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Utilization of pyrolysis oil in industrial scale boilers

Kyle D. Redfern
Iowa State University

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Utilization of pyrolysis oil in industrial scale boilers

by

Kyle Redfern

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Terrence R. Meyer, Major Professor

Song-Charng Kong

Thomas Ward

Iowa State University

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ABSTRACT

The performance of pyrolysis oil in a large-scale combustion system is investigated to determine the feasibility of displacing fuel oil or natural gas in current heating and power infrastructure. A commercial 600 kW building heating boiler was installed and retrofitted to burn pyrolysis oil and pyrolysis oil mixtures at controlled conditions. The boiler was equipped with the necessary fuel systems and instrumentation to enable accurate and independent control of the pilot light, natural gas flow, and liquid fuel system parameters, while maintaining standard boiler safety cutouts. Exhaust analysis equipment was installed to allow measurements of particulate matter (PM), NO, CO, and unburned hydrocarbons (HC). Shadowgraphy spray imaging and phase-Doppler particle analysis (PDPA) was performed on non-reacting fuel sprays to investigate atomization phenomena. Ethanol was mixed with the pyrolysis oil at various concentrations and tested to determine the ideal concentration for spay and combustion performance. Combustion tests were conducted in the boiler using #2 fuel oil, natural gas, pyrolysis oil, and mixtures of ethanol and pyrolysis oil. Ethanol pyrolysis oil mixtures were primarily investigated while varying nozzles and nozzle conditions, overall equivalence ratio, and ethanol content of the mixture utilizing a natural gas pilot light and a natural gas co-fire to increase flame stability and broaden the range of stable conditions. Combustion results showed very high emissions with a pressure atomizing nozzle and low emissions with an air atomized nozzle, agreeing with spray imaging results. By optimizing atomization air pressure and equivalence ratio, PM, CO, and HC were brought down to levels near typical fuel oil combustion emissions with ethanol content as low as 20%. NO was relatively unaffected by nozzle conditions, equivalence

ratio, and ethanol content. These data show the feasibility, range of conditions, and fuel injection strategies for clean combustion of bio-oil and displacement of natural gas or fuel oil in large-scale commercial boilers.

CHAPTER 1. INTRODUCTION

1.1 Motivation

In recent years there has been growing interest in alternative energy sources to fossil fuels due to limited supply as well as environmental impact. In the United States, roughly 85% of energy consumed for transportation, heating, and industrial use comes from burning fossil fuels.[1] Pyrolysis oil offers an alternative to these fossil fuels, especially to liquids such as fuel oil. Pyrolysis oil is made from non-food-based lignocellulose biomass such as wood or corn stover. Pyrolysis oil is produced by heating the biomass to high temperatures in a reduced oxygen environment and by condensation of vapors that are released into a liquid fuel product.

Because pyrolysis oil can be transported, stored, and injected in a similar manner as fuel oil, it is a candidate for use in heating and power generation applications such as industrial boilers and home scale heating applications. However, pyrolysis oil has several properties that make it more challenging to use than fuel oil, such as its corrosive properties toward some materials, its instability, and its spray and combustion characteristics. If measures can be taken to address these challenges on new as well as retrofitted boilers, then pyrolysis oil may be a viable replacement for fuel oil for these applications.

Several studies have been conducted demonstrating the use of pyrolysis oil for a variety of applications including boilers,[31,32,33] reciprocating engines,[65,66,67] and gas turbines.[59,60,61] Work has also been conducted on spray characteristics of pyrolysis oil[44,45,46]

and single droplet combustion.[71,72,73,74,75] One promising solution to the high viscosity, low combustion stability, and low heating value of pyrolysis oil is to add ethanol, another renewable fuel. This reduces viscosity and enhances spray and combustion characteristics. Mixtures of pyrolysis oil and ethanol have been investigated,[2] but not in a large-scale boiler. In addition, thorough studies of spray, combustion, and emissions characteristics at this scale have not been conducted. The goal of this work is to investigate the feasibility and performance characteristics of a large-scale boiler while utilizing pyrolysis oil, including the evaluation of several strategies used to address the challenges associated with flame stability and emissions. In this effort, strategies that minimized changes to the current boiler infrastructure were of particular interest to maximize the potential for adoption of the proposed modifications on a commercial scale. Specific objectives are enumerated below.

1.2 Objectives

Objective 1: To demonstrate that pyrolysis oil can be successfully utilized in existing large-scale (district heating) boilers without exceeding the pollution output and while maintaining the safety standards of current technologies.

Objective 2: To investigate the challenges of utilizing pyrolysis oil with current liquid-fuel boiler infrastructure.

Objective 3: To understand spray characteristics and combustion properties of pyrolysis oil.

Objective 4: To optimize boiler and fuel nozzle design and operation for ideal combustion performance.

1.3 Dissertation Outline

Chapter 2 begins with a background on flames, sprays, nozzles, and pollutant formation in flames. This is followed by a summary of recent related works in the field of pyrolysis oil combustion. Chapter 3 describes apparatuses used for this study including the boiler and gas analyzers, as well as the spray apparatus and other fuel property measurement systems. Chapter 4 presents the results of the spray and combustion tests, as well as relevant fuel property results. Chapter 5 presents a summary of results and conclusions as well as directions for further investigation.

CHAPTER 2. LITERATURE REVIEW AND BACKGROUND

2.1 Boiler Combustion Background

Combustion is a process in which energy from fuel is released in the form of heat through exothermic oxidation reactions. The region where the reaction and the heat release take place is known as the flame zone. A flame can be characterized as fuel rich, fuel lean, or stoichiometric by the parameter λ in equation (1).

$$\lambda = \frac{\left(m_{air}/m_{fuel}\right)_{Actual}}{\left(m_{air}/m_{fuel}\right)_{Stoichiometric}} \tag{1}$$

For λ = 1, the flame is said to be stoichiometric because the mass of air is equal to the theoretical amount needed to oxidize all of the fuel. For λ < 1, the flame is said to be fuel rich, or simply "rich," and some fuel will remain in the products while all the oxidizer is consumed. Likewise, for λ > 1 the flame is said to be fuel lean, or just "lean," and all fuel will be consumed and some excess oxidizer will remain. In cases where the fuel and air are introduced separately into the combustion chamber, the value of λ locally in the flame zone is not necessarily equal to the overall λ and is dictated rather by the local mixing of the fuel and air. This is the case for most commercial boilers operating on liquid fuels, which utilize direction injection of the fuel into the combustion chamber. Most liquid-fueled combustors run overall lean or near stoichiometric because excess air is often necessary to ensure complete combustion of soot and carbon monoxide.[3] In addition, it is important to maximize

fuel consumption as it is typically the more costly reactant, and operating lean or near stoichiometric helps to ensure complete combustion of the fuel. Because most spray flames are fuel lean, it is often useful to consider a parameter known as excess air, particularly in the boiler industry. Excess air is a percentage of air beyond what is needed to combust all of the fuel. This is related to λ by equation (2).

$$Percent\ Excess\ Air = 100\% * (\lambda - 1) \qquad (2)$$

In practice and in this work, this is determined by measuring the oxygen content of the exhaust and comparing this to the oxygen content of intake air, which at atmospheric conditions is very close to 21%.[4] While lean conditions are advantageous for ensuring complete combustion of the fuel and reduced emissions, it is important to stay well above the lower flammability limit[5] locally to ensure sufficient flame stability and avoid incomplete combustion due to flame extinction. This flame extinction occurs if the heat released from combustion of a lean mixture is not be sufficient to overcome the activation energy of the incoming reactant mixture. In steady state applications, such as gas turbine combustors and boilers, the reactants and products move through a stationary flame zone, rather than the flame propagating in space. In this case, the nature of the mixing process determines whether the reactant mixture is premixed or non-premixed and locally lean or rich prior to reaching the flame zone.

2.1.1 Premixed Flames

Premixed flames occur in boilers when the liquid fuel has sufficient time to vaporize and mix with the incoming air prior to meeting the flame front. Heat released from

combustion transfers to the fresh reactants via a recirculation, causing them to reach the activation energy and combust. Flames propagate through reactants in a sheet known as a flame front. The flame front is often irregular in shape, but locally the propagation is normal to the sheet at an approximate rate known as the laminar flame speed.[6] In premixed flames the flame speed is governed by the reactivity of the fuel and the rate of heat transfer from combustion products to the upstream reactants. The composition of reactants, such as pyrolysis oil, can have a significant effect on the flame speed; for instance mixtures with lower activation energy require less heat to transfer before the flame can propagate, while mixtures with a lower heat release will have slower heat transfer because of the smaller temperature gradient, resulting in slower propagation. The ratio of oxidizer to fuel has a strong effect on flame speed with a maximum usually at stoichiometric conditions. If the flame blows out, the injected fuel will reach a premixed state within the combustor, and it is important to purge the combustor to avoid a rapid pressure rise and damage to the combustor. This is incorporated into the boiler safety system.

2.1.2 Diffusion Flames

Diffusion flames occur at interfaces between fuel and oxidizer where the mixing rate is controlled by diffusion of the two substances. In these cases, the flame propagates through mixed reactants much more quickly than reactants are added to the combustion process. As a result, the flame will be confined to a location where the fuel and oxidizer mixture is most reactive. One disadvantage of pure diffusion flames is that much of the combustion will occur in areas of the flame where there is more fuel than oxidizer locally present, or where more oxidizer than fuel is present. This can contribute to incomplete combustion and

pollutant formation. It is often useful to partially premix reactants by establishing the flame downstream of the region where the liquid fuel is introduced. In the case of air atomized nozzles, the fuel and air are in direct contact even before entering the combustion chamber, which leads to greater partial premixing. Indeed, most modern combustion processes exhibit a mixture of premixed and diffusion flame characteristics.[5]

2.1.3 Spray Flames

Liquid spray combustion is a process where a nozzle is used to atomize liquid fuel into fine droplets and mixed with a flow of oxidizer, usually air.[7] The fine droplets have a very large surface area to encourage vaporization of the fuel so that mixing will occur between the fuel and oxidizer to allow combustion. One of the main advantages of spray combustion over other types of combustors is that less volatile fuels can be effectively vaporized to sustain combustion.[8]

Two extreme models of spray combustion can be generally described as homogeneous combustion and heterogeneous combustion,[8] but most flames behave as a combination of the two. Homogeneous spray flames as described by Williams occur when fuel droplets completely vaporize before entering a flame zone. This type of combustion behaves essentially the same way as a premixed gaseous fueled flame because both reactants are in gaseous phase and are well mixed upon entering the flame zone. This model typically applies to light fuels such as gasoline, but heavier fuels can be made to behave in this way as well. When very fine atomization occurs such that droplets are around 10 μm or smaller,[6] then flames using fuels that are relatively nonvolatile, such as #2 fuel oil, can be utilized under homogeneous combustion conditions. Heterogeneous flames occur when fuel aerosols

remain present within the flame zone. In this case, combustion is best characterized as a diffusion flame surrounding each droplet. Components of the fuel droplet are evaporated and diffuse away from the liquid droplet until they meet oxidizer and combust. Often times, heavier components of the fuel are vaporized last and in some cases solids will remain, resulting in combustion at the surface of the now solid particle. This final phase of the combustion behaves like a solid fueled combustion process, similar to a coal fueled process. Heterogeneous combustion is better for describing combustion of heavy fuel oils, especially when rudimentary nozzles are used, producing relatively large droplets.

Studies performed by Onuma and Ogasawara et- al. show that in most cases droplets are fully evaporated before reaching the flame front.[9] Early studies that compared kerosene spray and propane non-premixed flames showed similar flame speed, flame structure, and emission compositions, suggesting that all fuel droplets are vaporized before reaching the flame front[9]. This result prompted further studies with heavier fuels and the results also showed evidence that the fuel is vaporized, despite the lower volatility of the heavy fuel oil.[10] Other studies have shown that sprays can behave even as premixed flames in terms of flame speed.[11] In the case of pyrolysis oil, poor atomization can lead to diffusion flames around droplets that survive into the flame, thereby affecting the total pollutant emissions.

2.1.4 Characterization of Sprays

Liquid fuel sprays have been studied extensively for combustion applications. Sprays are produced by nozzles which are specially designed to create fine droplets of fuel or other liquids depending on the application. Nozzles can be made to produce a wide variety of spray patterns and function over a variety of operating conditions. A few of the important

parameters of a spray in terms of combustion are the spray angle, the Sauter Mean Diameter (SMD), the spatial distribution, and the fuel flow rate.

Perhaps the most important, the SMD is a representation of the surface area to volume ratio of droplets produced in a spray. The SMD is defined as the diameter of a droplet which shares the overall surface area to volume ratio with that of the spray. Since sprays generally consist of droplets of a variety of diameters, the SMD is used as a way to quantify the distribution down to a single representative value[12]. The surface area of a spray has a strong effect on droplet evaporation and so it is useful to quantify sprays for flames by such a measure. This is accomplished mathematically by summing the volume of droplets and dividing by the sum area of the droplets or sample of droplets as shown in equation (3).

$$SMD = \frac{\sum nD^3}{\sum nD^2} \qquad (\textbf{3})$$

For combustion applications, a spray is generally a hollow or solid cone, depending on the design of the nozzle. Both types of cones allow fuel to be spread out across a flow of gaseous oxidizer. The spray angle of a nozzle is the angle of the cone of fluid droplets as it leaves the nozzle. A wider spray angle permits shorter combustors since the fuel does not need to travel axially a great distance before it is spread wide enough to mix with oxidizer.

2.1.5 Spray Nozzles

For proper atomization, surface tension must be overcome to turn a flow of liquid into a mist of droplets and generate substantial new surface area. The surface tension of a fuel is affected by its composition and is expected to vary depending on the pyrolysis oil mixture. The process of overcoming surface tension takes place through the use of a nozzle, and

energy must be input to do the work required to overcome this surface tension. Typically, nozzles used for combustion are either pressure atomizing or air atomized depending on the source of this energy. In this work, both types of nozzles are of interest, with the former being common for fuel oil applications and the latter being used for heavier oils.

Spray nozzles typically generate flow patterns where the fluid is formed into ligaments which ultimately break up into droplets through stretching and necking processes. When the ligaments are sufficiently long and disturbances are present, surface tension forces will act to neck narrow points of the strand until the strand is broken.[13] The elongation of ligaments is driven by inertial effects generated by the action of the nozzle, acting against the surface tension which acts to shorten the ligaments until they condense back to a single sphere. The ratio of inertial effects to surface tension is quantified by the Weber Number as shown in equation (4).

$$We = \frac{\rho v^2 D_0}{\sigma} \qquad \text{(4)}$$

The Weber number of a spray is affected by several parameters. The characteristic length (D_0) of the spray is the diameter of the ligaments or jet in the spray. The density (ρ) and the surface tension (σ) compete, so denser fluids will have higher weber numbers while fluids with stronger surface tension will have lower weber numbers given the same conditions. Since velocity (v) is a squared term, there is a strong effect from velocity. A high Weber Number spray will tend to produce more completely atomized sprays, while low Weber Number sprays may not properly break up as intended and will leave large droplets in the spray.[14]

Pressure atomizing nozzles use high pressures to do the work of breaking the fuel into droplets. The simplest style of pressure atomizing nozzle is a simple orifice which produces a high velocity jet of fuel. As the fuel jet travels from the nozzle, it is affected by aerodynamic disturbances and inertial and surface tension effects until it forms the ligaments which break up as previously described. Simple orifice nozzles can produce only very narrow spray angles and is thus limited to certain specialized applications where this is acceptable or desired.

The simplex swirl nozzle is one of the most common pressure atomizing nozzles for combustion use and is the type used, in part, for this study. A simplex swirl nozzle has a swirl chamber with tangential entrances and a single central outlet. As fuel enters, it spirals around the chamber forming a spinning hollow cylinder due to centripetal acceleration. When the inner wall of this cylinder reaches the outlet hole, it spills out retaining both an axial velocity and a tangential velocity. This forms an axially symmetric hollow cone of fuel leaving the nozzle into the combustion area. As the cone moves away from the nozzle and its diameter increases, its walls become thinner until it forms ligaments which then break into droplets. The spray angle is primarily determined by the design of the nozzle. The fuel flow rate in these nozzles is typically proportional to the square root of the pressure applied to the fuel. These nozzles work well only for relatively narrow range of fuel flow rates since a certain pressure is required to produce a fine spray, and a large increase in pressure is required to produce an increase in flow. This type of nozzle is also very sensitive to solids in the fuel since a small disturbance or blockage in the fine passageways or in the swirl chamber can disrupt the fragile swirl pattern that must match up to the outlet to produce the spray.

Air atomized nozzles are fed fuel as well as a stream of pressurized air or steam. Most of the energy used to atomize the fuel comes from the atomizing air stream. These nozzles generally do not need such a high pressure to operate properly since there is substantial energy available in pressurized gas. In this type of nozzle, the air is fed through one or more channels where is reaches a high velocity. Fuel is then fed in roughly normal to this stream where droplets are sheared off and entrained into the air flow. In the case of the air atomized nozzle used in this study, three such streams feed into a plenum surrounding a swirl chamber. The gas streams combine then enter the swirl chamber through six tangential channels, before exiting the orifice as a solid cone of fuel droplets, fuel vapor, and atomizing air. The swirling chamber both shapes the cone and encourages further mixing between the entrained fuel and air in order to produce finer, more evenly distributed droplets. Because of the way the fuel and air mix, it is necessary to have the fuel and the air at nearly the same pressure. Fuel pressure is not substantially affected by fuel flow rate so a fuel metering system must be employed. Since the atomizing energy comes primarily from the air, fuel flow can be varied all the way down to zero without sacrificing atomizing performance. The SMD is usually inversely proportional to the difference in velocity between the atomizing air and the fuel.[15] In most cases this difference is the velocity of gas, which controlled mainly by the pressure of the gas.

Since the atomizing gas is much less dense than fuel used in the pressure atomizing nozzle, passages are much larger. There is a turbulent flow pattern in the swirl chamber rather than the precise fluid cylinder of the pressure atomizing nozzle. The exit orifice is also much larger. All of these make the nozzle much more robust against clogging. Air atomized nozzles allow for a wide range of fuel flow rates because they can achieve fine atomization

for a range of fuel flow rates. However, air atomized nozzles are more costly because a source of atomizing air and a fuel flow control system are needed.

2.1.6 Flame Stabilization

In order for a flame to remain steady and ensure proper performance, it must be stabilized. Typically this means designing the combustor in such a way as to control, usually to increase, the mixing between fuel and air. Rapid mixing and turbulence as well as recirculation will have effects of both reducing emissions and providing a flame that is robust even in high throughput conditions.

One of the most common methods of flame stabilization, especially for liquid fueled heating applications, is to use an air swirler. In this style of combustor, combustion air passes through angled vanes surrounding the fuel nozzle. This causes the air to spiral outward, but also to recirculate backwards up the center axis of the flow due to the pressure gradient created by the centripetal acceleration of the spiraling flow. This flow has effects on aerodynamic breakup of the spray, but also has the effect of achieving strong turbulent mixing of the flame, increasing the flame speed drastically and creating a more robust flame by using the recirculating products to help relight incoming reactants. The recirculation can also have the effect of increasing residence time of the flame. It is known that matching and aligning the nozzle to the swirler can significantly reduce pollutants and increase flame stability.[16] As the breakup and vaporization properties of pyrolysis oil can differ substantially from fuel oil, it is of interest to evaluate the effects of the air swirler geometry on combustion performance of pyrolysis oil.

2.2 Pollutant Formation

There has been significant effort to understand and control the formation of pollutants in combustion exhaust due to their potential harmful effects. Combustion processes can produce hundreds of compounds, but trace pollutants that have been particularly targeted for study and reduction include particulate matter (PM), oxides of nitrogen (NOx), oxides of sulfur (SOx), and incomplete combustion compounds such as carbon monoxide (CO) and unburned hydrocarbons (HCs). There have also been measures to combat carbon dioxide (CO2) emissions, and of course, the use of pyrolysis oil with carbon derived from the atmosphere is one way to do this. However, it is important that the other pollutant emissions remain low during combustion of pyrolysis oil.

2.2.1 Pollutant Measurement Techniques

To analyze the amount of pollutants produced, most tests rely on instruments which draw a small sample from the exhaust stream to be analyzed for a particular pollutant species concentration. In applications like boilers, the amount of energy produced is normally proportional to the amount of fuel consumed. Since pollutant standards are normalized to energy output, the concentration levels can be compared directly, so long as excess air is accounted for in the concentration. For applications where this is not the case, the total flow rate of the exhaust gas should also be measured, and the total emissions from the test can be determined by multiplying the concentration by the flow rate. Many sensors can produce time resolved results which is particularly useful for measuring emissions when the exhaust

flow is transient, so that concentrations during times of higher exhaust flow can be more heavily weighted in the final result. Batch sampling techniques, such as those commonly used to measure PM, present a challenge since the time resolution is lost when the sample is cumulatively collected into one measurement. This can be corrected for by sampling at a flow rate proportionally to the instantaneous exhaust flow rate, such that less sample is collected at times when less exhaust is being released from the process.

2.2.2 Particulate Matter

Particulate matter (PM) is defined by the United States Environmental Protection Agency as solid and liquid aerosols present suspended in exhaust gases collected under very specific conditions.[17] These specific conditions are required to produce repeatable results since there are many constituents of PM that will evaporate or deposit onto sampling device surfaces under differing conditions. For official PM tests such as for engine certification, isokinetic sampling is required from the exhaust stream, which means that a sample is extracted from the flow without significantly changing velocity. The sample is then transported to and passed through a filter which collects PM. The tubing from the sample probe to the filter must be controlled to a specified temperature. The filter is weighed before and after the test to determine how much PM was collected during the sampling period, and this can be extrapolated to determine how much PM was produced in the entire exhaust stream. For transient operations, the sampling flow rate must be proportional to instantaneous exhaust flow rate since the measurement is a batch technique. This also has the effect of matching the sample inlet velocity to the exhaust stack velocity, maintaining isokinetic sampling.

