1498	367	84	58

4.0 Discussion

There are three major outcomes discussed in this report. First, research pellets were fabricated with wood varieties and diverse synthetic materials to simulate emissions from WUI fires. Second, these research pellets were combusted and analyzed in real time and off-line to evaluate the resultant emissions. The goal of these analyses was to characterize particles, chemicals, and metal constituents of emissions in high resolution. Third, a novel collaboration was established between WVU and CIRI scientists to increase the impact of our assessments.

Sawdust from wood species from four distinct regions of the United States were collected: the Northeast – red oak, Quercus rubra; the Southeast – loblolly pine, Pinus taeda; the Northwest – Douglas fir, Pseudotsuga menziesii; and the Southwest – ponderosa pine, Pinus ponderosa. Additionally, three widely used synthetic building materials (oriented strand board, foam board insulation, and vinyl flooring) were ground into suitable sizes for pellet formation. The percentages of synthetics added to each pellet were chosen based on maximizing synthetic amounts balanced against pellet structure integrity and preventing equipment overload. It should be noted that while the wood types are common in the indicated regions, they are not comprehensive, as other woods types are used elsewhere (e.g. yellow pine). Similarly, the synthetics used herein are not specifically representative, nor conclusive. Future studies should explore additional materials' variability and proportions.

The combustion processes developed herein were complex procedures that tended to be mutually exclusive per trial. Great effort was made to combust all pellet materials at comparable temperatures between three trials for any given pellet type. However, it should be noted that some variables were not controllable (e.g. atmospheric pressure, pellet integrity during feed to crucible, combustion patterns). Pellets were combusted at a fixed rate (~6 g/min) during each trial. The purpose of this was to ensure that at least three successful trials were performed for 30 minutes, and to be able to uniformly compare the measurement assays across the different types of pellets. For these studies, emissions were pulled from the flue. A custom 10-port manifold developed for this project allowed simultaneous sample collection for particles and/or chemicals. While it was theoretically possible to attach up to 10 pieces of sampling equipment, physical space in front of the generator system is finite. As such, there were typically four to six pieces of equipment attached during each trial.

To provide complete characterization of the combustion emissions, we segregated our analyses into particles, chemicals, and metals. The iTOX Inhalation Facility has the capacity to measure aerosols in real time to determine particle and chemical concentrations. Aerosol sampling is performed for gravimetric measures and electron microscopy. Advanced assessment of particles determined size distributions and with electron microscopy, particle morphology. Off-line chemical assessments were achieved with a water trap. This permitted chemical speciation of the emissions via GC/MS. We initially attempted traditional methods by injecting aerosols into the headspace autosampler coupled with GC/MS; however, due to the considerable instability of complex volatile chemicals present in the emissions, this could not accurately and consistently evaluate emissions. As positive controls for some materials, we directly injected materials into the air-tight headspace vial to qualitatively analyze material specific emissions on combustion. This was an effective approach for range finding and technique development.

To assess the possibility of contamination between pellet trials, we conducted "hot" (with two high wattage electrical heaters to produce a similar amount of heat without any combustion) and "cold" (air being fed into the system with the input fan and other moving parts without combustion) air sampling to evaluate residual of particles and total volatile chemicals using the CPC and TVOC 2, respectively. For both the "hot" and "cold" tests, VOC levels were extremely low and essentially in the "noise" range (0.047 and 0.031 PPM for the cold and hot test, respectively). GC/MS analysis during these tests did not identify any VOCs beyond detection limits. Surprisingly, the "hot" test resulted in nano-sized particles. However, the size distribution of these particles was very different from our typical combustion aerosols. Subsequent assessment with SEM confirmed that the heaters, themselves, released these particles when a voltage was applied. Based on these tests, we concluded that any particles and/or VOCs produced by residual residue from previous runs were negligible.

During the course of this project, it became apparent that a considerable amount of floor ash was produced by a single trial. This ash contains a mixture of emissions that did not escape the combustion chamber, agglomerates that grew and became too large to remain aerosolized, ash and non-combusted materials. For most of the trials reported herein, a sample exists in this novel "ash library." Going forward, great effort will be made to expand this "ash library" and study

these samples for several reasons. First, a respirable fraction exists in this ash. Second, if possible, to separate this fraction, a relevant emission component will be available for in vitro and analytical assays with particles directly relevant to human inhalation exposures. Third, even considered as total ash, the samples are important as third hand exposures do occur when humans come into contact with ash (e.g. inspectors, children), and it can also be used to determine impacts on the ecosystem. These floor ash samples were provided to CIRI scientists, and we plan to continue doing so on a greater scale in future experiments.

Novel and productive collaborations have been established with CIRI scientists. The most immediate result of this is unrealized potential for emissions assessments. Based on these interactions, we have customized hardware and software to sample emissions for VOCs including aldehydes and metals with cassettes, TD tubes, and DNPH cartridges. These systems are available for future studies and are capable of evolving to increase the scope and depth of the collaboration. Our regular communications with CIRI scientists to schedule, troubleshoot, discuss results, and share inputs have increased the impact of this project. It is our opinion that this foundation with CIRI scientists has increased the trajectory of this project to expand the scientific considerations for future research proposals.

5.0 Conclusion and Future Direction

Three conclusions can be made from the observations made in this project.

- First, only subtle differences in size distributions were observed among the four wood types. These differences could have been due to nominal differences in combustion, as well as the equipment used to characterize the aerosols. It is our observation that when synthetics are mixed into the raw materials, pine woods tended to press into stronger pellets. While three synthetics were effectively mixed in our pellets, it is currently unknown what the upper limit is for more synthetically diverse pellets.
- Second, a substantial amount of floor ash can be reliably and repeatedly collected in our systems. This ash is a combination of trapped emissions that agglomerated and never left the combustion chamber, and debris that bounces from the crucible and is never combusted. This ash has direct relevance to the first, second, and third hand human exposures that occur post-WUI fires. A challenge exists in separating the respirable portion of this ash for various in vitro applications. Given our technical expertise, we are confident that techniques to separate these fractions will be used in future efforts.
- Third, the duration of combustion and sampling time are variables that can influence the measured outcomes. In certain cases, samples collected were below detection limit. In others, measurements were made in real time that precluded identifying how emissions chemistry would change with distance from the source. It remains to be determined how time influences these emissions.

Future studies should take advantage of these conclusions as many questions remain, and new challenges will develop as construction and materials is ever changing. Modern buildings use more than three synthetic materials, and at varied concentrations around the country. The development of a generic “house pellet” with pine at its core, could unify modern combustion emission research. Given the unprecedented reach of modern wildfires and WUI fires, it would be critical to study the impact of time/age on house pellet combustion emissions. Finally, the resultant ashes from these pellets could be used for diverse analytical and in vitro assessments if the respiratory fraction can be effectively separated.