PM usually consists of four major components including soot, ash, polycyclic aromatic hydrocarbons (PAH) and liquid hydrocarbons remaining from the fuel or other hydrocarbon sources such as lubrication oil in engines.[18] Soot is composed primarily of elemental carbon that forms as a solid during gas-phase condensation reactions of fuel constituents in the flame. Soot is typically formed in areas of a flame that are locally fuel rich. Fuels with a higher percentage of aromatic constituents are more likely to form soot, even in flames that are slightly lean overall.[19] Generally, many nucleated particles will agglomerate to form larger irregular shaped soot particles,[20] but soot particles can also continue to grow as material is deposited on their surface as the gaseous reactions continue. The black carbon content of soot causes it to act as a blackbody in terms of absorption and radiation. This is responsible for much of the coloration in flames, especially in visibly orange and yellow colored flames, and can contribute significantly to radiation heat transfer in the combustion zone of boilers. The soot concentration emitted from the process is much lower than the maximum concentration of soot found within the flame, suggesting that soot is oxidized within the flame. This effect is increased in high temperature flames with long residence times. It has been shown that the hydroxyl radical (OH) in the flame zone is primarily responsible for oxidizing the soot and is more effective than free O_2.[20] This means that soot which can escape the flame zone will not easily be oxidized despite high temperature and presence of oxygen, and so these remaining particles will likely be emitted in the process exhaust.

PAH is formed in a manner similar to soot.[20] It is produced by the polymerization of fuel constituents. PAH is usually found adsorbed onto the surface of soot particles, but is chemically different from soot. PAH tends to be present in fuels with aromatic components.

It has been shown by diluting fuel air mixtures with inert gases that PAH formation is decreased with lower temperatures in the fuel rich zones. Vigorous mixing of the fuel and oxidizer can decrease both PAH and soot production by reducing the presence of fuel rich areas within the flame, encouraging combustion of the fuel rather than heating of the fuel in fuel rich areas.

Other solid particles caused by polymerization of fuels which can contribute to PM emissions, especially in the combustion of heavy oils or pyrolysis oil, are cenospheres. Cenospheres are hollow spheres created as fuel droplets evaporate. Heavier constituents of the fuel are left at the surface of droplets as lighter constituents are boiled off. The heavier components polymerize into larger molecules and ultimately to solids. This phenomenon is more common for fuels with high viscosity. Typically the cenospheres can be in a size range that is similar to the original diameter of the drop, but may even be slightly larger due to expansion caused when the inner light components bubble and stretch the surface. These Cenospheres present mostly the same problems as other forms of PM, including being pollutants and fouling heat exchange surfaces or causing wear to moving parts, although they are much larger and therefore more likely to form deposits. Cenospheres can be burned up in the flame, but because of their solid nature their combustion rates are much slower than that of fuels which evaporate before burning.[8] Another problem with cenospheres when they reach large quantities is that their energy is not released in the flame, reducing combustion efficiency. Cenospheres can contain up to 10% of the mass of their original fuel droplet[8], which is significant from an efficiency standpoint. Fuels high in asphaltene and fuels with high viscosity have the greatest likelihood to form cenospheres, but fuels can be more precisely characterized by a Conradson carbon number test, which is a test of residue formed

by pyrolysis under specific conditions. Volatile fuels will tend to leave behind little or no residue, while heavy fuels may leave behind a coke or char which is responsible for forming cenospheres during combustion.

Ash consists of inorganic impurities in the fuel such as metals, silica, and salts which cannot be combusted in a normal flame. The primary way to reduce emissions of ash is to reduce the content of these impurities in the fuel.

Hydrocarbons in PM are simply reactants which did not completely burn. This is often caused by low combustion temperature, poor fuel atomization, or by contaminants entering the exhaust stream at a point after combustion has occurred, such as engine lube oil leaking past exhaust valve seals. Fine fuel atomization, excellent mixing of fuel and oxidizer, and high combustion temperatures are used to combat all forms of PM.

2.2.3 Oxides of Nitrogen

Nitrogen Oxides (NOx) include several gaseous phase molecules consisting of nitrogen and oxygen. There are three primary ways that NOx is formed in a flame, known in literature as Thermal NOx formation, Prompt NOx formation, and fuel bound nitrogen oxidation.[21] The latter is of particular concern for pyrolysis oil combustion because of the non-negligible amount of nitrogen bound in the oil.

Thermal NOx formation is governed by a set of equilibrium reactions known as the Zeldovich mechanism.

$$O + N_2 \rightleftharpoons NO + N \tag{5}$$

$$N + O_2 \rightleftharpoons NO + O \tag{6}$$

$$N + OH \rightleftharpoons NO + H \tag{7}$$

Diatomic nitrogen is present in oxidizing air and is the most stable of the participants in this reaction and so reaction (5) is typically the limiting reaction for the production of thermal NOx. High temperatures are required to break the strong bonds of the N_2 molecule, making thermal NOx production very dependent on flame temperature. Once the reaction has occurred and the reactants leave the flame zone, the instances of collision between NO and O or H are uncommon because O and H are radicals only found in the flame zone, so the thermal NOx in the exhaust is normally frozen at the peak thermal NOx in the flame, rather than returning to the low temperature equilibrium levels. One way to reduce the production of NOx is to decrease the peak temperatures and residence time in the flame. This is contrary to what is favorable for low PM emissions, often resulting in a trade-off between NOx and PM.

Prompt NOx is also formed through similar pathways, but the N radical that is needed for reactions (6) and (7) instead comes from the reaction between the CH radical and the N_2 molecule.

$$CH + N_2 \rightleftharpoons HCN + N \tag{8}$$

The CH radical comes directly from hydrocarbon fuel, and the N_2 again comes from the oxidizing air. The hydrocyanic acid (HCN) molecule will continue to combust but does not play a further role in prompt NOx production.

Fuel bound nitrogen oxidation occurs by nitrogen in the fuel being directly oxidized during combustion.[22] This is typically dependent primarily on the mass concentration of nitrogen in the fuel, but can also be affected by combustion conditions. This mechanism is generally not sensitive to what molecule the nitrogen is bound to in the fuel. It has been shown that rich combustion reduces the severity of fuel bound nitrogen oxidation, again contrary to conditions favorable for reducing PM. It has been shown that staged combustion can reduce fuel bound nitrogen oxidation while maintaining overall lean combustion. It has also been shown that fuel bound nitrogen can produce HCN and ammonia (NH_3) which can further react to form NOx in the exhaust. For this reason, it is desirable to have lower nitrogen contents in fuels, and this is a challenge for biomass-based fuels.

2.2.4 Oxides of Sulfur

Oxides of sulfur or SOx are composed of a variety of sulfur containing molecules primarily consisting of SO_2, SO_3, and H_2SO_4.[22] SOx emissions are usually present in their final molecular form in the fuel, and escape the process chemically unchanged. Since they are not created by flame conditions, little can be done to reduce the SOx emissions short of reducing fuel sulfur content and reducing fuel consumption. Sulfur compounds are particularly harmful to catalyzed particulate filters used on modern diesel engines, leading to rapid catalyst degradation. Heavy petroleum distillate fuels can contain up to 7% sulfur compounds. Biofuels including pyrolysis oil tend to have very low sulfur content, and so they produce very little SOx in comparison to petroleum based fuels.[23] This is a potential advantage for the use of pyrolysis oil in commercial scale boilers.

2.2.5 Carbon Monoxide and Hydrocarbons

Carbon monoxide (CO) and gaseous phase hydrocarbons (HC) are incomplete combustion products.[5] Carbon monoxide is commonly produced in large quantities during rich combustion, in which there is not enough oxygen available to fully combust carbon to CO_2. CO is present in all combustion flames as an intermediate between reactants and products and its production and destruction are considered kinetically controlled reactions. CO is normally combusted into CO_2, but if the flame is rapidly cooled, equilibrium reactions may fail to reach the normally very low equilibrium concentrations expected in the exhaust, resulting in higher CO emissions. Competing reactions can also consume radicals responsible for combusting CO, thereby increasing residual CO in the exhaust. Gaseous hydrocarbons can exit flames under similar conditions to CO, if the flame is quenched or if poor mixing occurs such that the hydrocarbons are not fully combusted. Gaseous-phase hydrocarbons are separate from PM in that they are gaseous under sampling conditions, making their measurement similar to that of other gaseous species. Both CO and HC emissions are reduced by maintaining a well-mixed, lean combustion process at sufficiently high temperatures and residence times to yield complete combustion. While these design characteristics are desirable for reducing PM, they are not ideal for minimizing NOx.

2.3 Fast Pyrolysis Process

Fast Pyrolysis is the process of heating biomass feedstock in a low oxygen environment to decompose the organic material into vapors, aerosols, and char. The vapors

are separated into fractions via staged cooling and condensation. . The pyrolysis oil produced has a much greater density than raw biomass, making it more practical as a fuel in terms of storage and transportation.[24,25] Gaseous and solid fractions can be combusted, in part, to provide heat for the process, or they can be utilized for other applications. The solid fraction, known as bio-char, is rich in nutrients and can be used as a fertilizer for soil. This can potentially replace nutrients removed from the field through growing plants for biomass production.[25,26,27] The reuse of less desired feedstock components to provide heat can reduce or eliminate the need for external energy input to the process. The fast pyrolysis process is usually adjusted to maximize liquid fuel production by controlling the heating temperature and residence time. The temperatures used for fast pyrolysis are 450-650 °C, and the residence time is typically around two seconds.[28] The liquid yield can be as high as 75% of the biomass feedstock.[25] The process is compatible with a wide variety of cellulose biomass feedstocks such as corn stover, which represents the largest share of cellulose biomass feedstock production in the U.S.[25,29]

2.4 Liquid Fuel Properties

There are several properties of liquid fuels that can affect performance in combustion applications. Energy content or higher heating value (HHV) is important because it determines how much mass of the fuel must be produced, stored, transported, and consumed in order to meet a given heat demand. High fuel energy density is desirable for storage and transportation since more mass of fuel can fit in the same vessel.[25] Properties such as viscosity, surface tension, and volatility affect atomization in combustion sprays, which can

have effects on combustion performance. Chemical properties of fuels must be considered because system components that come into contact with the fuel must be chemically compatible with the fuel.

2.4.1 Properties of Pyrolysis Oil

Pyrolysis oil can have a range of properties depending on feedstock and the process used to produce it. The density is typically around 1200 g/ccm. Pyrolysis oil is significantly more dense than petroleum derived fuel oils (by 20-30%). The HHV for pyrolysis oil can be up to 19 MJ/kg, compared to most petroleum fuel oils which are near 44 MJ/kg. This low energy content can be partially attributed to the high water content of pyrolysis oil ranging from 15-35 wt%. Pyrolysis oil also contains oxygenated components which tend to have lower energy content than hydrocarbons. However, because of its high density, the HHV of pyrolysis oil is about 50% that of petroleum fuel oil on a volumetric basis.

The viscosity can have a very wide range depending on conditions during the production and the fraction selection method, but the most desirable fuel samples for spray atomization tend to have lower viscosity, as low as 15cP.[24,30] This is more viscous that #2 fuel oil, but less viscous than #6 fuel oil at room temperature, however #6 fuel oil is typically heated before spraying to reduce viscosity and improve atomization characteristics. Attempts have been made to produce nozzles that are optimized for the viscosity range of pyrolysis oil.[31,32,33]

Pyrolysis oil is corrosive to many materials because of its low pH and its strong solvent components. Whetted components must be made from stainless steel or polymers compatible with pyrolysis oil such as polypropylene, polyethylene or polytetraflouroethylene

(PTFE). Metals such as aluminum, non-stainless steel, and several kinds of rubber are quickly damaged by contact with pyrolysis oil, resulting in leaking or failure of the parts. Solid constituents in pyrolysis oil can agglomerate in small passages such as those in nozzles, causing clogs. Many researchers have found it difficult to remove solids from pyrolysis oil by filtering in its raw form.[34,35,36]

Oasmaa et- al. has studied fuel properties of pyrolysis oil extensively and has determined that a few characteristics are most important in the product for it to be used as a fuel.[37,38,39,40] These properties are flash point, tendency to separate, water content, solid content, and homogeneity. Solid content is most important with regard to clogging. Water content was shown to increase the flashpoint while lowering heating value and decreasing stability, but had beneficial thinning effects on viscosity. Flash point is a critical property for both material hazard status as well as fuel combustion properties. Flash point measurements are a challenge when the flash point is greater than the boiling point of water since water has a tendency to leave the sample before the test.[41] A desirable property of fuel is to resist separation to ensure consistent performance from run to run and from beginning of a tank to the end. Pyrolysis oil has been shown to become more viscous as it ages and separates.

2.4.2 Properties of Pyrolysis Oil Mixtures with Ethanol

Pyrolysis oil is miscible with ethanol. The addition of ethanol to pyrolysis oil can substantially improve the combustion performance of the solution by acting in several ways. Ethanol can substantially reduce the viscosity of the solution, which allows better atomization through conventional spray nozzles. Ethanol can also accelerate filtering processes by lowering viscosity. Adding ethanol contributes to a higher volatile content in

the solution.[42] The low boiling point of ethanol within droplets may further contribute to

droplet breakup when the more volatile components of the fuel droplet boil within the droplet

during the combustion process, contributing to a phenomenon known as micro-explosions.[43]

Micro-explosions can be present in any liquid fuel composed of components with different

boiling points.

2.5 Spray Studies of Pyrolysis Oil

Several studies have been conducted targeting sprays of pyrolysis oil[44,45,46] and

emulsions of pyrolysis oil with other liquids. These studies seek to quantify the spray

characteristics of pyrolysis oil when compared to conventional fuels to better understand the

atomization process for combustion applications. Several of these have shown that pyrolysis

oil sprays can be attained that are fine enough to be used for combustion. Current work does

not show spatial distributions of droplets or visual characteristics of pyrolysis oil sprays.

Sauter mean diameter (SMD) is one of the most important parameters to quantify spray

quality.

Garcia-Perez et al. has published work focused on droplet breakup, studying such

parameters as SMD and nozzle volumetric flowrate characteristics.[44] Conventional pressure

atomizing nozzles were used with vacuum produced pyrolysis oil from softwood bark. SMD

was measured using a Malvern Master-sizer 2600 Series Particle Sizer. It was shown that the

pyrolysis oil behaved as expected from other Newtonian fluids. Sprays were produced with

droplets as fine as 50 μm SMD, comparable to many fuel oil sprays in modern applications.[44]

Many conditions produced droplets as large are 150 μm which require longer residence times

to fully burn out. It was shown that the flow rate of fuel through the nozzles was governed by a square root function of the pressure drop across the nozzle, as is true of conventional Newtonian fluids for this kind of nozzle.[12]

Chiaramonte et al. has investigated the SMD of pyrolysis oil as well as fuel oil, water, and emulsions of fuel oil and pyrolysis oil.[46] Fiber Optic Quasi Elastic Light Scattering was used to determine SMD. This technique as applied does not provide a visualization of the spray. A variety of existing Delevan nozzles were used in this study. This study showed it was possible to attain reasonable SMD with pyrolysis oil using conventional pressure atomizing nozzles.

Weimer et al. performed spray tests on surrogates of pyrolysis oil, but did not use pyrolysis oil itself. The surrogate fuel was a mixture of water and glycol with similar spray properties to pyrolysis oil through an air atomized nozzle. Measurement techniques included Laser Doppler Anemometry (LDA), Particle Image Velicometry (PIV), and Phase Doppler Particle Analysis (PDPA). Results and findings were limited, but it was shown that SMD was affected by the fuel-to-atomizing air ratio in the nozzle, which is not predicted by the idealized model of the air atomized nozzle, where SMD is solely dependent on velocity difference between fuel and air at the point of mixing.

Overall, detailed studies of sprays utilizing ethanol mixed with pyrolysis oil are lacking, especially with air atomized nozzles. In addition, spray visualization and phase-Doppler particle analysis (PDPA) of droplet sizes and velocities is generally lacking for pyrolysis oil sprays.

2.6 Combustion Studies in Swirl Stabilized Combustors for Heating

Several studies have been performed on the combustion of pyrolysis oil and pyrolysis oil mixtures in swirl stabilized combustors, which are the most common style of combustor for heating and stationary power generation applications. These are summarized below.

2.6.1 Combustion Studies of Pyrolysis Oil in Swirl Stabilized Combustors

Pyrolysis oil has been studied as a potential alternative fuel for several applications including home scale heating,[47] and industrial scale boilers larger than 200 kW.[31,32,33,34,35,40,48,49,50,51,52,53] Applications of pyrolysis oil for industrial boilers have often used fuel heating to reduce viscosity and improve spray performance, as is typical with heavy fuel oil. Many of these investigators faced challenges under some conditions with pyrolysis oil polymerizing in the nozzle (coking) or otherwise forming clogs.[32,33,34,35,36,47,48,49,51] Most of these combustors were started on pilot fuels before being switched to pyrolysis oil.[31,32,33,34,35,36,48,49,50,51,52]

Several studies have been able to successfully use pressure atomized nozzles on industrial boiler scales.[34,35,48,50] Gust et al. used a standard pressure atomized nozzle for combustion but was unable to match the droplet size distribution of light fuel oil even when running heated pyrolysis oil at higher than standard fuel pressures.[34,35]

Studies using air atomized nozzles have also been successful in burning pyrolysis oil. Shihadeh et al. found that steam atomization had less problems with fuel coking when compared to air atomization.[36] Van De Kamp et al. found that coking could still occur when

using steam at low flow rates.[33,51] Preto et al. compared a commercially available steam atomization nozzle for heavy fuel oil to a custom designed steam atomization nozzle originally developed for spraying water-coal slurries. The heavy fuel oil nozzle allowed droplets to persist through the combustion zone until they landed in the bottom of the combustor, while the water-coal slurry nozzle allowed complete combustion of the pyrolysis oil droplets.[32] Investigators who used custom nozzles had better results with the custom nozzle than with commercial nozzles.[31,32,33]

Flame stability was also an issue for these tests and some studies took additional measures to improve stability. Kyto et al. implemented an enhanced swirler to generate stronger swirl in order to stabilize the flame.[48] Gust et al. and Oasmaa et al. experimented with radiant devices designed to put more energy back into the flame and into the spray to improve stability with some success.[34,35,49] Pollutant emissions were also studied and in most cases the results were compared with typical results for the light or heavy fuel oil that the pyrolysis oil would replace. Generally, CO emissions were found to be slightly higher for pyrolysis oil than for light fuel oil,[31,33,36,51,54] but some studies found substantially higher CO,[49,53] while Gust et al. found that CO levels were nearly the same for both fuels.[34,35] NOx was also generally found to be slightly higher for pyrolysis oil than for light fuel oil.[31,34,35,36,49,54] Oasmaa et al. found that NOx was lower for pyrolysis oil than for heavy fuel oil.[49] Van De Kamp et al. found that NOx was higher for pyrolysis oil than light fuel oil for the same combustion conditions, but that substantial reduction in NOx could be achieved through staged combustion, indicating that fuel bound nitrogen oxidation was a major contributor.[33,51] PM was found to be higher for pyrolysis oil than for light fuel oil for all of these studies, and much higher for most.[31,34,35,36,48,49,50,54] Rossi et al. found that PM levels

from pyrolysis oil were lower than for heavy fuel oil,[50] but Van De Kamp et al. and Oasmaa et al. found that PM was higher than heavy fuel oil.[33,49,51] SOx was measured in only a few of these studies because it is well known that SOx emissions are directly related to fuel sulfur content which is low for biomass fuels. Huffman et al. and Rossi et al. confirmed low SOx emissions from pyrolysis oil.[31,50,54]

Wissmiller et al. conducted research regarding combustion of pyrolysis oil in a home heating scale swirl stabilized combustor.[47] The experimental setup included optical accessibility for several in-situ measurements including flame luminosity measurements and planar laser measurements such as Planar Laser Induced Incandescence (PLII), Planar Laser Induced Fluorescence (PLIF) and Mie Scattering inside the combustor. Gaseous emissions including HC, NOx, and CO were quantified as well as PM. Scanning electron microscope images of PM samples show that PM consisted of primarily cenospheres rather than typical soot agglomerations. Air atomized nozzles showed significant advantage over pressure atomizing nozzles for reducing PM. Other parameters such as combustion air preheating, fuel water content, and fuel fixed carbon content did not show significant effects on emission performance. This study focused primarily on combustion of pyrolysis oil and did not include mixtures of ethanol. The heat rates in these studies did not exceed 30 kW.

2.6.2 Combustion Studies of Pyrolysis Oil Mixtures with Ethanol in Swirl Stabilized Combustors

Pyrolysis oil solutions with ethanol are desirable because the properties of the solution are substantially changed from those of pure pyrolysis oil.[42,43] Advantages include a

reduction in viscosity and increase in volatility, as well as other potential phenomena which may improve combustion performance.

Tzanetakis et al. has recently investigated the combustion of pyrolysis oil and ethanol solutions in swirl stabilized combustors.[42,55,56] These investigations were carried out in a burner sized for a 10 kW flame. A mixture of 80% pyrolysis oil and 20% ethanol was used and other parameters were investigated as means of minimizing emissions and achieving good flame stability. It was found that PM consisted of mostly cenospheres and ash, although cenospheres were largely eliminated under ideal conditions.[56] It was found that high amounts of atomization air were very important to achieving good atomization and combustion, while swirl air helped flame stability. Air and fuel preheat were also utilized to reduce CO and HC emissions. NOx levels were attributed primarily to fuel-bound nitrogen oxidation.[56] The results of this study demonstrate an investigation of relatively small-scale applications for pyrolysis oil ethanol mixtures.

Stamatov et al. has published work on pyrolysis oil and pyrolysis oil mixed with ethanol for use in home heating scale burners.[57,58] NOx emissions were studied in particular and it was found that NOx levels were higher than predicted by thermal NOx models, but that NOx could be reduced by mixing pyrolysis oil with ethanol. Ethanol had the effect of decreasing the radiant heat flux from the flame which is important for some heat exchangers, but is less important for heat exchangers that rely on convection. These studies did not report findings for PM.

Moloodi et al. completed a MS dissertation studying the combustion of pyrolysis oil mixtures with ethanol in a lab scale swirl stabilized combustor.[2] This study found that CO and HC emissions were reduced with the addition of ethanol and that flame stability

increased with ethanol concentration. The study also investigated the sources of PM including ash. These findings are important, but there are differences between lab scale studies and practical applications in existing real world equipment.

2.7 Combustion Studies of Pyrolysis Oil in Gas Turbines

Some studies have been carried out using pyrolysis oil for gas turbines.[59,60,61,62,63,64] Like works in boilers, these studies have utilized fuel heating to reduce the viscosity of pyrolysis oil to improve spray characteristics. These studies also used a pilot fuel to start up before switching to pyrolysis oil. Gas turbines present additional challenges over boilers due to the high performance turbine blades moving in the exhaust. This is particularly a problem for particulates which may strike the blades at high speed forming deposits and corrosion.

Andrews et al. carried out tests on an Orenda GT2500, 2500 kWe turbine with an experimental dual-fuel nozzle designed to improve spray quality. They found that deposits formed on many of the combustion surfaces, including turbine blades.[59,60,61] It was found that these deposits could be removed by running conventional fuels in the turbine, but corrosion had occurred on the turbine blades, even in the relatively short duration of the tests.

Strenzoik et al. performed similar tests on a Deutz T216 75kWe gas turbine.[62] They were not able to sustain operation with pure pyrolysis oil, but instead used a dual-fuel nozzle to co-burn light fuel oil with pyrolysis oil. They also noted that deposits formed in the combustion area and on the turbine blades but were unable to remove the deposits by switching fuels. NOx, HC, and CO data were collected showing slightly increased CO and

HC and slightly decreased NOx compared to light fuel oil. It was also shown that turndown ratio could not match that of light fuel oil.[62]

These studies indicate that is it typical to rely on combustion enhancement with conventional fuels in industrial scale combustion devices, if not through mixing then through dual-fuel strategies.

2.8 Combustion Studies of Pyrolysis Oil in Reciprocating Engines

Several studies have been done on pyrolysis oil for use in reciprocating engines.[65,66,67,68,69,70] This is desirable since a large portion of the world's energy consumption is in the form of transportation fuels burned in reciprocating engines. These studies have all been for compression ignition diesel engines because pyrolysis oil is more similar to diesel fuel than to gasoline in terms of volatility. Common problems involved the corrosive nature of the fuel and clogging by the solid components in pyrolysis oil. Clogging is particularly an issue with the very fine passages in diesel fuel injectors as compared to lower pressure, higher flow nozzles found in boilers and gas turbine applications.

Solantausta et al. ran a stationary high speed diesel engine on pyrolysis oil.[66] A pilot injection of light fuel oil was used to ensure reliable ignition. Significant wear resulted in the fuel pump and fuel injector in a short time. The results of emissions tests showed increased CO production, but they were able to successfully reduce CO to normal levels by using a commercially available catalytic converter.

Shihadeh et al. was able to burn pyrolysis oil in a diesel engine and quantify parameters such as ignition delay and heat release rate which are studied for conventional

fuels in order to optimize engine operation. Shihadeh found that there was a longer ignition delay with pyrolysis oil and that ignition was less reliable with pyrolysis oil. In order to combat the ignition reliability, preheated combustion air was utilized, which increased the robustness of ignition of pyrolysis oil. It was also determined that the heat release rate was lower for pyrolysis oil than for diesel fuel and this was attributed to slower combustion kinematics than that of diesel fuel.[68] As #2 fuel oil very similar to diesel fuel, it is anticipated that longer ignition delay and lower heat release rate may pose similar challenges for when replacing fuel oil with pyrolysis oil in boilers. In the current work, it is hoped that mixing with ethanol can help to alleviate these challenges.

2.9 Single Droplet Combustion Studies

Several important studies have been carried out characterizing the evaporation and combustion processes of a single droplet of pyrolysis oil.[71][72][73][74][75] These studies have focused on how PM is formed, as well as observing other phenomena such as micro-explosions that can be better understood to enhance combustion performance. Several of these single droplet combustion tests place a droplet onto a thermocouple so that the temperature of the droplet can be measured throughout the combustion event.[71,72]

D'Alessio et al. utilized high speed optical measurement of combustion of droplets in a temperature controlled furnace. Simultaneous temperature measurements indicate stages of evaporation as light components are boiled out of the droplet before heavy components boil. This results in observed micro-explosions which eject some mass from the droplet, but do not

completely destroy the droplet. As components boil away, they reach air and react with a flame.[72]

Shaddix et al. carried out single droplet studies on a variety of fuels examining the effects of additives such as methanol and the presence of water on the burnout time of droplets.[74] This study showed that methanol did not have as strong of an effect on droplet burnout time as water, but that water would cause further delayed microexplosions which were more effective at shortening droplet burnout time.[74] This study also considered the effects of bio-char content in the fuel on droplet burnout time.

These studies show the potential benefits of utilizing ethanol in pyrolysis oil to enhance droplet break up without significantly reducing droplet burn-out time. However, it is difficult to relate single droplet studies with the realistic boiler combustion environment.

CHAPTER 3. EXPERIMENTAL SETUP

The purpose of this investigation is to characterize and understand pyrolysis oil combustion for use in existing industrial boilers, and to understand what accommodations must be made to substitute pyrolysis oil for conventional fuels. A commercial boiler was installed in order to facilitate combustion testing with pyrolysis oil, and modifications were made to various systems to study effects on the combustion performance of pyrolysis oil. The boiler was fitted with exhaust gas analyzers that are typically used for industrial fuel oil boilers to quantify combustion performance from an emissions standpoint.

Fuel properties tests are also a crucial part of understanding pyrolysis oil combustion. In this study, parameters such as viscosity and volatility are examined, as well as simulated aging tests for stability. Samples were tested for higher heating value and Thermo-Gravimetric Analysis (TGA) was performed to determine fuel composition.

Fuel sprays are a critical part of pyrolysis oil combustion performance. Spray nozzles were installed in a non-combustion apparatus and the sprays were studied using shadowgraphy and a Phase-Doppler Particle Analyzer (PDPA). These sprays used the same nozzles used in combustion tests and used both surrogate fuels and pyrolysis oil ethanol mixtures.

3.1 Boiler Combustion Rig

For this study, a building heating boiler was provided for use by the State of Iowa Capitol Complex to investigate the combustion of pyrolysis oil. The boiler could not be

installed into a steam load since there was no accommodation at the facility to incorporate the boiler into the facility steam system. However, this should not affect the evaluation of combustion performance. The fuel system was largely replaced to accommodate both pressure and air atomized nozzles for pyrolysis oil. Other modifications, described below, were also made to better accommodate pyrolysis oil and to study the effects of operating parameters.

3.1.1 Boiler

The boiler used in this study is a Burnham 4F-240 three-pass boiler. This boiler is rated for up to 60 BHP, which equivalent to about 600 kW heat rate. The boiler was originally installed to burn natural gas to heat a building within the State of Iowa Capitol Complex. This model of boiler is normally sold configured for either liquid or gaseous fuel. In this case, many of the components for operation for liquid fuel were never installed because the unit was sold configured for natural gas. In addition, when the boiler was uninstalled from its original location, many of the systems were disabled.

The three-pass design employed a combustion chamber as the first pass. Gases traveling from the combustion chamber loop around to a set of fire tubes, which constitutes the second pass. The gases reverse direction one more time into a second set of fire tubes to make the third pass. These fire tubes are submerged in water to maximize heat transfer from the gas to the water chamber. The water chamber also surrounds the combustion chamber to further increase the heat transfer area and to reduce heat lost to the boiler room.

Several systems had to be brought back up to operation when the boiler was installed for this study. The control system had to be reinstalled and all of the safety cutouts had to be

checked and brought back to operation. In addition, since the boiler had never been configured to burn liquid fuels, a few new components had to be installed including a liquid fuel nozzle and the rest of the experimental fuel system.

3.1.2 Installation of the Boiler at Iowa State University

Boilers rely on a system of supporting equipment to operate properly to provide the needed heat to the building. At the very least a normal boiler system requires electrical power, feed water, steam line, radiators in the buildings, and fuel. Electrical power needed for the main fan and for control systems and pumps was readily available, but the rest of these accommodations could not be provided since there was not actually a building radiator system to heat during the tests.

3.1.2.1 Water handling system

The water side of a boiler normally operates as a closed loop, where water is boiled into steam in the water chamber of the boiler and exits to the steam pipe. It then travels to radiators in the buildings, and after the energy is extracted, it returns to liquid phase. It then travels back to the boiler as water, typically driven by some kind of a pump and control system to maintain a near constant level of water in the boiler and radiators. New water must be let into the system when the water returning from the radiators does not match the amount of water leaving the boiler as steam due to leaks or other effects. This system will involve water treatment to remove contaminants from the water which could lead to corrosion and

deposits. Normally this closed loop operates under pressure of up to 15 psig for a low-pressure boiler, as used here.

In this installation, there was no demand for steam, so the conventional method of sending steam to the radiators and receiving water from them was not feasible. Instead, steam was vented at atmospheric pressure out of a tube through the roof of the building alongside of the combustion exhaust tube. This water leaving the system was made up for with tap water, filtered to reduce sediment. This was less than ideal as dissolved contaminants could still get through the water filter, but for the low number of test hours required from this boiler this was not an issue. Another slight drawback of this setup was that the boiling point of the water was lowered without the steam pressure. Between atmospheric pressure and 15 psig, the boiling point of water changes by 21°C. This was not considered as a problem for this combustion study since the temperature change of 21°C is small compared to the large temperature difference between the flame temperature and the boiling temperature on the water side. The water feed was controlled by a solenoid valve which was triggered by the high level switch of one of the low water safety cutout switches, so that when the water level fell below full, the water was turned on and water from the tap flowed into the boiler. Since the water coming in was not heated, this may have led to cooler areas in the water side of the boiler, although this was assumed not to affect combustion. Furthermore, steam output from the boiler was not observed to change with the cycling of the fill water flow, indicating this did not have a significant effect on heat flux.

3.1.2.2 Control system modifications

For the purposes of the combustion study, it was necessary to make several modifications in order to gain independent control of combustion parameters of the boiler, while leaving safety measures operational. Safety systems on this boiler include an air purge cycle before startup, a flame detector to shut down fuel in the event of flame blowout, and low water cutoffs.

The control unit normally controls when the inlet air fan powers on and off, as well as all fuel valves including the natural gas pilot and ignition transformer. It is also normally responsible for adjusting firing rate to match heat demand. This authority normally allows it to fully control procedures such as the pre-combustion purge cycle and the safety cutout, as well as to adjust both fuel and air flow to match firing rate demand. In the current setup, solenoid valves were placed in all fuel lines, including newly installed liquid fuel lines, to ensure that the controller maintained the authority to shut off fuel if a problem was detected. Under normal operation, an actuator controlled by the control unit mechanically operates a damper to control air flow, while a butterfly valve controls the main flow of natural gas. Pilot natural gas flow is normally controlled by an orifice nozzle. For the current experiments, it was necessary to have direct control over fuel flow parameters while leaving the control unit capable of operating solenoid valves for safety, as discussed later in Section 3.1.2.3 Fuel system.

Airflow is one of the main parameters that must be controlled for combustion tests. The damper which is normally used to control airflow was still used, but it was disconnected from the actuator and connected to a fixed bracket to allow the damper to be set to specific repeatable settings. These settings were calibrated by measuring airflow with a hot wire

anemometer in the exhaust outlet during fan tests without fuel. The results of this calibration can be found in Appendix A.

During preliminary tests, the standard ultraviolet flame detector triggered some false alarms, failing to detect the pyrolysis oil flame even when the flame had not blown out. The control unit would then shut off fuel and indicate a flame blowout. This was difficult to diagnose because after each instance of failure to detect flame, the flame was extinguished by the fuel shutoff. Fortunately there is a grace period of several seconds when the flame detector loses signal before triggering the alarm to safeguard against false alarms caused by a flicker. Flame was observed through the viewing port during this grace period, indicating that the flame detector was falsely identifying a flame blowout. To remedy the problem, an alternate infrared flame detector was installed and caused no further issues.

3.1.2.3 Fuel system

It was necessary to construct a fuel system which would allow independent control of main combustion natural gas, pilot natural gas, and liquid fuel nozzle parameters. Different systems were needed to accommodate pressure atomized nozzles and air atomized nozzles due to the differing pressure and flow characteristics of these kinds of nozzles. Pyrolysis oil is challenging to measure and control because of its corrosive nature and because of its inconsistent viscosity and other properties.

Normally, the natural gas is metered by the control unit through the use of solenoid valves, orifices, and actuator-controlled butterfly valves. Solenoid valves provide a positive shutoff but cannot regulate the flow rate, while the butterfly valve does not positively seal but can be adjusted to produce different flow rates. In the main natural gas flow, these valves are

normally used in series to vary the natural gas flow from zero to the desired load. The pilot flame circuit for natural gas is normally regulated by a solenoid valve and a fixed orifice, since the pilot light does not need to accommodate turndown.

In the setup used for this investigation, the natural gas entered the facility at a relatively high pressure compared to the design pressure for the butterfly valve, so the main natural gas flow rate and that of the pilot flame was controlled by rotameters with large pressure drops in the needle valves built into the units. The pilot light was needed for many combustion conditions, even when the control unit no longer called for it. Simply bypassing the pilot solenoid valve would not allow the controller to properly use the pilot light in the startup sequence or to disable the pilot in the event of a flame blowout. A system was implemented as shown in Figure 1.
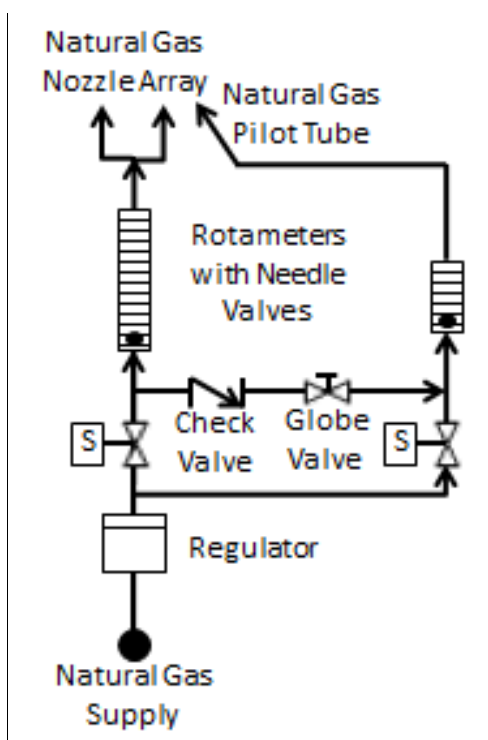
Figure 1: Natural gas schematic.

A bypass with a check valve and a manual globe valve was placed between the main natural gas line and the pilot rotameter in order to supply the pilot light with gas when either the pilot or main natural gas solenoids were open. This still allows the pilot light to be disabled when both solenoid valves are closed, or when the manual globe valve is closed and the pilot solenoid is closed by the control unit.

To quantify pyrolysis oil fuel flow, which could not easily be measured directly, an automotive wideband oxygen sensor was installed in the exhaust duct. The oxygen sensor is an Innovate Motorsports MTX-L Wideband O_2 Sensor. This sensor was capable of indicating the overall λ value anywhere from rich conditions through very lean conditions with a resolution of ± 0.01. With the air flow rate known from the damper calibration, the λ value was used to determine and adjust the fuel flow rate. Since natural gas flow rates were measured by the rotameters, they could be subtracted from the overall fuel flow equation to determine how much liquid fuel was consumed. Controlling fuel flow rate manually, the λ value could be maintained at $\pm 5\%$. Finer control was usually not attainable due variations in the uniformity of the pyrolysis oil, which caused the flow rate through the controlling system to drift slightly.

To supply fuel to pressure atomized nozzles, it was necessary to pressurize the fuel to 100 psi or higher. Pumps compatible with the viscosity and chemical properties of pyrolysis oil for these pressure ranges are costly and may not offer consistent performance for combustion tests. Instead, liquid fuels were placed into sealed stainless steel containers which could be pressurized with nitrogen gas from a compressed gas cylinder. The pressure forced the fuel through the lines and valves up to the nozzle and into the combustion chamber. Pressure atomizing nozzles generally have a fuel flow rate controlled by fuel

pressure and nozzle design, so controlling the pressure controlled the flow. Nitrogen was used for pressurizing the fuel so that there was no risk of combustion occurring inside the tank. A single nitrogen line was used to pressurize multiple tanks to the same pressure, allowing for switching from one tank to another rapidly via T-valves in order to switch from one fuel to another.

A similar setup was used at a much lower pressure to supply fuel to the air atomized nozzle, but the flow had to be controlled with a separate needle valve because unlike for pressure atomizing nozzles, the fuel flow rate for air atomized nozzles is not a well-behaved function of fuel pressure. The same pressure tanks were used, but a stainless steel needle valve was placed before the nozzle and adjusted manually to control the fuel flow rate based on the real-time oxygen sensor readings. The fuel tank pressure was set above the intended atomization air pressure so that fuel would be driven toward the nozzle and air would not propagate from the nozzle to the fuel tank. Atomization air was provided through a pressure regulator by a shop air line from the facility. The pressure regulator was used to adjust the atomizing pressure.

3.1.2.4 Fuel pump

It was desirable to investigate the feasibility of using pyrolysis oil in a conventional pump, since the pressurized tank system is not suitable for continuous operation. In order to test feasibility with current technologies, a commercial fuel pump designed for heavy fuel oil was implemented in place of the pressurized tank system. The pump produced a constant fuel flow, which was relieved through a pressure release valve into a bypass stream which circulated back to the original fuel tank, as consistent with the intended operation. The flow

could be adjusted by changing the relief valve settings or by adjusting a needle valve in the fuel line. This setup allowed the pump to operate at full bypass if there were a nozzle clog or if the fuel cutout valve was closed in an emergency without causing excessive back pressure. The pump was wired in series with the blower fan, so it also ran during the startup and purge sequences, but fuel was simply routed back to the tank.

The fuel pump also produced atomizing air, by drawing air in from the room through an inlet filter/silencer. This side of the pump was lubricated with a flow of motor oil from another reservoir. Atomizing air became laden with oil droplets in the pump, so it was routed back to the reservoir where it was passed through steel wool screens which captured oil droplets from the air to be recirculated. Air left this chamber through another hose which led to the air atomized nozzle. A stopcock was placed at the top of the chamber to vent some of the atomization air to adjust the atomizing air pressure. This entire system was plumbed consistently with installation instructions for the pump as it was designed to be used on heavy fuel boilers.

The pump was able to operate in this way for 3-4 weeks of testing before problems began to arise. Ultimately this was probably only a few hours of operation over the course of this time, but the whetted parts were exposed to pyrolysis oil nearly the entire time. Ultimately, the pump was again replaced with the tank system when the airflow output began to degrade and it would no longer maintain atomization air pressure for the desired conditions. It is not clear what the cause was for this degradation. It is possible that the pyrolysis oil may have damaged the pump through its corrosive or abrasive properties, or failed to provide adequate lubrication during operation. There may also have been unintended deviation from proper maintenance or priming procedures which could have

caused damage as well. It does not appear that the mechanical seals of the pump ever failed because no pyrolysis oil was found to leak from the shaft seal or between the air and fuel systems. The oil in the air pump system maintained its level and did not appear to be contaminated with pyrolysis oil. The pump proved too costly to replace or investigate further when the tank system enabled adequate performance.

3.1.2.5 Fuel nozzles

Fuel nozzles included both pressure atomized and air atomized nozzles provided by Delevan. The pressure atomized nozzles used in these tests were Delevan WDA pressure atomizing simplex swirl nozzles. These nozzles are sized with a rated fuel flow rate for fuels at 100 psi, however they can operate at many different pressures with flow rate varying approximately with the square root of pressure for low-viscosity fluids and at moderate flow velocities. The pressure atomized nozzles utilized in this work produce a hollow cone with a design spray angle of 70°. The air atomized nozzle tested was a Delevan AIRO nozzle, rated for a range of flows up to 60 gph. The conditions tested with this nozzle were well below the maximum flow capabilities of the nozzle, but with air atomized nozzles, the quality of atomization is controlled by the air pressure and is decoupled from the fuel flow rate, allowing for a very wide turndown ratio. This style of nozzle produces a solid cone, with angle varying slightly depending on conditions. The two nozzles are pictured in Figure 2.
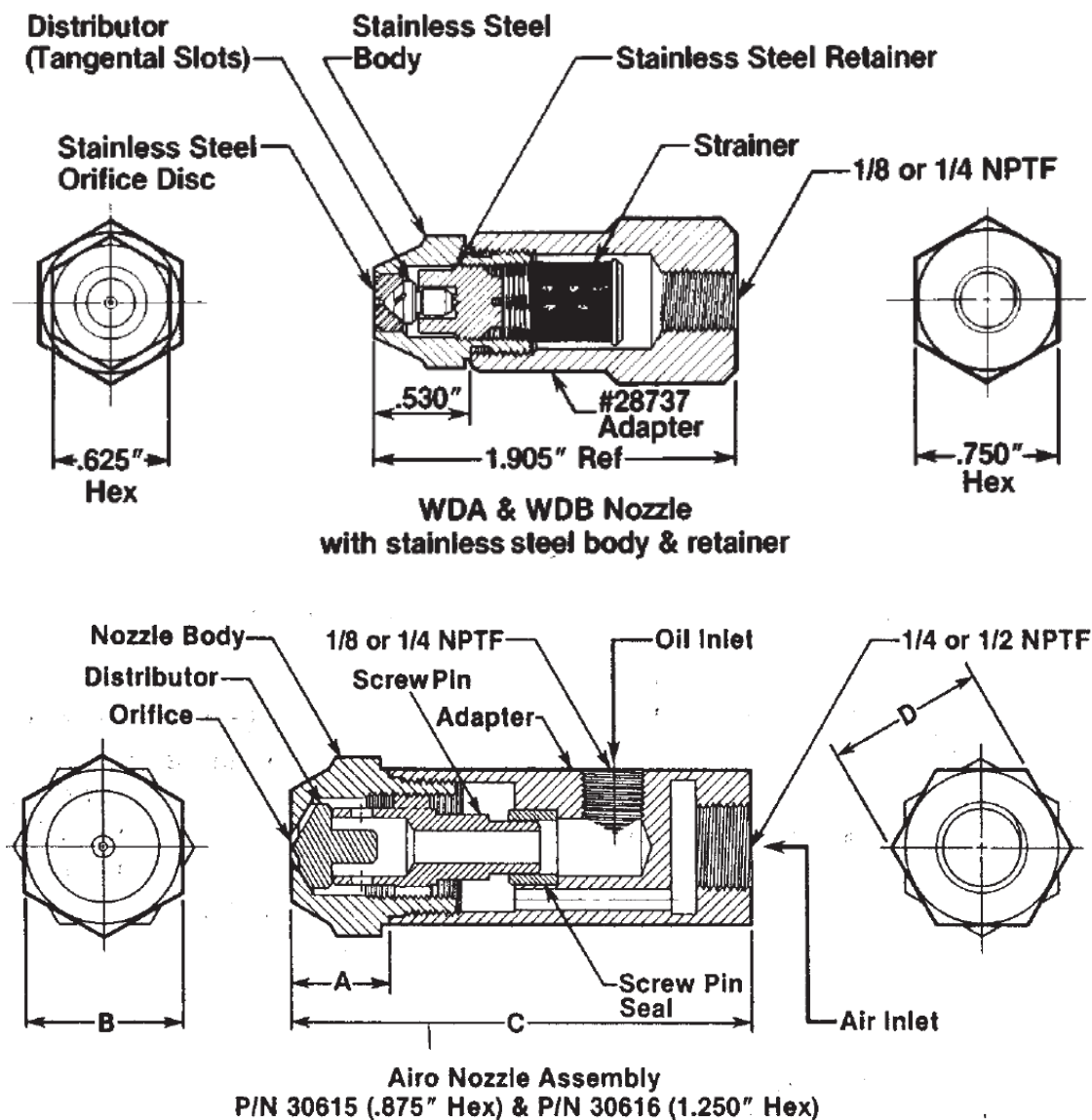
Figure 2: Delevan WDA pressure atomizing nozzle (top) and AIRO nozzle (bottom).[76]

3.1.2.6 Modified swirler

Previous studies have demonstrated improved performance of pyrolysis oil combustion by modifying the construction of the swirler. For this study, a replacement swirler was fabricated that has more pronounced swirl vanes and a greater effective flow area. Effective flow area measurements and other information, including pictures of the

swirler, can be found in Appendix C. The new swirler fits as a direct replacement part so that either swirler can be easily substituted for different test conditions.

3.1.3 Exhaust Analysis Equipment

One of the objectives of this study is to ensure that pyrolysis oil emissions levels can be competitive with fuel oil emissions levels. The emissions measured include PM, CO, NOx and HCs. Samples are taken from the exhaust gas and analyzed by instruments specialized for each of these species. These samples are taken from the vertical section of the exhaust stack about three feet above the exit of the heat exchanger. It is assumed that exhaust gases are well mixed after passing through all three passes of the boiler.

3.1.3.1 PM analyzer

PM was measured by an AVL 415 which is designed to measure black carbon soot. A sampling probe was installed in the exhaust stack at the sampling point according to recommendations in the AVL 415 operators manual. During each measurement, it takes a fixed volume sample of exhaust gas from the sampling probe through a temperature controlled sample train, passing the sample through a white filter paper. The instrument then moves the filter paper onto an apparatus which shines light onto the paper and measures the reflectance of the paper. The amount of soot collected on the paper is related to the amount of light absorbed. A correlation has been developed by AVL between sample volume, reflectance, and PM levels. From reflectance, a number known as Filter Smoke Number (FSN) is produced, and from this number the software calculates a concentration of soot in

mg/m^3. FSN can indicate the level of loading on the filter paper, which can indicate whether a larger or smaller sample volume is needed for subsequent tests and ensure that the filter loading is in a range that can be accurately correlated by the algorithm. These samples were taken in triplicate for each measurement point to provide insight into the variability and precision of the measurement. This algorithm was developed for PM generated by fuel oil, so it may not be an exact correlation to PM produced by pyrolysis oil. Because all results are reported with the same method, this serves as at least a relative measurement.

3.1.3.2 Gaseous analyzer

Gaseous emissions such as CO, HC, and NOx are typically measured on industrial boilers only when they are installed and serviced. These emissions are minimized to ensure that the boiler is operating properly. Because of this, it is typical in the industry to utilize portable gaseous analyzers that boiler service technicians use during boiler visits. The instruments used were two IMR 1400 units, one for NO and the other for CO and HC, which were available from the same supplier used by the personnel that serviced boilers at the Capitol Complex. These gas analyzers measure the concentration of pollutants as well as the concentrations of O_2 and CO_2 to determine a corrected pollutant concentration. This concentration is normalized to the fuel consumption, correcting for the diluting effect of excess air on pollutant concentration. The corrected values are used in this study to normalize readings between conditions that have dissimilar equivalence ratios, so that more lean conditions are properly compared to less lean conditions without bias due to simple air dilution of the emissions. The measurement of O_2 also serves as a redundant measurement to

verify the λ value reported by the wideband O_2 sensor and used for determining the fuel flow rate.

The sampling procedures for gases are less rigorous than PM because gases do not have a tendency to deposit on surfaces or change phase with temperature. Gases also do not tend to separate based on inertial effects because of the very low density and strong propensity to diffuse to a uniform composition across a volume of gas. Because of this, it is only necessary to ensure the gas is well mixed before sampling; in this case, isokinetic sampling is not important. The sample for gaseous species is taken from near the PM sample point, but slightly closer to the boiler because the AVL 415 utilizes a purge cycle where shop air is introduced into the exhaust stream. By sampling upstream of the PM probe, the possibility of sample dilution by purge air is avoided.

3.2 Fuel Property Measurements

Several measurements were collected to quantify fuel properties and determine what is responsible for the combustion performance observed in the boiler. These tests were performed for samples of pyrolysis oil and on mixtures with ethanol using specialized equipment. The viscosity of solutions with respect to ethanol concentration was measured with a viscometer. Higher Heating Value (HHV) of samples was measured using a bomb calorimeter. Thermo-gravimetric Analysis (TGA) was used to quantify constituents of samples by boiling point. The Ried vapor pressure test was applied to pyrolysis oil and mixtures with limited success.

3.2.1 Sample Preparation

The pyrolysis oil used for this study was made from pine derived cellulose biomass. This sample was left over from a much larger scale test and was in storage for roughly 4 years before it was used in this study. This could cause it to differ slightly from a newly made sample, due to the potential aging effects of pyrolysis oil, but it was assumed that this would not be a problem so long as the sample was well mixed.

This type of fuel study requires repeatable fuel sample compositions that can yield stable results. There were several obstacles in reaching this type of performance which were overcome using a variety of strategies. Pyrolysis oil was supplied to Iowa State University in the form of a single 350 gallon container, containing about 250 gallons initially upon arrival, creating several practical problems of dealing with such a large single container in a lab setting. Samples had to be prepared in small batches mixed to the right ethanol content. Furthermore, particulates in the pyrolysis oil are sporadic in nature and tend to cause clogs in a manner that is highly disruptive to testing, if not managed.

To deal with such a large container of pyrolysis oil, several processes were developed. To help pull consistent samples from the container, the container was stirred before use with a large paint mixer on a power drill. This mixer had to be modified to fit through the relatively small opening of the container, but proved to be the best option for mixing such a large container. The mixer had a long shaft which was capable of reaching near the bottom of the tank and had angled blades to encourage vertical movement of the fluid, specifically to mix heavier components from the bottom of the tank with lighter components at the top. Despite this mixing, a small variation between samples persisted.

To extract a manageable sample from the tank following mixing, several techniques were employed. A metal manual pump was used to extract one set of samples, but the pyrolysis oil attacked the pump during the time before the next use, so it was replaced with a polyethylene pump, which proved to be chemically resistant. As larger volumes were needed for more tests, the manual pumping of the thick liquid proved quite demanding and a siphon system was developed to allow gravity to do the work. A thick hose was attached to a spigot at the bottom of the tank and routed to the basement below, so that a sample would flow freely when the spigot was opened.

Mixing ethanol with pyrolysis oil is a relatively straightforward process, since ethanol is miscible with pyrolysis oil. Ethanol was measured into a 7 gallon jug using a 1 liter flask, then the jug was filled to a marking representing the final volume. This jug was manageable enough to shake vigorously to ensure uniform mixing between the ethanol and pyrolysis oil.

Several methods were used to prevent interruptions due to clogs, especially in the nozzles. Inline filters were employed, but the capacity for collecting solids was low, requiring frequent servicing and interrupting tests when the inline filters had filled with particles. They were also limited in pressure or flow rate. It was determined that the best method would be to filter the pyrolysis oil mixture after mixing with ethanol using disposable polypropylene felt filter bags rated for 100 micron particle size. The ethanol lowered the viscosity, increasing the rate of filtering. This was usually completed within a few days before running a test condition.

3.2.2 Viscosity Measurement

The viscosity of several liquid samples were measured using a Brookfield DVII+ viscometer. The samples included pyrolysis-oil/ethanol mixtures and several other oils which would later be used as surrogate liquids for spray testing. The apparatus includes a sample cup which holds the sample and has a known diameter and volume. A rotor is suspended from above this cup such that the end of the rotor with a calibrated shape is submerged in the sample in the cup. When the rotor is turned at a known rate, it creates a film of known thickness between the rotor and the walls of the cup based on Taylor-Couette flow. The rotor is turned at a known rate by a stepper motor which allows very precise control of angular velocity. Reaction torque on the motor is measured, enabling calculation of the stress of the fluid in the Taylor-Couette flow. These measurements allow for calculation of strain rate as well as stress in the fluid, so a stress vs. strain rate relationship can be quantified to extract viscosity. The rotation speed can be varied to determine if viscosity measurements are affected by strain rate, indicating if the fluid is Newtonian or Non-Newtonian over the strain rate regimes tested. To improve the quality of the measurements, the sample is temperature controlled by circulating water through a water jacket around the sample cup at a range of temperatures from room temperature and above. This is necessary because many fluids change viscosity substantially with temperature. Before placing samples into the viscometer, the samples are thoroughly mixed with a vortex mixer to ensure that the sample is representative of the contents of the sample container.

3.2.3 Thermogravimetric Analysis

Several samples were prepared for composition testing using thermo-gravimetric analysis (TGA). The instrument used was the Mettler Toledo TGA/DSC 1 thermogravimetric analyzer operated under procedures specified by ASTM D5142. A small crucible is cleaned and pre-weighed for each sample. Each sample for each measurement, roughly 100 mg, is put into the pre-weighed crucible and the crucible is loaded into the instrument. Again, the vortex mixer is used before extracting the sample from the sample container. When the sample is loaded, the weight of the crucible is entered by the operator and is assigned to the sample. The instrument is capable of holding multiple samples simultaneously and feeding them through the measurement chamber one at a time to maximize utilization of the instrument. When a sample is queued, it is moved by the instrument into the measurement chamber which is temperature controlled and has a sensitive scale to continually monitor the weight of the sample over the course of the test. The temperature of the chamber is slowly raised from room temperature to a pre-selected final temperature over the course of 30 minutes or more. At the end of the test oxygen is introduced to the chamber to burn off any remaining combustible hydrocarbons such as bio-char. The weight is recorded as various constituents of the sample evaporate and are vented away from the sample. The mass vs. temperature profile of the sample can be used to quantify constituents based on their boiling points. The distribution can be divided into four main areas including water content, volatiles, fixed carbon, and ash. Indicated water content will also include substances such as ethanol that have boiling points lower than water. Volatiles are considered any substances which evaporate above 105 C during the test, up to

the final temperature. When oxygen is introduced, remaining fixed carbon is removed by combustion, leaving only ash.

3.2.4 Higher Heating Value

To determine the energy content of a fuel, the best method is to burn a sample in a calibrated, well-insulated, sealed combustion chamber known as a bomb calorimeter. The particular unit used for this study is the Parr 1341 Oxygen Bomb Calorimeter operated under procedures specified by ASTM D240. This instrument also has a sensitive temperature measurement probe to measure the temperature of the chamber before and after combusting the sample. A sample is weighed and put into a crucible, since higher heating value is an intrinsic value. The sample size is divided out, so the sample size is not important so long as enough energy is released to be accurately analyzed. The vortex mixer is again used to ensure a representative sample. The amount of energy released in the test is the same as the heat capacity of the sample times the temperature change. There is an igniter system which puts a known amount of electrical energy into a wire in the combustion chamber. A cotton thread is placed on this heated wire and also contacts the sample in order to initiate combustion when the test is started. The heat from the wire and thread can be subtracted from the total heat easily because of the uniform heat input by these from run to run. There is also a system for metering oxygen into the sample volume to combust the sample, because the oxygen must be let in slowly during and after ignition to avoid violent reactions that could splatter the sample.

3.2.5 Aging Study

There has been some concern that pyrolysis oil is not stable over time, especially in regard to formation of solid precipitates containing fixed carbon. This test was created to assess whether or not ethanol mixtures with pyrolysis oil would have different stability performance than pure pyrolysis oil for the current tests. A series of sample mixtures were prepared in 50 ml containers to undergo the aging test. The test was carried out under elevated temperatures for a relatively short time of 30 minutes, in order to accelerate any aging phenomena so that the study could be completed in a timely manner while capturing possible conditions during storage and delivery of the fuel to the combustion chamber. To help validate this method, several different temperatures were selected including one set 'aged' at room temperature for a relative measure. These sets were aged by placing the sealed sample tubes into a large beaker of water on a hot plate as shown in Figure 3. The temperature of the water was controlled by a PID controller cycling the hot plate on and off based on a thermocouple suspended by a ring stand to keep it from touching the bottom or sides of the beaker. It was assumed that over the course of each test, the samples quickly reached the water temperature do to the intimate thermal contact between the water and the tubes. After aging, the samples were sent to the TGA to be analyzed, with fixed carbon being of particular interest as a product of aging.
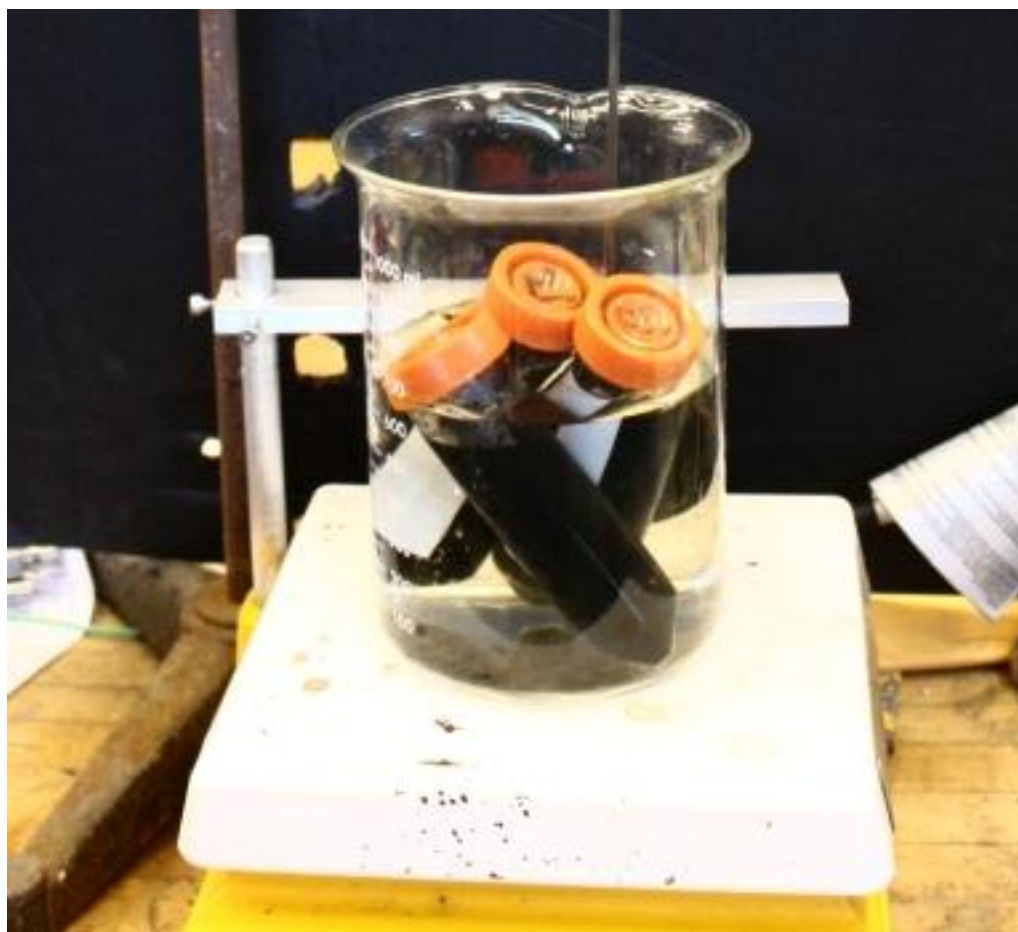
Figure 3 Pyrolysis oil mixed with ethanol in aging setup.

3.3 Nozzle Spray Testing

One of the biggest challenges of utilizing pyrolysis oil is producing an adequate spray comparable to typical fuel oil sprays. This portion of the study is intended to further investigate the effects of different spray nozzles and nozzle operating parameters and to study spray phenomena of pyrolysis oil mixtures. A spray chamber with optical access not intended for combustion was constructed to study the sprays. Surrogate fuels also were

examined to see if properties of pyrolysis oil could be matched by other liquids to help isolate properties of pyrolysis oil that are particularly important to sprays.

3.3.1 Spray Chamber

To perform optical diagnostics on the sprays, an optically accessible chamber was created. These measurements were not possible inside the combustion chamber because the walls of the chamber are opaque except for a few small sight glass windows that are often obscured by condensation or contaminated with particulates during combustion tests. Optical access ports were added by cutting holes in the chamber where needed. As pyrolysis oil mixtures with the current sprays could not sustain combustion without a continuous pilot flame, it was determine that the chamber could consist of an inexpensive, polyethylene open container.

3.3.2 Mist Handling System

Sprays created by nozzles will tend to spread to outside their intended areas if measures are not taken to prevent this. This is a particular problem with optics near the open ports of the spray chamber. To prevent droplets from leaving the optical access ports of the chamber, a mist handling system was employed. This system utilized a fan, a filter element, a settling chamber, and some ducting to create a very slight negative pressure inside the spray chamber. Droplet laden air in the spray chamber travels through a flexible duct into a large settling chamber where some droplets settle. Air is pulled out of this chamber through a filter element by the fan and directed out of the facility through a spark-resistant exhaust

hood. The filter is to help remove droplets that may not have settled to reduce fouling in the hood and contamination of the lab by any gas that escapes from the exhaust hood system.

3.3.3 Shadowgraphy Setup

To obtain useful images of the spray, the image must be frozen in time to resolve droplets and structures. This was done by using a diffuse strobe backlight and a long exposure on a digital camera. An etched glass diffuser was placed behind one of the optical ports, as shown in

Figure 4, with the strobe light placed to illuminate the diffuser to create the pulsed backlight. A translucent ruler was placed inside the chamber through another port and illuminated with a white paper diffuser to provide a scale. The camera was held on the opposite side of the chamber so that the spray and nozzle were illuminated by the backlight as shown in Figure 5. The nozzle and camera were adjusted to show just the tip of the nozzle to maximize the amount of the spray visible in the pictures. The strobe was set to 2 Hz and the camera shutter was set to 0.35 s exposure to avoid the possibility of double exposures. Many pictures were taken and occasionally the 0.35 s shutter would fall completely between two strobe flashes, resulting in a black picture that was discarded. This was not a problem as most of the pictures captured a single flash, so there were enough images for the study.
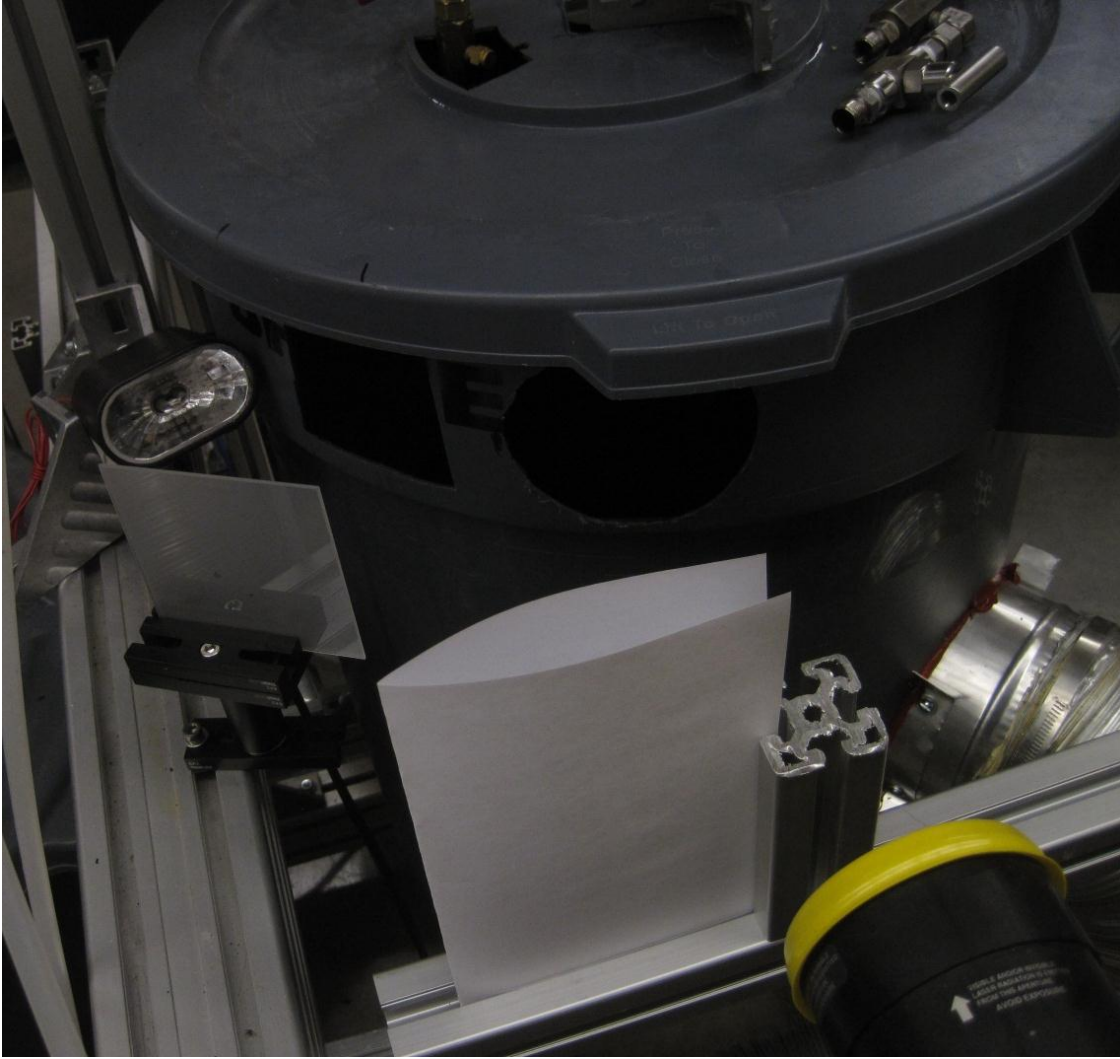
Figure 4: Side view of setup for Shadowgraphy.
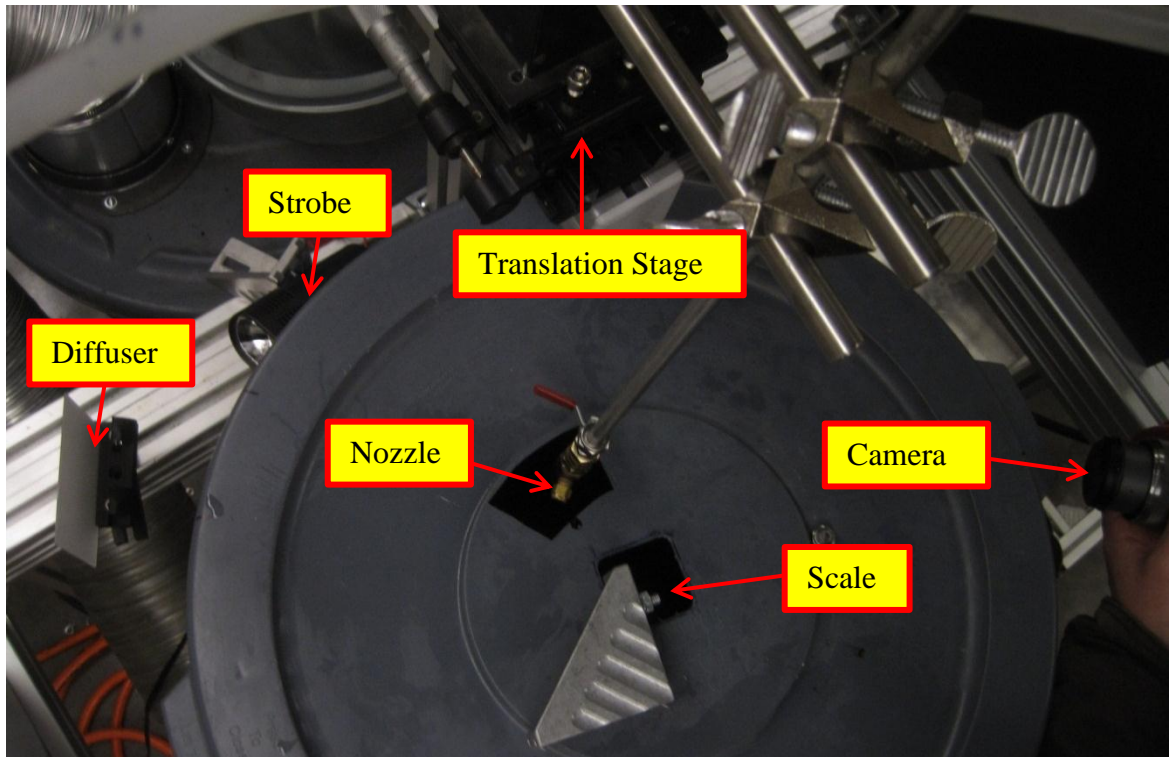
Figure 5: Spray test setup for shadowgraphy.

3.3.4 PDPA Setup

The TSI Phase Doppler Particle Analyzer (PDPA) is an optical point measurement system capable of measuring particle size and velocity in a variety of aerosols using a measurement technique known as Phase Doppler Interferometry. The instrument uses a laser source and a detector. The laser source focuses 4 beams onto a very small measurement volume, which is located within the spray. Only 2 beams are needed to measure droplet size and velocity in one component direction based on scattering pattern created by droplets passing through light and dark regions within the fringe patterned created at the crossing point of the 2 beams. The use of 4 beams allows velocity measurements in two component directions as well as redundant droplet size measurements using the size of the fringe patterns created by each pair of beams and projected from the droplets to the detector. The detector is

placed at a location 150 degrees from the source to optimize the amount of light reflected from the measurement volume by droplets that pass through. The size range that can be measured using this system is ~1 μm to ~200 μm. Round holes in the spray chamber match the lenses on the source and detector to provide optical access to the spray near the center of the chamber. The nozzle can be translated to probe different parts of the spray without disturbing the alignment of the PDPA system.

CHAPTER 4. RESULTS

4.1 Fuel Property Tests

Several properties of fuels can affect atomization and combustion performance. Tests were conducted to measure properties including viscosity, higher heating value (HHV), Ried vapor pressure, fuel stability, and thermo-gravimetric analysis (TGA). The viscosity results showed that viscosity is reduced from 165 cP to near 40 cP by mixing only 20% ethanol by volume with pyrolysis oil. The HHV testing of samples of various mixtures of pyrolysis oil and ethanol showed a slight increase in energy content with the addition of ethanol, as predicted by direct replacement. TGA of mixtures showed an increase in moisture readings, due to the fact that ethanol evaporates in a similar temperature regime to water. There is a corresponding change in quantity of volatiles, ash, and fixed carbon proportional to the amount of pyrolysis oil in each sample. The Ried vapor pressure test is a test to measure the volatility of a fuel, but is normally used for refined fuels such as gasoline. For the mixtures tested, the final readings were the same as the value of the lightest component of the mixture. Full fuel properties and aging test results can be found in Appendix C.

4.1.1 Viscosity Results

Viscosity is one of the important parameters for fuel spray nozzle performance, particularly for pressure atomizing nozzles. The viscosity tests were selected to quantify the viscosity effects of mixing ethanol into pyrolysis oil, as well as measuring viscosity of some

other liquids that can be used as more readily available surrogate fluids for spray testing. Figure 6 shows the results for mixtures of ethanol and pyrolysis oil, as well as viscosity results for canola oil and soybean oil, which are inexpensive fluids widely available for spray testing.
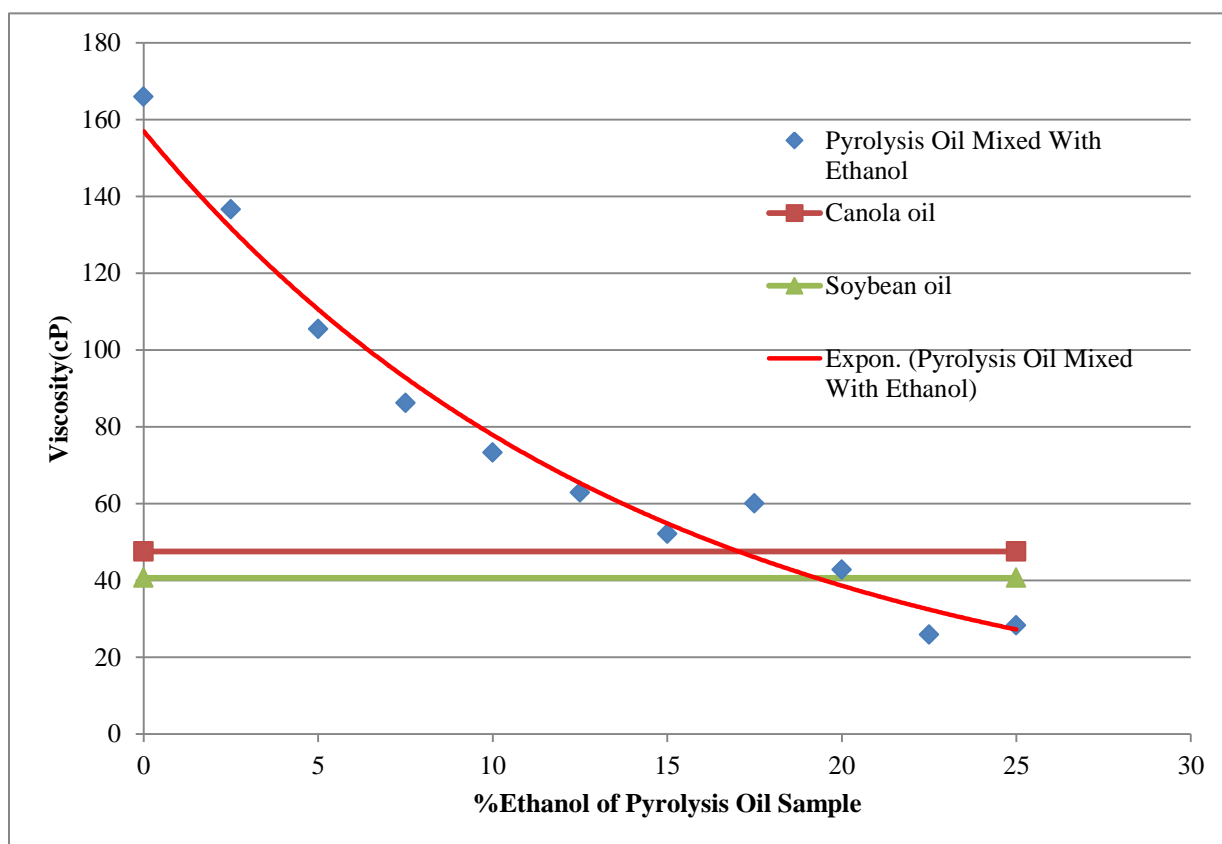
Figure 6: Viscosity of fuels at 30°C.

A temperature of 30°C was selected because this is a representative temperature for fuel that is sprayed without heat addition other than viscous effects from the pumping system and heat conduction from the flame. An exponential fit follows the trend of viscosity with respect to percent ethanol content. Points at 17.5% and 22.5% ethanol do not follow the trend as closely, but this is likely due to variation in sample composition, despite careful mixing intended to produce consistent samples. This result shows a significant decrease in

viscosity with the addition of only 20% ethanol. Indeed, in subsequent combustion tests, this allowed delivery of the pyrolysis oil without fuel preheating and instantaneous start-up of the boiler with a 20% ethanol mixture, which is a substantial benefit operationally. It is desirable to have as much pyrolysis oil in the mixture as possible while maintaining acceptable fuel properties to minimize the amount of other resources needed to make pyrolysis oil feasible. In this study, only a single shear rate was used. This does not provide information about whether or not the fluid behaves as a Newtonian fluid for very high and very low shear rates. This has been investigated by others who have found that pyrolysis oil does not behave as a Newtonian fluid in some circumstances.[47]

Also apparent in Fig. 6 is that the similar viscosity of soybean and canola oil with 20% ethanol in pyrolysis oil allows them to be utilized as surrogate oils for extracting qualitative features of the ethanol/pyrolysis-oil mixtures for a variety of operating conditions.

4.2 Spray Test Results

Spray testing was carried out in the spray chamber separate from the combustor so that optical techniques could be used to investigate the sprays produced using pressure atomized and air atomized nozzles for both actual fuels and surrogate fuels. This is an important step in understanding fuel droplet atomization and nozzle performance and can yield insight into combustion performance.

4.2.1 Shadowgraphy Results

Shadowgraphy was used to visualize sprays of interest for the study. While it is difficult to extract meaningful quantitative information from these images, it is possible to make qualitative observations about nozzle performance that are relevant for understanding differences in combustion behavior.

4.2.1.1 Air atomized nozzle performance

Water was used to examine the air atomized nozzle's performance with a low viscosity fluid and the possible effects of varying atomizing pressure.

Figure 7: Water spray with atomizing air at 25 psi (left) and 35 psi (right).

The images shown in Figure 7 compare two sprays of water, representing typical pressure conditions for this nozzle. Because atomization pressure is high enough in both conditions, there are relatively few large droplets or ligament structures in either spray, especially at downstream locations.

Canola oil was used as a surrogate fuel with similar viscosity to 20% ethanol pyrolysis oil mixture, as is shown in the viscosity measurement section. Canola oil also has a similar surface tension to pyrolysis oil,[47] making this a more useful surrogate.

Figure 8: Canola oil spray with atomizing air at 25 psi (left) and 35 psi (right).

The canola oil sprays shown in Figure 8 show two sprays at less ideal conditions. The spray with 25 psi atomization air shows a higher concentration of larger droplets and structures, which will lead to problems vaporizing in a combustion spray. With atomization air pressure increased to 35psi, this non-ideal behavior appears to be significantly reduced. This indicates that there is potential for a change in spray behavior to occur within this pressure range. It can be reasonably expected that these results may also apply at a similar pressure regime to the ethanol pyrolysis oil mixture because of the similar surface tension and viscosity.
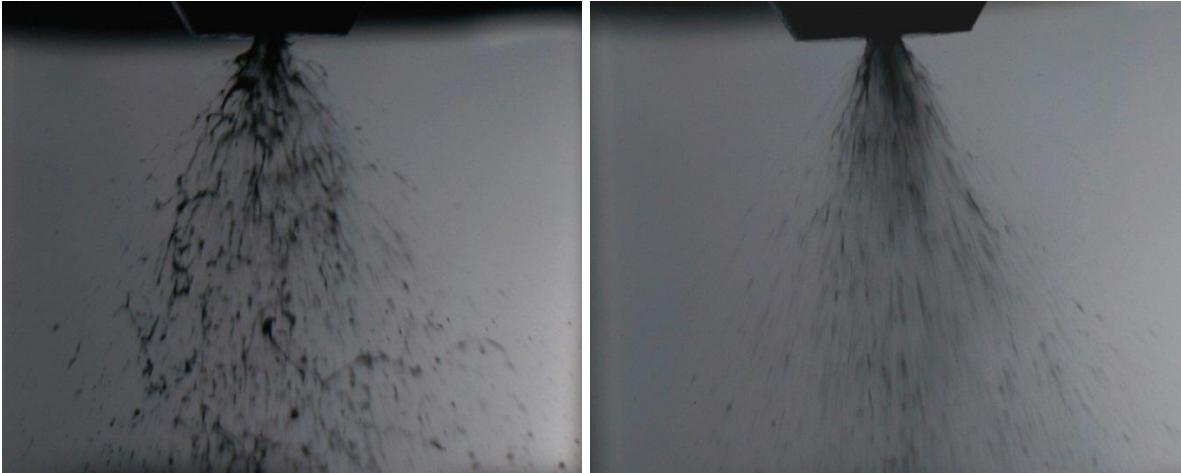
Figure 9: 20% ethanol in pyrolysis oil mixture with atomizing air at 25 psi (left) and 35 psi (right).

When the 20% ethanol in pyrolysis oil mixture is used under the same conditions as the two canola oil sprays, the trends are similar. Figure 9 shows the images of a poor spray of pyrolysis oil at 25 psi atomizing air, exhibiting large droplets and long ligaments still intact in the spray. These are highly undesirable because most of the fuel is contained in a few droplets with very low surface area to permit vaporization. The spray at 35 psi atomization air shows a well-atomized droplet field and almost no surviving ligaments. Certainly, the large structures seen in the 25 psi atomizing air spray are mostly eliminated at 35 psi. It is interesting to note that the effect of increasing atomizing air from 25 psi to 35 psi is much more pronounced for the 20% ethanol in pyrolysis oil mixture than for the canola oil, indicating that the combustion performance will be more sensitive to the atomizing air for pyrolysis oil, due perhaps to Non-Newtonian properties. However, the 20% ethanol in pyrolysis oil spray seems to have similar spray characteristics as canola oil at an atomizing air pressure of 35 psi.

4.2.1.2 Pressure atomizing nozzle performance

Water is again used to examine the spray structures that develop using a low viscosity

fluid, this time for the 16 gph pressure atomizing simplex swirl nozzle at different

atomization pressures.
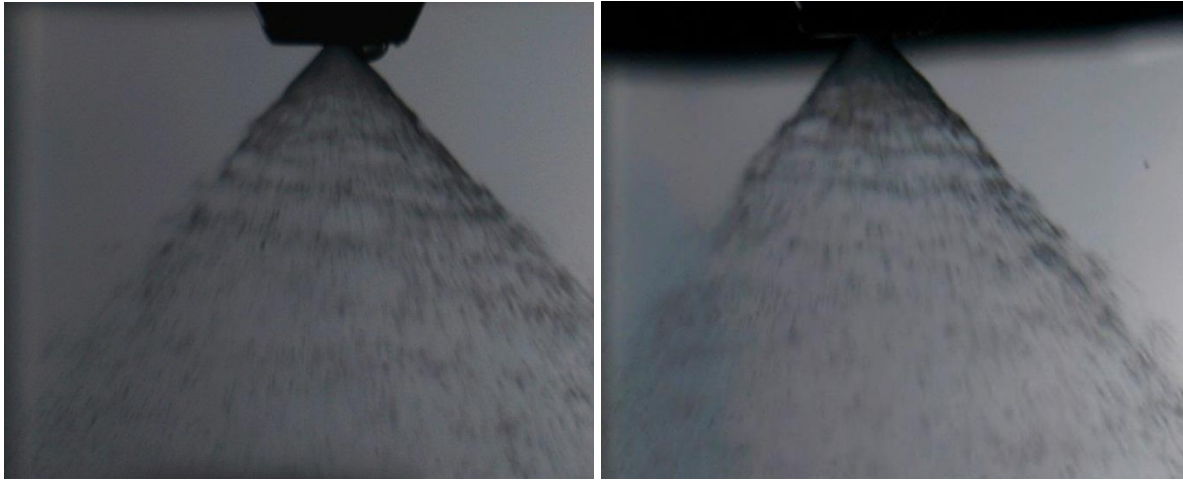
Figure 10: Pressure atomized water spray at 80 psi (left) and 100 psi (right).

In the images in Figure 10, it can be seen that the ideal flow structures of the simplex

swirl style nozzle are developed. The hollow cone can be seen radiating from the nozzle

orifice, then breaking into fine droplets at the edge. This is an example of a properly

functioning nozzle operating in a typical flow regime.
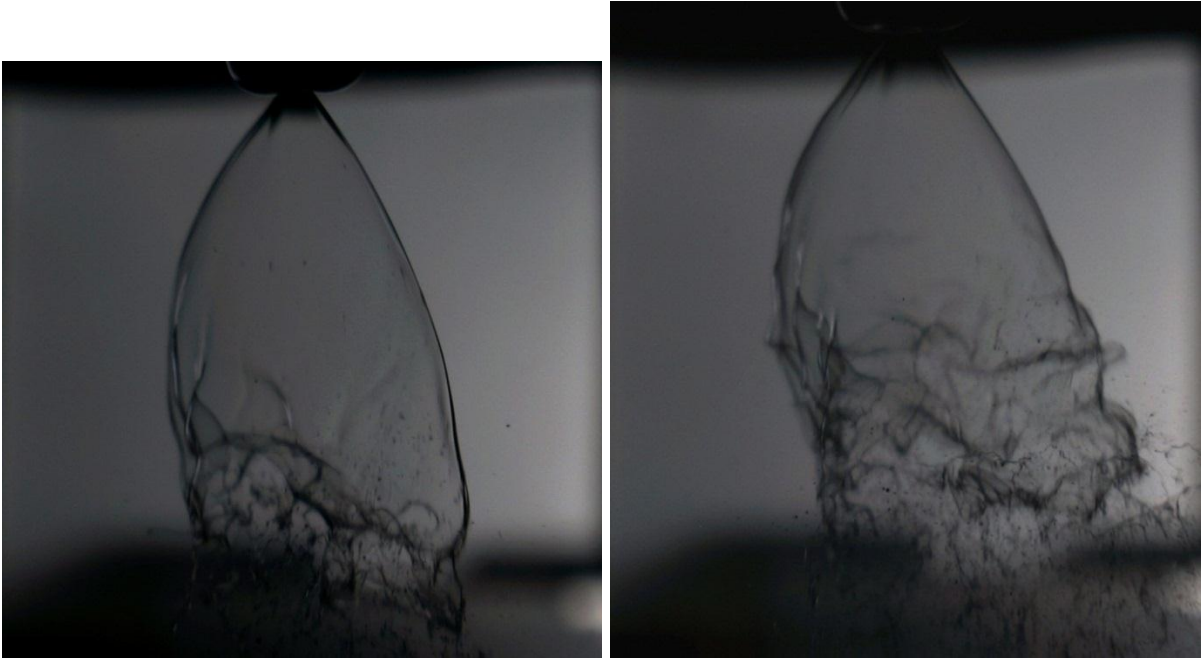
Figure 11: Pressure atomized canola oil spray at 80 psi (left) and 100 psi (right).

Canola oil is again used as a surrogate fuel for a 20% ethanol in pyrolysis oil mixture, but this time in a pressure atomizing nozzle. The two sprays shown in Figure 11 exhibit sprays from simplex swirl nozzles operating at too low of a Weber Number. The flow pattern was not very stable for these measurements, so the differences observed between these two particular spray images should not be used to draw conclusions. What can be seen in both is that the flow structure is properly developed within the nozzle in order to produce a hollow cone, but the inertial effects are not strong enough to overcome surface tension effects as the fluid travels away from the nozzle orifice. This results in inconsistent breakup that causes a wide distribution of droplet sizes, including many large droplets which are not desirable in a combustion spray.
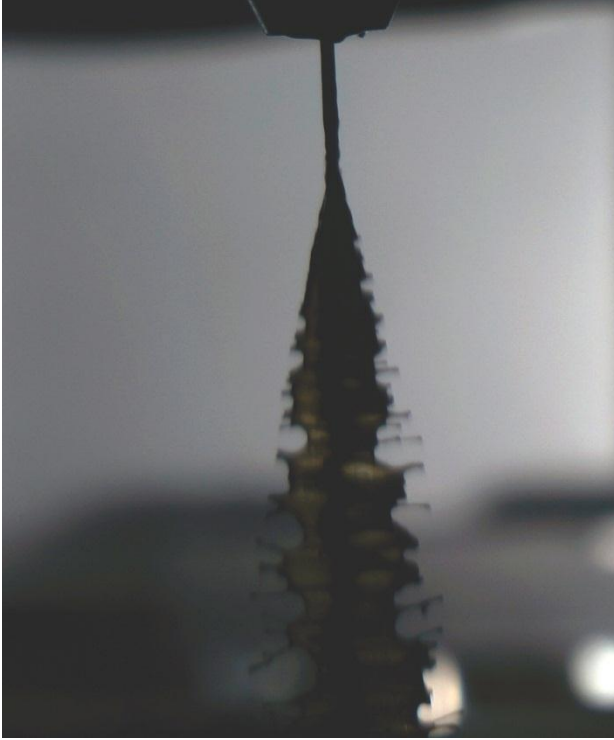
Figure 12: Pressure atomized spray of 20% ethanol in pyrolysis oil at 100psi.

When the 20% ethanol in pyrolysis oil mixture is tested under the same conditions as the canola oil in the pressure atomizing nozzle, the spray is very different. Figure 12 shows the spray from the pressure atomized nozzle, but the ideal structure of the simplex swirl nozzle is clearly not developed. It is known that simplex swirl nozzles operating at very low Weber Numbers can sometimes exhibit a simple jet spray because there is not sufficient centripetal acceleration to develop the hollow cylinder structure within the nozzle. This is not expected here because the Weber Number should not be significantly different than that of canola oil, which was at least able to develop the hollow cone flow structure within the nozzle. Again, we speculate that non-Newtonian properties of pyrolysis oil could be leading to these differences.

4.2.1.3 Shadowgraphy results summary

The results for air atomized nozzles indicate that there can be significant changes in spray structure caused by a change in atomization air pressure. It is expected that there should be a corresponding change in combustion performance due to the concentration of larger droplets and ligaments in the spray at lower atomization pressures.

The results of the pressure atomized nozzle tests indicate that good atomization will not be achieved at pressures the experimental rig is capable of delivering, which is up to about 120 psi. Poor combustion performance should be expected from the 20% ethanol in pyrolysis oil mixtures when used in combustion due to the extremely large droplets and the failure to spread to an appropriate spray angle for the combustor geometry. These effects will both lead to poor mixing between fuel and air since surface area is low, and the droplets will only interact with the center section of the total airflow in the combustion chamber.

Both air atomized and pressure atomized tests show that canola oil is not a perfect spray analog for this sample of 20% ethanol in pyrolysis oil mixture. The 25 psi atomization air cases show that pyrolysis oil has a higher propensity to retain ligament structures and large droplets under the same conditions. However, at 35 psi atomization air, the canola oil appears as a reasonable surrogate. The pressure atomized test shows that pyrolysis oil interferes with the development of the hollow cone flow pattern necessary for the simplex swirl nozzles to properly function. This is unexpected because the parameters such as viscosity and surface tension that normally control these flow phenomena are thought to be fairly close between canola oil and the 20% ethanol in pyrolysis oil mixture.

4.2.2 PDPA Results

The PDPA was only used for the air atomized nozzle, because the pressure atomized nozzles were not able to produce acceptable sprays with either pyrolysis oil or canola oil, as shown by the shadowgraphy results. Attempts were made to measure sprays with pyrolysis oil, but the opacity of the liquid interfered with data collection. Instead, sprays of water and canola oil were measured. Canola oil has similar viscosity to the mixture of 20% ethanol in pyrolysis oil and can be a reasonable surrogate liquid for spray testing.   The sample volume was placed 3" below the nozzle to obtain a measurement that is representative of droplets entering the flame zone and avoiding droplets that are still undergoing primary droplet breakup. Each run consists of measurements at a single point for 60 seconds, or until 5000 droplets have been measured in the sample volume. The time limit is imposed to prevent unnecessary expenditure of fluid for measurements with fewer, larger droplets.

Four sets of runs were collected with varying atomization air pressure. For both water and canola oil a set of runs was collected at the center of the spray and a set was collected near the edge of the spray cone. For the center measurement, the nozzle was not moved, but for the edge of cone measurements the nozzle was moved to keep the edge of the spray cone in the measurement volume. This adjustment was necessary for each run because the spray angle changes slightly with changes in flow conditions.

SMD is one of the most important parameters to combustion performance of liquid fuels. Sprays with large droplets, or high SMD, will have droplets which persist for a long duration, creating locally rich areas and increasing the residence time. These large droplets can contribute to increased pollutant formation and decreased flame stability. Ideal sprays will show smaller SMD values.

Table 1: PDPA results for SMD vs. atomization air pressure.

Edge of Cone Measurements				Center of Spray Measurements		
Fluid	Atomization Pressure (psi)	SMD (μm)		Fluid	Atomization Pressure(psi)	SMD (μm)
Water	35	110.7		Water	35	38.39
Water	30	112.94		Water	30	42.69
Water	25	120.7		Water	25	45.79
Water	20	140.64		Water	20	46.07
Water	15	154.14		Water	15	73.04
Water	10	164.87		Water	10	96.49
Canola Oil	35	136.92		Canola Oil	40	39.82
Canola Oil	30	137.84		Canola Oil	35	39.94
Canola Oil	25	155.36		Canola Oil	30	81.6
Canola Oil	20	157.38		Canola Oil	25	101.75
Canola Oil	15	164.04		Canola Oil	20	113.37
				Canola Oil	15	140.43
				Canola Oil	10	177.05
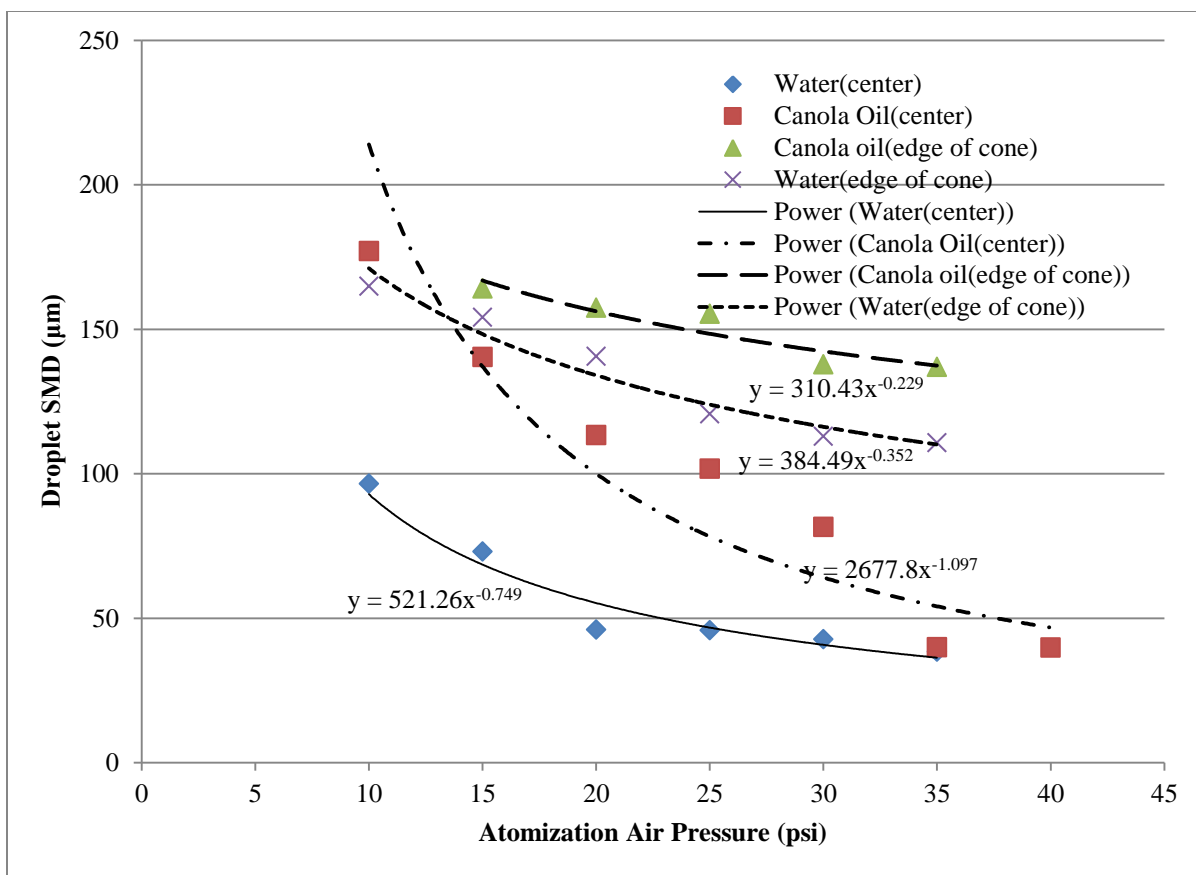
Figure 13: PDPA results for SMD vs. atomization air pressure with curve fits.

The results from the PDPA indicate that increasing atomization air pressure decreases the SMD. As atomization air pressure rises, this tends to have less of an effect. This trend is shown clearly with water and with canola oil at a higher pressure. This means that less viscous fluids can be atomized with less pressure, while more viscous fluids require a higher pressure to achieve optimal spray conditions. Because of this, it should be expected that there is a reduction in emissions associated with increasing atomization air pressure from 25 psi to 35 psi for the 20% ethanol in pyrolysis oil mixture.

Current literature on air atomized nozzles indicates that the SMD should be inversely proportional to the velocity of the atomizing air at the interface between liquid and atomizing air.[15] This is essentially just the velocity of the air, since the fuel enters at relatively low

velocity. The air velocity should be proportional to a square root function of pressure drop across the air passages of the nozzle. It should be expected that a power curve should correlate SMD to the -0.5 power of atomizing air pressure. Figure 13 shows that the SMD does not follow these trends very well. It can be observed that the very high atomization pressures and very low atomization pressures follow the trends the least. This is probably due to phenomena outside of the initial air assist breakup mechanism, which causes the nozzle to act differently as a system than predicted by a simple fundamental analysis, especially at conditions beyond the nozzle's intended operating range.

4.3 Combustion Test Results

Combustion tests in the boiler were carried out to study the effects of various parameters on exhaust emissions while maintaining flame stability. The tests focused primarily on parameters that affect fuel droplet atomization such as nozzle selection and operating condition, but global parameters such as overall λ value were also investigated. Several mixtures of pyrolysis oil and ethanol were tested to determine the effects of ethanol, but 20% ethanol was a primary focus because of the large drop in viscosity from pure pyrolysis oil to 20% ethanol mixture, with higher ethanol concentrations having less dramatic reductions in viscosity. Both air atomized and pressure atomized nozzles were investigated, along with substitution with the modified swirler. Preliminary results showed that a wider range of stable conditions could be examined when pyrolysis oil is co-fired with natural gas and a natural gas pilot light. It is likely that liquid pyrolysis oil would be implemented as a base loading fuel for these types of applications, with natural gas used in a co-firing mode to

accommodate peak demands. This allows designers to avoid the complexities associated with varying the liquid fuel flow with load, which is further complicated by the inconsistent liquid properties of pyrolysis oil. Most of the tests used in this study have a constant 3 SCFM natural gas co-fire along with a natural gas pilot flame, which accounts for about 17% of the energy contribution. The combined heat rate is around 260 kW, which is just below half of the maximum output of the boiler, the base load condition.

4.2.1 Fuel Oil and Natural Gas Baselines

Prior to boiler testing, personnel from the company that services the boilers at the Capitol Complex of the State of Iowa inspected the boiler for safety and to ensure proper operation. The latter was accomplished, in part, by ensuring that CO emissions were minimized. Baseline fuel oil tests were then conducted to establish the typical levels of PM that are present for boilers in current use. Typically #2 fuel oil boilers utilize pressure atomized nozzles due to the simplicity and cost of the system over air atomized nozzles. Air atomized nozzles were also tested with fuel oil to observe any changes over pressure atomizing nozzles. Natural gas conditions were also sampled, again for comparison of PM emissions. The results of measurements are shown in Table 2.

Table 2: Fuel oil and natural gas baseline runs.

Fuel	Nozzle Type	λ	PM mg/m^3
Fuel oil	Pressure	1	524.83
Fuel oil	Pressure	1.32	7.23
Fuel oil	Pressure	1.42	1.80
Fuel oil	Pressure	1.5	0.70
Fuel oil	Pressure	1.58	0.41
Fuel oil	Air (25 psi)	1.36	70.51
Fuel oil	Air (25 psi)	1.5	4.13
Fuel oil	Air (25 psi)	1.58	0.90
Natural Gas	N/A	1.37	0.19
Natural Gas	N/A	1.38	0.09

The results in

Table 2 highlighted in green represent typical operating conditions for properly adjusted #2 fuel oil and natural gas boilers. Off of normal operating conditions, soot output can reach very high levels. Soot levels for fuel oil are very dependent on λ value, with leaner conditions being more ideal, at the cost of moving more air through the boiler for a given heat rate. Contrary to expectations, there is not a dramatic decrease when switching to the air atomized nozzle. This may be caused by the fact that the pressure nozzle is a hollow cone spray, while the air atomized nozzle is a solid cone spray, leaving a more locally rich area in the center of the flow. With the nozzles normally used for this type of system, typical PM concentrations for fuel oil flames in this boiler are around 0.4-0.7 mg/m^3. Natural gas is capable of attaining even lower soot levels due to the lower sooting propensity of the lighter, lower carbon content, natural gas species, but either level is considered acceptable for typical boiler operation.

4.2.2 Runs without Natural Gas Co-fire

Flame stability was impaired for conditions without natural gas co-fire. As a result, very few of these runs were conducted, and a pilot light was still used. The 20% ethanol in pyrolysis oil mixture was unable to sustain stable combustion without the slight natural gas co-fire, even under ideal conditions. With the higher concentration of ethanol, other fuel mixtures were capable of sustaining a flame at least long enough to record data without the use of the co-fire. These results are shown in Table 33, again for cases without natural gas co-fire. All other data presented subsequently to Table 3 all used a fixed natural gas co-fire at a rate of 3 SCFM to help stabilize the flame and ensure repeatable flame conditions for a wider range of λ and atomizing conditions.

Table 3: Emissions for pyrolysis oil/ethanol mixtures without co-fire with natural gas. Higher levels of emissions are highlighted.

λ	Fuel	Atomization Pressure	PM mg/m^3	CO ppm	NO ppm
1.5	70/30	35 psi	0.27	73	136
			0.29	79	146
			0.19	102	147
	60/40		0.31	100	136
			0.13	94	137
			0.19	83	138

These data show the ability to achieve low PM with pyrolysis oil mixtures even without co-firing with natural gas. The CO emissions are similar for both mixtures with 30% and 40% ethanol in pyrolysis oil and are close to same levels seen with the natural gas co-fire, indicating that the natural gas does not inherently affect the CO emissions so long as the flames are stable. NO is slightly higher for these runs than for runs with the co-fire, which may be due to the fact that more pyrolysis oil mixture is used in these runs to keep the same heat rate and λ value without natural gas.

4.2.3 Pressure Atomizing Nozzle Runs

These runs were intended to test the capabilities of traditional pressure atomized nozzles of two different flow rates as compared to a run with the air atomized nozzle for the case of 20% ethanol in pyrolysis oil. Very few of these conditions were run due to the high pollutant output and poor flame stability. It was also challenging to control λ, since fuel flow rate is a function of fuel pressure. As a result, one very rich condition was run unintentionally, and the results are included in Table 4 below.

Table 4: Emissions for 20% ethanol in pyrolysis mixtures using pressure atomized vs. air atomized. Higher levels of emissions are highlighted.

λ	Nozzle	Pressure	PM mg/m^3	CO ppm	NO ppm	HC ppm
1.5	Air	35 psi	0.58	120	109	0
			0.90	166	113	0
	16 gph rated pressure atomizing nozzle	80 psi	83.92		46	
			64.75		54	
			78.94		52	
1.25		95 psi	308.81	724	96	723
			240.88	684	97	852
			266.51	>2000	92	869
1.5	9.5 gph rated pressure atomizing nozzle	80 psi	35.29	1234	82	0
			42.24	1472	80	0
			40.16	1349	87	0
		100 psi	100.85	>2000	76	932
			107.34	>2000	76	236
			121.78	>2000	62	134

From Table 4, it can be observed that pressure atomized nozzles for the 20% ethanol in pyrolysis oil produces substantial incomplete combustion products including PM, HC and CO, each at unacceptable levels. It is interesting to note that NO is slightly lower for pressure atomized nozzle conditions, but this does not outweigh the emission levels for the

other pollutants. One would expect poor pressure atomized combustion results from the 20%

ethanol in pyrolysis oil mixture, correlating to the poor atomization observed in the spray

testing.

4.2.4 Fuel Comparison

In this section, fuels are compared at a series of overall λ values. This is to form a

basis of comparison between existing #2 fuel oil emission levels and the pyrolysis oil ethanol

mixtures studied in this work. Overall λ value has a strong impact on fuel oil emissions, so it

is important to study these fuels across a range of possible λ values. A finer control over λ is

attainable with fuel oil than with pyrolysis oil mixtures due to drift in the fuel flow through

the controlling needle valve, so more data points are available for fuel oil. For this set of

data, the air atomized nozzle was used and the atomizing air pressure was set to 35 psi in

order to provide constant conditions across the array of tests. Figure 144 shows two side by

side images of a 20% ethanol in pyrolysis oil mixture flame and a similar fuel oil flame.
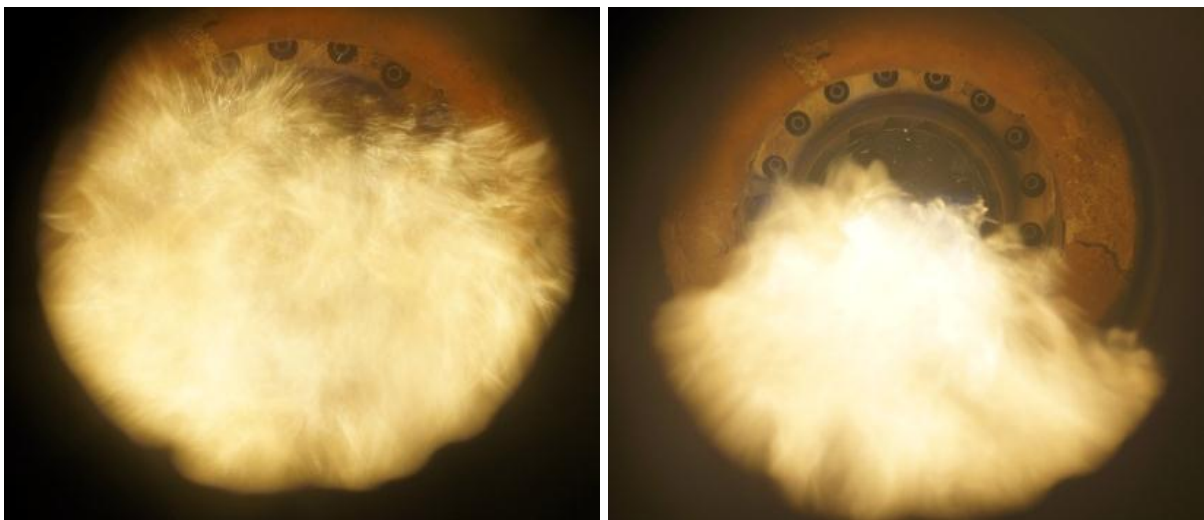
**Figure 14 Pyrolysis oil flame with 3 SCFM natural gas co-burn (left), and fuel oil flame
with 3 SCFM natural gas co-burn (right).**

In Figure 14 it can be seen that there is a different flame structure between fuel oil and pyrolysis oil. This is consistent across many conditions. It is observed that the pyrolysis oil flame is more uniformly distributed in the combustion chamber and contains many distinct "sparklers" or particles of fuel traveling about the combustion chamber as they burn.

Table 5: Comparison of emissions for #2 fuel oil and different mixture of pyrolysis oil and ethanol. Higher levels of emissions are highlighted.

Atomizing Pressure	λ	Fuel	PM mg/m^3	CO ppm	NO ppm
35 psi	1.2	#2 fuel oil	38.89	1743	34
	1.3	#2 fuel oil	2.11	89	43
		80/20 Bio	0.58	120	109
		60/40 Bio	0.04	45	97
	1.4	#2 fuel oil	0.01	48	61
	1.5	#2 fuel oil	0.07	117	62
		80/20 Bio	0.45	49	131
		60/40 Bio	0.05	95	102
	1.6	#2 fuel oil	0.00	187	69
	1.7	#2 fuel oil	0.11	285	69
		80/20 Bio	0.55	108	121
		60/40 Bio	0.24	271	96
	1.8	#2 fuel oil	0.08	459	66

The results shown in Table 5 reflect a potential for pyrolysis oil mixtures to have comparable emissions with #2 fuel oil. Fuel oil reaches very high levels of PM under conditions that are more fuel rich. It is observed that pyrolysis oil conditions offer lower PM than the fuel oil condition at λ = 1.3. Although the #2 fuel oil emissions for air atomized nozzles are lower for λ = 1.4 – 1.8 than for pressure atomized nozzles, likely due to fine atomization tat the 35 psi atomization air pressure, more typical fuel oil PM levels from pressure atomized nozzles are around 0.4 – 0.7 mg/m^3, as shown previously in Table 2. Hence, the PM levels reported in Table 5 are acceptable for pyrolysis oil mixtures from λ =

1.3 – 1.7. As pyrolysis oil has a narrower range of flammability, this may prevent combustion in regions where too little oxidizer is present and help to limit soot production. This has the effect of decreasing soot produced at locally rich sites within the flame compared to fuel oil, reducing overall PM levels for these conditions. CO emissions are lower for pyrolysis oil mixtures than for fuel oil in most cases. Each fuel seems to have a local minimum for CO emissions which can be targeted with subsequent optimization tests. NO is higher for pyrolysis oil than for fuel oil for most conditions, but still within a reasonable range. Nonetheless, this is may be a target for future optimization studies.

4.2.5 Test Matrix for Ethanol Concentration and Atomization Pressure

Table 6 focuses on atomization air pressure effects for three different ethanol concentrations of ethanol pyrolysis oil mixtures in order to determine optimum conditions for each ethanol level. Ethanol concentration is suspected to have an effect on atomization through its viscosity effects, in addition to atomization air pressure. The λ value is fixed at 1.5 for these conditions to focus solely on atomization conditions. Triplicates were not run for gaseous emissions for the 30% ethanol pyrolysis oil mixture in order to save resources for more focused tests.

Table 6: Emissions data with varying atomization pressure and ethanol content in pyrolysis oil. Higher levels of emissions are highlighted.

λ	Fuel	Atomizing Pressure	PM mg/m^3	CO ppm	NO ppm	HC ppm
1.5	80/20 Pyrolysis oil	20 psi	0.16	86	124	42
			0.24	82	117	45
			0.32	73	123	48
		25 psi	0.10	48	134	0
			0.20	46	133	0
			0.24	48	133	0
		30 psi	0.11	54	129	0
			0.16	50	130	0
			0.16	48	133	0
		35 psi	0.29	42	136	0
			0.28	41	136	0
			0.34	37	134	0
		40 psi	0.25	60	130	0
			0.11	53	129	0
			0.02	58	130	0
	70/30 Pyrolysis oil	20 psi	0.28	76	122	0
			0.13			
			0.23			
		25 psi	0.15	36	123	0
			0.08			
			0.04			
		30 psi	0.28	76	115	0
			0.26			
			0.21			
		35 psi	0.25	102	126	0
			0.28			
			0.31			
		40 psi	0.20	80	128	0
			0.31			
			0.21			
	60/40 Pyrolysis oil	20 psi	0.29	64	95	0
			0.34	61	97	0
			0.25	69	94	0
		25 psi	0.19	75	107	0
			0.22	63	101	0
			0.22	65	104	0
		30 psi	0.30	69	107	0
			0.39	58	105	0
			0.09	59	105	0
		35 psi	0.08	60	109	0
			0.14	54	109	0
			0.14	66	106	0
		40 psi	0.21	67	100	0
			0.21	80	102	0
			0.24	114	108	0

It can be observed that PM is below 0.40 mg/m^3 for all runs in this chart, which is comparable to fuel oil emission levels for the baseline runs. It is interesting to note that there is not a large decrease in PM with increasing atomizing air pressure, as might be expected from the change in spray behavior observed in spray testing. This indicates that increasing atomizing air pressure is only useful up to a certain point, and going beyond this has little impact on combustion performance. The variance between PM measurements for these points is substantial compared to the low levels of PM that are measured. Variability shown between these conditions is mostly within the measurement noise.

A minimum can be seen in CO at 35 psi for both 20% and 40% ethanol pyrolysis oil mixtures. The changes between conditions are larger than the noise within each run, indicating that these are real results and not noise. It is also interesting that for these two sets, both low CO and PM are attainable from 25 psi to 35 psi atomization indicating that there is not a strong effect from atomizing pressure, so long as there is enough atomizing pressure to properly atomize the fuel. The minima in CO is not found in the 30% mixture, but there is only a single measurement point for that condition, so it may not have been as accurate as for the other two fuels, and any trend is likely drowned out in the measurement noise.

There are detectable emissions of HCs only for low atomization pressures of the 20% ethanol pyrolysis oil mixture. This indicates poor combustion, which is likely the reason that NO is also low for this run. This agrees with spray testing that indicates a deterioration of spray performance below 25 psi atomization for 20% ethanol in pyrolysis oil mixtures. The higher ethanol mixtures are likely immune to this phenomenon until a lower pressure level due to reduced viscosity caused by the ethanol.

NO is not strongly affected by atomization air, but there is a slight decrease with increasing ethanol content. This is consistent with NO readings in Table 5. This is likely because ethanol contains no fuel bound nitrogen. By replacing pyrolysis oil with ethanol, less fuel bound nitrogen is available to be oxidized.

4.2.6 Effects of λ and Atomization Pressure

This table employs a constant fuel composition, but varies λ at two different atomization pressure levels, to study the effect of λ for each atomizing condition. Two runs were taken at each condition on separate days, which serves as a measure of reproducibility for the measurements.

Table 7: Emissions for 20% ethanol in pyrolysis oil while varying λ for two different atomization pressures. Higher levels of emissions are highlighted.

λ	Atomizing Pressure	PM mg/m^3	CO ppm	NO ppm
1.3	25	0.42	135	102
		0.50	167	107
	35	0.58	120	109
		0.90	166	113
1.5	25	0.29	50	120
		0.41	53	119
	35	0.45	49	131
		0.55	42	135
1.7	25	0.28	109	119
		0.43	101	111
	35	0.55	108	121
		0.44	64	133

This dataset shows little effect from atomization pressure. A strong minimum of CO is shown at λ=1.5 for both atomization pressures. With the exception of one point, all of

these conditions have PM under 0.60 mg/m^3 which is in the same range as the baseline runs for #2 fuel oil. It is worth noting that for the rich condition NO is lower than for the other two conditions at both atomization levels, while CO is higher. This tends to indicate lower flame temperatures or combustion with less oxygen content available for NO production, possibly caused by a stronger tendency to have locally rich areas in the flame.

4.2.7 Air Swirler Comparison

This dataset examines a small range of conditions for both the factory and custom air swirlers. The results from Table 8 and Figure 15 show that there is very little difference caused by the swirler at any conditions. In fact, the custom swirler, which has a higher effective flow area, may even slightly worsen gaseous emissions on average. This is slightly surprising since previous studies in a smaller scale combustor (~20 kW) showed that this type of design modification significantly increased flame stability and reduced emissions.[47] Perhaps for a larger boiler of this type, there is less sensitivity due to more significant heat release per unit surface area of the flame zone, or it may also be that the baseline flow of natural gas eliminated the advantages of the design modification. Although there are many factors in the air intake that may affect combustion performance, it was not possible in this study to extract specific information about the effects of air swirl and effective flow area for the two available swirlers. However, it is possible that some combination of swirler features could improve combustion performance. Since there was no substantial change, this variable was not investigated further.

Table 8: Comparison of two different swirlers for combustion of 20% ethanol in pyrolysis oil. Higher levels of emissions are highlighted.

Swirler	Atomizing Pressure	PM mg/m^3	CO ppm	NO ppm	Swirler	Atomizing Pressure	PM mg/m^3	CO ppm	NO ppm
Factory	20	0.16	86	124	Custom	20	0.32	133	119
		0.24	82	117			0.28	115	121
		0.32	73	123			0.32	112	123
	25	0.1	48	134		25	0.28	68	128
		0.2	46	133			0.25	66	125
		0.24	48	133			0.09	66	126
	30	0.11	54	129		30	0.14	52	133
		0.16	50	130			0.11	52	137
		0.16	48	133			0.16	49	133
	35	0.29	42	136		35	0.08	43	140
		0.28	41	136			0.15	44	139
		0.34	37	134			0.24	47	138
	40	0.25	60	130		40	0.25	42	150
		0.11	53	129			0.23	42	150
		0.02	58	130			0.13	40	150
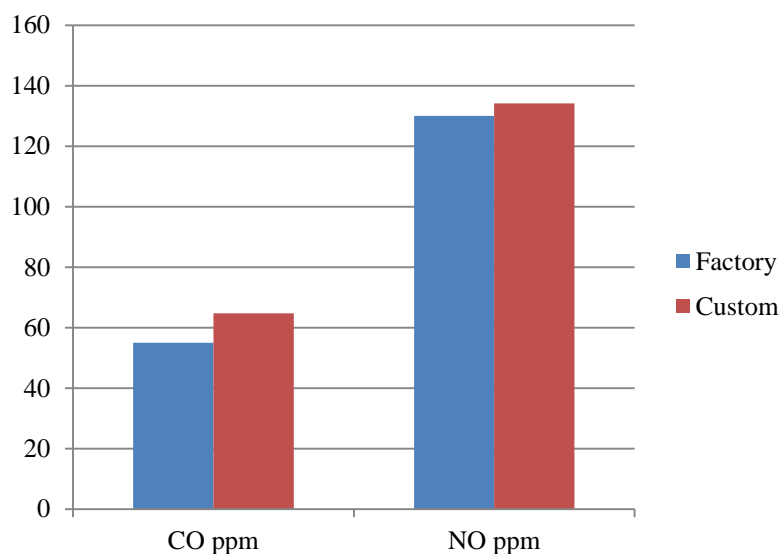
Figure 15: Average gaseous emissions comparison for two different air swirlers for combustion of 20% ethanol in pyrolysis oil.

CHAPTER 5. SUMMARY AND FUTURE WORK

A building heating boiler has been modified for testing and optimizing combustion properties of pyrolysis oil and ethanol mixtures under a variety of conditions. This boiler was able to sustain a pyrolysis oil flame with emissions near those of a typical fuel oil flame, but required a small baseline level of natural gas for ethanol concentrations of 20% or lower. This demonstrates that it is possible to use pyrolysis oil to displace substantial amounts of fossil fuel combustion for boiler applications.

Pyrolysis oil mixtures with ethanol were characterized for several properties, most notably for viscosity, which can have a major effect on spray performance. A thorough set of samples was tested and it was determined that a large drop in viscosity occurred between 0% and 20% ethanol, with less viscosity change at higher ethanol levels. This allowed operation with pyrolysis oil without fuel or boiler preheating, a key advantage for on-demand boiler operation. Hence the range of tests included ethanol concentrations of 20% to 40% for comparison of pollutant emissions, with the primary goal of maximizing the pyrolysis oil fraction in the mixtures.

Pressure atomized nozzles were compared with air atomized nozzles for their performance with pyrolysis oil mixtures using both optical techniques for cold spray characteristics and for combustion tests. Air atomized nozzles were found to be much more effective at atomizing pyrolysis oil than pressure atomized nozzles. Spray imaging shows that pressure atomized nozzles cannot properly develop the delicate exit flow patterns needed to effectively atomize the ethanol/pyrolysis oil mixtures. This is reflected in combustion

performance in the form of high concentrations of incomplete combustion products including PM and HC for pressure atomized nozzles.

Through spray imaging of air atomized nozzle sprays, it was found that atomizing airflow had an impact on atomization performance, especially for pyrolysis oil mixtures. Imaging results show ligaments and larger droplets leaving the nozzle in spray conditions with atomization pressure as low as 25 psi, compared to fully developed spray patterns at 35 psi. Surprisingly, however, combustion PM results were fairly similar for atomizing air pressures between 25 psi to 35 psi, although CO emissions appeared to be lower at 35 psi. The results of lower atomization pressures show slight changes in PM and CO, though still maintaining near acceptable levels. This may be because ligaments visible in spray images end up breaking into smaller droplets before combustion. As a result, these may not have severe effects on the combustion performance. Hence air atomized nozzles appear to allow a wide range of operating pressures and certainly much lower emissions than pressure atomized nozzles.

The effects of overall λ value on combustion performance were shown to be fairly important to flame stability and emissions levels. Stable flames were easily attainable with natural gas co-fire with the ethanol/pyrolysis oil mixtures for λ values ranging from 1.3-1.7, with $\lambda = 1.5$ being optimal for flame stability and emissions performance. PM emissions in this range appeared to be lower for air atomized pyrolysis oil mixtures than for pressure atomized #2 fuel oil at the same overall λ. CO emissions were minimized for $\lambda = 1.5$ as well. For rich conditions, this increase in CO can be explained by reduced oxidizer availability. For lean conditions, the low combustion temperatures are less able to fully combust CO.

A variety of concentrations of ethanol mixtures with pyrolysis oil were tested to determine the effects of ethanol content. NO levels were reduced by an amount expected for replacement of pyrolysis oil, while PM was not significantly affected, and CO levels were increased with increasing ethanol content. These results are not favorable for increasing ethanol concentration beyond 20% ethanol, which was able to easily produce acceptable emission levels and flame stability under proper conditions.

Some studies have found that swirler characteristics can be important to swirl stabilized pyrolysis oil combustion. A custom swirler was constructed and substituted with the factory installed swirler in order to investigate possible effects based on these prevous studies. These tests showed no appreciable effect from the new swirler on emissions. Hence, the custom swirler was not investigated further, although a full range of design parameters may still lead to some improvement and would be a possible area of future study.

For all operating conditions with PM emissions comparable to typical fuel oil conditions, HC emissions were below the detection limit of the instrument. This shows that HC is not likely to pose a major issue for pyrolysis oil applications, so long as PM conditions are satisfied. This, combined with low CO emissions, is indicative of high combustion efficiencies.

NO was not strongly affected by any variables other than the fraction of pyrolysis oil in the flame. This suggests that the primary method of NO production is fuel bound nitrogen oxidation rather than thermal NOx or prompt NOx. The low adiabatic flame temperatures due to the high moisture content and low energy content in pyrolysis oil will not tend to produce high levels of thermal and prompt NOx, providing further support for this claim.

An off-the-shelf fuel pump was used for some of the conditions before pump performance began to degrade; thereafter, a laboratory fuel system was reintroduced relying on a pressurized tank. The off-the-shelf fuel pump was selected because of compatibility with #6 fuel oil and had accommodations for atomizing air, but was by no means designed for pyrolysis oil use. The pump was able to fulfill pumping needs for a few weeks before showing problems. It is likely that with different materials choices, a pump could be designed specifically for use with pyrolysis oil, making use of stainless steel whetted components and pyrolysis-oil compatible seal materials, but this redesign was outside the scope of this project. Hence, material compatibility in the fuel pumping system is a potential issue that still needs to be resolved before pyrolysis oil can attain widespread use.

Another possible issue is the tendency for pyrolysis oil to separate during long periods of storage. In this experiment, the problem was partially resolved by vigorously mixing the fuel before taking samples and before use. This is possible with current technologies, but is not commonplace in fuel systems. In addition, the 20% ethanol acted as a solvent and effectively kept the pyrolysis oil components in solution.

The biggest hurdles to overcome with regard to the feasibility of pyrolysis oil are the fuel properties and combustion performance. This investigation has demonstrated that these can be overcome with existing technologies by utilizing air atomized nozzles, mixing ethanol with the pyrolysis oil, filtering the fuel before use, and utilizing some natural gas baseline flow for lower ethanol concentrations. This investigation shows that pyrolysis oil is a viable replacement for fuel and can displace natural gas to reduce overall carbon emissions in the energy supply of the future.

APPENDIX A. COMBUSTION AIR DAMPER CALIBRATION

The amount of combustion air is a crucial variable for these combustion conditions, since fuel flow is controlled by equivalence ratio. This makes fuel flow rate proportional to air flow rate for a given condition. It is useful to maintain the control system employed on actual boilers to ensure that conditions are accurately represented. To maintain the factory mechanism for controlling air but to have the ability to control the airflow during the investigation, the linkage controlling the airflow damper was disconnected from the electronic actuator and connected to a fixed bracket. Marks were put on the linkage so that it could be adjusted to provide varying levels of airflow. In order to calibrate these markings, the airflow out of the exhaust was measured with a hot wire anemometer during cold tests of the fan with no combustion. For each damper setting, five measurements were collected at different locations across the exhaust tube and were averaged to determine a flow rate for that setting. The results of this test are shown in Figure 16.
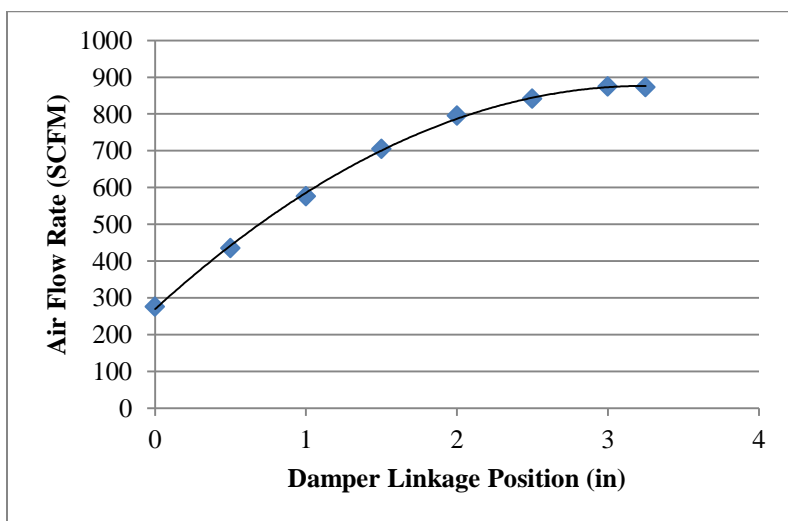
Figure 16: Air flow rate for damper setting calibration curve.

APPENDIX B. PDPA UNCERTAINTY ANALYSIS

The PDPA measurement is subject to several sources of variance. Preliminary data show that droplet size distribution is highly dependent on location within the spray. This is a possible source of error because the positioning of the nozzle was performed by observation of the probe volume in the spray. Another issue is that the spray angle changed slightly in response to changes in operating conditions, including both fuel type and atomization air pressure. These can cause changes in readings for errors in nozzle placement.

Table 9: PDPA preliminary results for water.

Atomizing Air Pressure(psi)	Axial Distance(in)	Radial Distance(in)	SMD(μm) Run 1	SMD(μm) Run 2	SMD(μm) Run 3	COV
25	3	0	38.38	36.13	35.41	0.0655
35	3	0	27.82	28.85	28.16	0.0097
25	3	1	43.14	45.92	42.51	0.0750
35	3	1	37.88	35.83	36.01	0.0352
25	3	2	103.07	103.82	103.51	0.0013
35	3	2	91.51	92.37	90.62	0.0083
35	2	0	37.22			
35	2	1	51.32	52.89	54.39	0.0445
35	2	2	102.13			

The data shown in Table 9 are SMD readings for a variety of locations within two different atomization pressure sprays of water. For most of these points, three runs were taken sequentially without adjusting nozzle location, atomization pressure, or any other parameters to confirm that each measurement was repeatable. This is shown by the low coefficient of variance (COV) for each set of three runs, with all COV values less than 0.08. It can be accepted that the measurement of each point is repeatable.

Geometric trends in the spray can also be observed from Table 9. Looking at the coordinates of the measurement, it can be seen that the spray consists of much smaller droplets in the center than at the edge of the spray, with varying sizes in between. It can also be observed that this distribution is much different at a plane 2 in. from the nozzle than 3in. This shows that measurements will be sensitive to sampling locations within a spray.

The large droplets at the edge of the spray are likely to have an effect on combustion performance because large droplets can lead to poor atomization, long burnout time and locally rich areas. These problems contribute to poor flame stability and increased production of emissions, especially PM. This means that the SMD at the edge of the spray can impact combustion performance and should be measured during the spray testing.

Another challenge is that the spray angle of the nozzle changes with changes in operating conditions. An issue arises because a fixed point in space may not correspond to a representative comparison between two sprays, for instance a point at the edge of one spray could lie completely outside of the cone of a narrower spray. This is corrected by observation for each run, especially in cases where the sampling point is to be at the edge of the spray cone. Measurements along the axis of the spray are not subject to this sensitivity, but are still subject to errors caused by misalignment. It is shown that the measurement of each point is repeatable, but that any error most likely comes from imperfect positioning of the nozzle or judgment errors in determining representative points to sample.

APPENDIX C. MODIFIED SWIRLER

Other researchers have found that the swirl plate of swirl stabilized pyrolysis oil flames can have a substantial effect on flame stability and pollutant emission.[47] A swirler was made with the intent of enhancing the swirl to reduce emissions. The new swirler was made to be interchangeable with the factory original swirler to facilitate comparison tests. The factory swirler had small swirl vanes that protruded into the combustion area, while the new swirler had wider, more open swirl vanes that were recessed away from the combustion area, with the intent of creating a more airfoil shaped swirl vane to further enhance swirl effects. These two swirlers are shown side by side in Figure 177.

Figure 17: Original factory swirler (left) and modified custom swirler (right).

The factory and modified swirlers were characterized by their effective area in an orifice flow system by measuring pressure drop across the swirler with respect to air mass flow rate through the swirler. Airflow was controlled by an Alicat mass flow controller,

while pressure was measured with an oil manometer. Effective area can be calculated by solving for area in the orifice flow equation. The flow needs to be increased until a set of conditions is reached where the swirler behaves like an ideal orifice, with the calculated effective area leveling out to a constant value between conditions.

$$Q = C_d A_e \sqrt{\frac{2\Delta p}{\rho}}$$

Q is the volumetric flow rate of air, and ρ is the density, in this case 1.24 kg/m^3. C_d is the discharge coefficient which is applied to known structures in order to correct for different geometries given a characteristic length. In this case, the characteristic length is the subject of study, and C_d is assumed to be 1. This is consistent between both swirlers, so it is a useful comparison.

Table 10: Δp and Ae for varying air flow rate for factory and custom swirlers.

| Airflow Q (m^3/s)	Δp (pa)	Δp (pa)	Factory A$_e$ (m^2)	Custom A$_e$ (m^2)
0.0000	0	0		
0.0017	0	0		
0.0033	0	0		
0.0050	2.49	0	0.00249	
0.0067	2.49	2.49	0.00333	0.00333
0.0083	4.98	2.49	0.00294	0.00416
0.0100	7.47	2.49	0.00288	0.00499
0.0117	9.96	2.49	0.00291	0.00582
0.0133	9.96	2.49	0.00333	0.00665
0.0150	14.94	4.98	0.00306	0.00529
0.0167	17.43	4.98	0.00314	0.00588
0.0183	19.92	7.47	0.00323	0.00528
0.0200	22.41	7.47	0.00333	0.00576
0.0217	27.39	9.96	0.00326	0.00541
0.0233	29.88	9.96	0.00336	0.00582
0.0250	34.86	12.45	0.00333	0.00558
	Average A$_e$ of last 5 runs		0.00330	0.00557

As shown in Table 10, the effective area for the custom swirler is larger than for the factory swirler. This is due to the larger, more open swirl vanes in the custom swirler, which was found in previous work to encourage a smaller flame cone angle and increased mixing rates.[47]

APPENDIX D. FUEL AGING TESTS

This section discusses a set of samples that were analyzed using instruments previously described to measure higher heating value (HHV) and to perform thermogravimetric analysis (TGA). These samples were aged at various temperatures using the hot plate apparatus discussed in experimental setup and then sent to the Biorenewables Research Laboratory (BRL) at Iowa State University. The sample set included one that was "aged" at room temperature and provides some insight into the fuel properties aside from any possible effects from the elevated temperature aging process. Therefore, these results are applicable to fuel samples used for combustion and spray testing.

Table 11: Higher heating value test results for aged samples.

| Sample Ethanol Percentage	Aging Temperature, 30 Minutes			
	20 °C	30 °C	40 °C	50 °C
100% Pyrolysis Oil	4015	3926	4039	4038
90% Pyrolysis Oil, 10% Ethanol	4242	4233	4224	4236
80% Pyrolysis Oil, 20% Ethanol	4387	4437	4437	4478
50% Pyrolysis Oil, 50% Ethanol	5006	5109	5029	4882
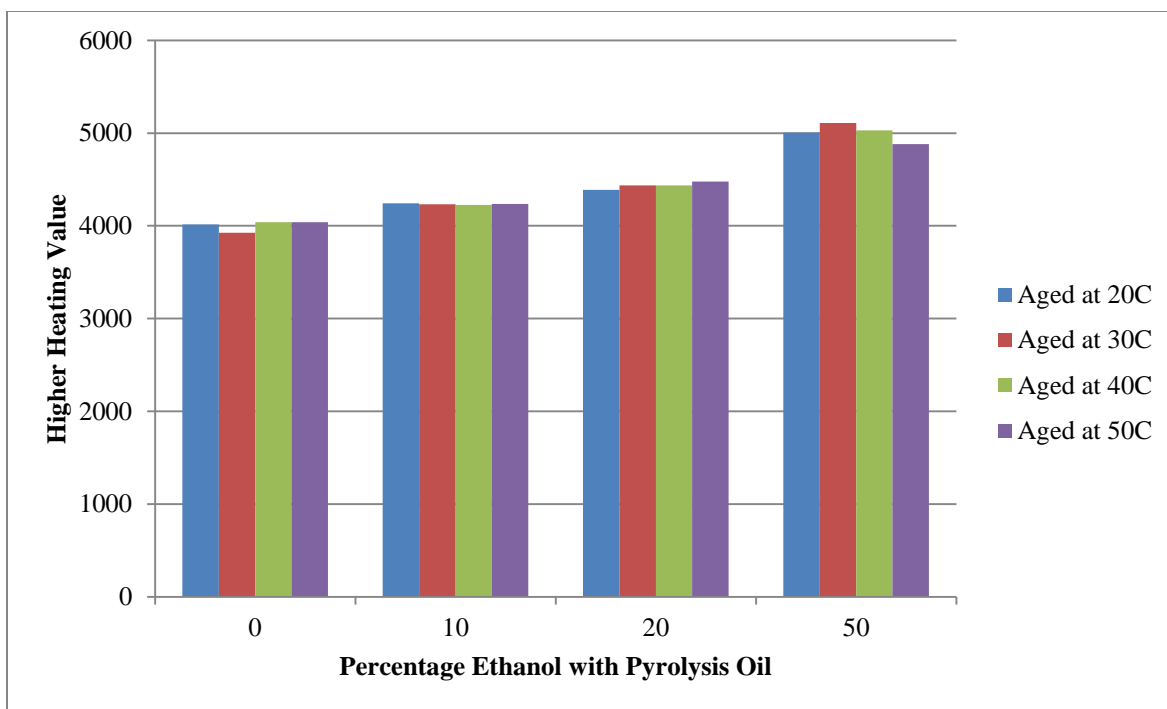
**Figure 18: Higher heating value test results for aged samples.**

The results of Figure 18 and Table 11 show that there is very little effect correlated to the aging process applied. This is likely because the samples were aged for only a relatively short time so that very little change could occur. It is also possible that changes took place but did not have a significant effect on HHV, much the way that hydrocarbon distillates all tend to have very similar HHV, despite being very different fuels. Some increase is observed with increasing ethanol content, due to the higher HHV of ethanol than pyrolysis oil.

Table 122 shows the full TGA results for the samples. There was a problem with the measurement of the 10% ethanol pyrolysis oil mixture that was aged at 40°C; the percentages did not add up to 100. Moisture is defined as constituents that evaporate before 105°C. This includes water, added ethanol, and any other substances originally contained in the pyrolysis oil which evaporates in the temperature range. Fixed carbon includes substances which do
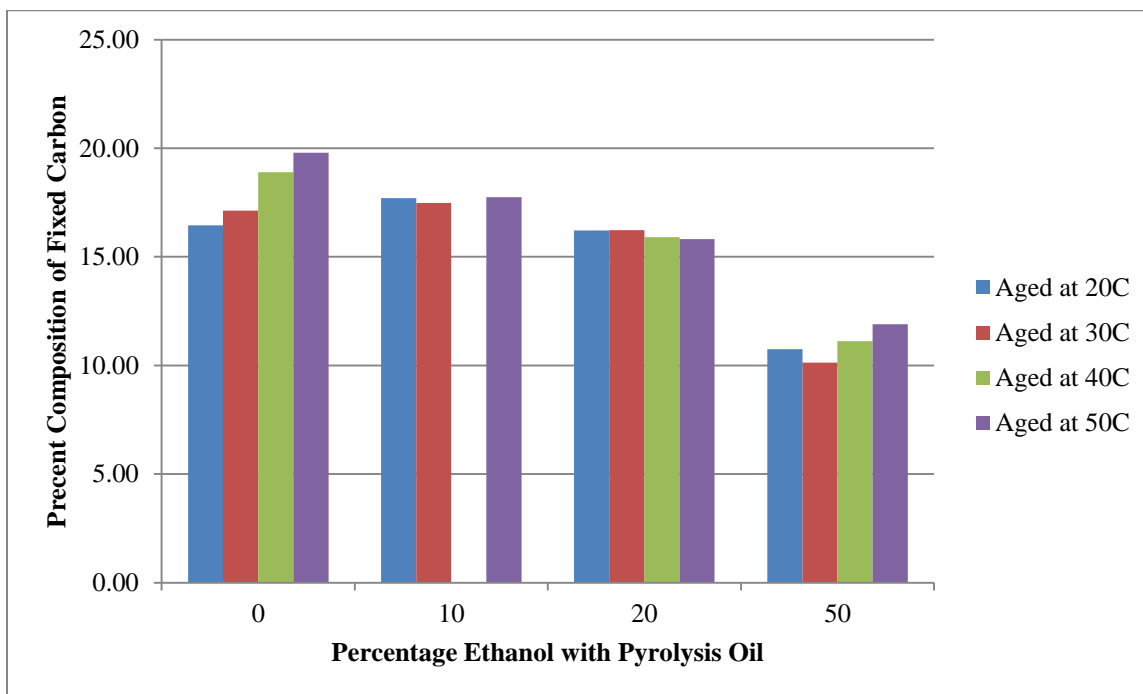
not leave the crucible until oxygen is introduced to allow combustion, and ash is what remains after combustion.
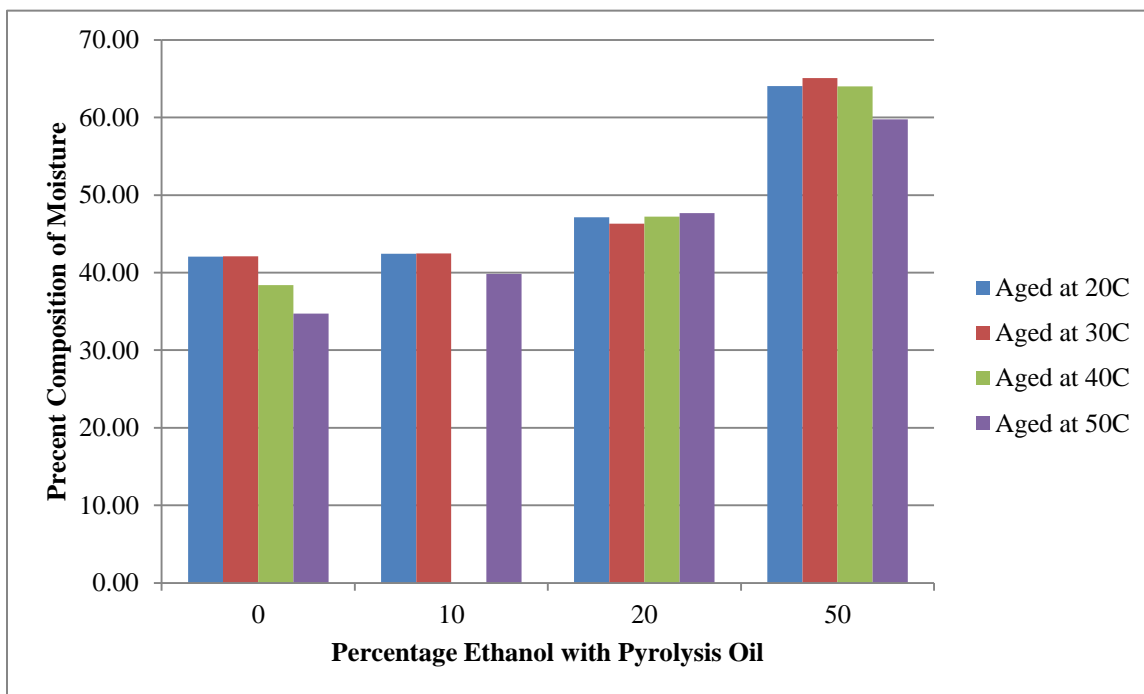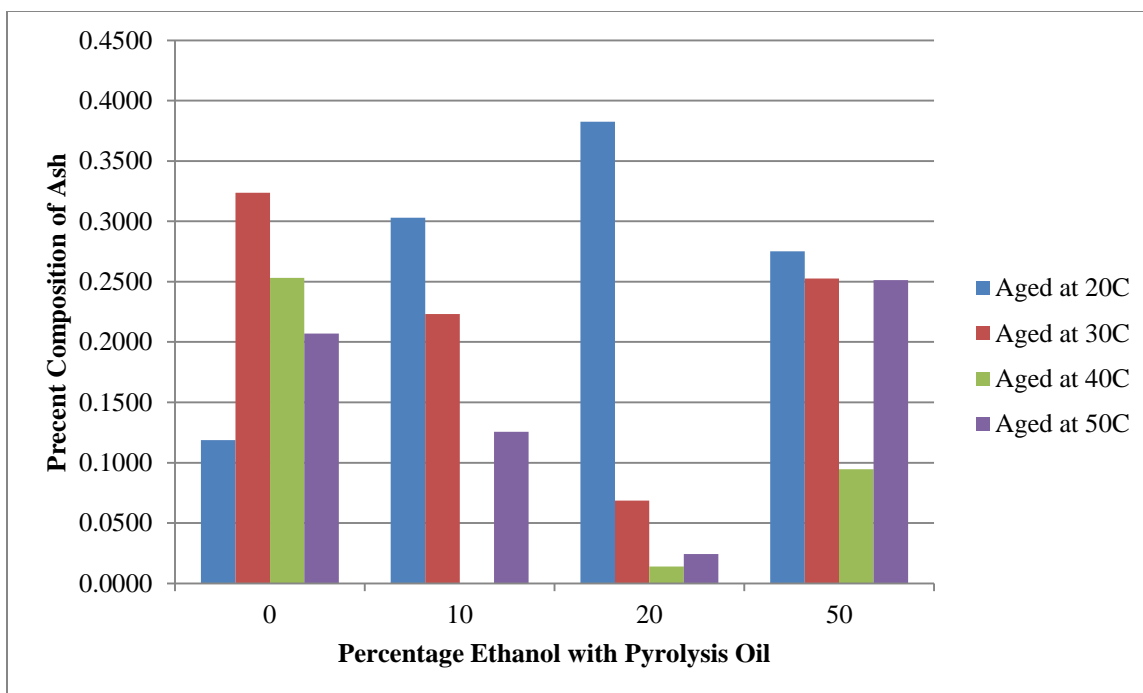

Figure 19: Weight percentage of moisture in aged samples.
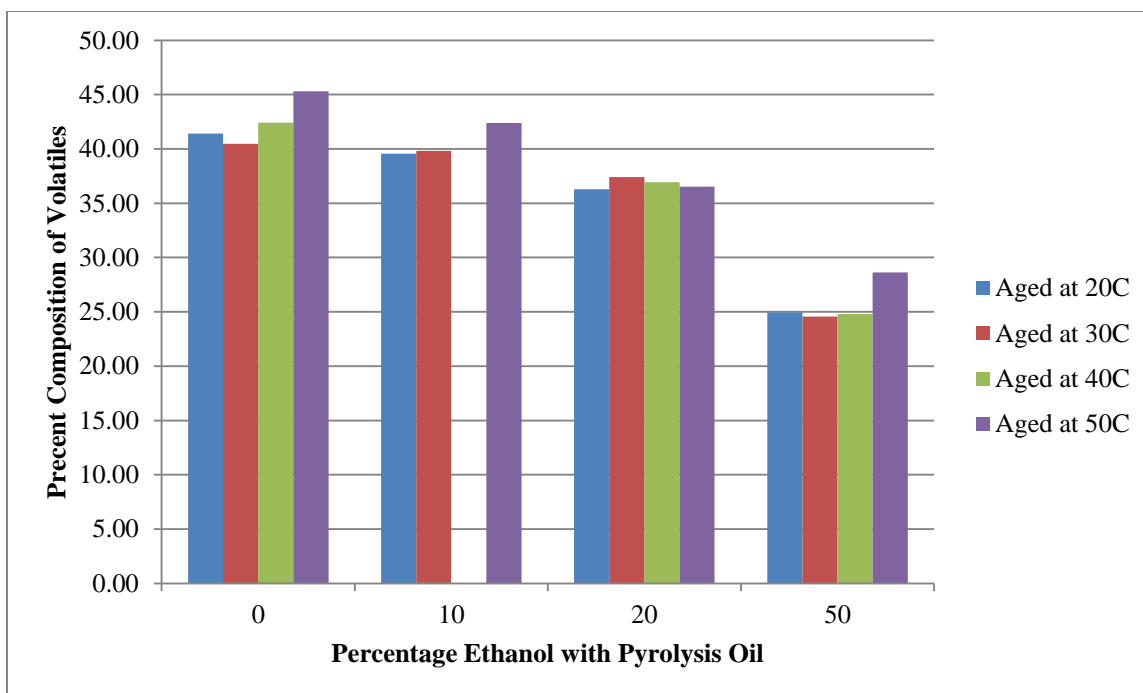
Figure 20: Weight percentage of volatiles in aged samples.

Figure 21: Weight percentage of fixed carbon in aged samples.

Figure 22: Weight percentage of ash in aged samples.

Table 12: Full TGA analysis for aged samples.

Sample	Moisture (wt%)	Volatiles (wt%)	Fixed Carbon (wt%)	Ash (wt%)
100% Pyrolysis Oil 20 C	42.05	41.41	16.45	0.1187
10% Ethanol 20 C	42.45	39.57	17.71	0.3031
20% Ethanol 20 C	47.13	36.29	16.22	0.3825
50% Ethanol 20 C	64.04	24.95	10.75	0.2751
100% Pyrolysis Oil 30 C	42.11	40.47	17.12	0.3238
10% Ethanol 30 C	42.49	39.84	17.47	0.2233
20% Ethanol 30 C	46.30	37.42	16.24	0.0685
50% Ethanol 30 C	65.08	24.55	10.13	0.2527
100% Pyrolysis Oil 40 C	38.41	42.42	18.89	0.2532
10% Ethanol 40 C	x	x	x	x
20% Ethanol 40 C	47.21	36.93	15.90	0.0140
50% Ethanol 40 C	64.01	24.79	11.11	0.0945
100% Pyrolysis Oil 50 C	34.72	45.30	19.79	0.2069
10% Ethanol 50 C	39.83	42.38	17.75	0.1257
20% Ethanol 50 C	47.66	36.52	15.82	0.0244
50% Ethanol 50 C	59.75	28.62	11.90	0.2514

These figures graphically depict the levels of composition of the four component groups. These figures do not show substantial differences between samples that were aged differently. Figure 19 shows that moisture percentage increases with the addition of ethanol. This is because ethanol is evaporated in the same temperature regime as water, causing it to be analyzed as moisture by this procedure. The resulting amounts are proportional to the effects caused by dilution with ethanol. The volatile components shown in Figure 20 are shown to be reduced by the addition of ethanol by an amount attributed to replacement of pyrolysis oil with ethanol, which would evaporate in the volatile regime. Fixed carbon, shown in Figure 21, is also reduced with ethanol in the same manner. These results indicate that the aging process used and mixtures with ethanol do not have effects outside of diluting the sample. The results for ash, shown in Figure 22, are far too inconsistent to be conclusive. This large variance is caused by the very small amounts of sample which remain in the form of ash compared to other constituents. It is also possible that ash is not nonuniformly distributed amongst the samples at the time they were prepared, despite mixing practices.

APPENDIX E. REID VAPOR PRESSURE TESTS

The Reid Vapor Pressure test (RVP) is an industry standard normally used to determine the quality of light distilled fuels such as gasoline to analyze their volatility performance. This is useful in adjusting composition for seasonal changes, for instance, a 'winter blend' will call for a higher volatility to help facilitate cold starting in automobiles. The apparatus used for the test consists of a set of temperature-controlled pressure chambers with pressure gauges. The procedure used for the test is specified by ASTM D323. A sample is cooled to 0° C (32° F), then put into the bottom segment of the chamber, shown in Figure 23, which is also cooled to a matching temperature beforehand. This chamber is then sealed and the apparatus is raised to a final temperature of 37.8° C (100° F), agitating periodically. The fuel is allowed to evaporate inside the chamber until reaching equilibrium vapor pressure. The total gauge pressure measured at the equilibrium represents the volatility measurement of the fuel. This test is different than the actual equilibrium vapor pressure because interactions between fuel and air in the chamber can affect the result, producing more useful results for certain applications.

Figure 23: Reid vapor pressure test apparatus, including water bath (left) and chamber (right).

The Reid Vapor Pressure test is a widely accepted measurement technique for studying the volatility of certain fuels as it pertains to combustion. Because of this, a set of samples was prepared for testing to better characterize the fuels used for this study. Samples included pure pyrolysis oil, 20% ethanol in pyrolysis oil, and #2 fuel oil, and pure ethanol for a comparison to the pyrolysis oil mixture. Unfortunately, the pure pyrolysis oil sample became too thick to pour in a timely fashion as called for the ASTM procedure, so the test

was applied only to the other three samples. The results are shown in Table 13: Reid vapor

pressure test results.

Table 13: Reid vapor pressure test results.

Fuel Sample	Measured Pressure (psi)
#2 Fuel oil	0.30
Ethanol	1.87
20% Ethanol Bio-oil	1.85

The results of this test are interesting in that there is a large difference between fuel

oil and pyrolysis oil mixtures that does not seem to have a large impact on combustion

properties. This is because the temperature ranges used for the test represent a very different

set of conditions than those seen by fuel droplets in a spray combustion environment. The

Reid Vapor Pressure test is used for volatile fuel such as gasoline where fuel is fully

evaporated in relatively cool air before entering the combustion chamber. This is not the

case in spray flames where droplets are often still evaporating even inside the flame zone,

with surrounding temperatures much higher than 100°F.

Another interesting finding of this test is that ethanol and mixtures of ethanol and

pyrolysis oil seem to have the same result. This is again due to an unusual application of a

test which has been developed for refined fuels. In refined fuels, all components have similar

vaporizing characteristics, because that is how they are sorted at the refinery. This causes the

substance to display a total vapor pressure that is representative of the whole sample. For a

mixed sample such as this one, the lighter components will continue evaporating until an

equilibrium is reached for that species, while heavier species contribute little to the vapor

composition. This results in a measure of only the most volatile substances in the mixture.

From this result and understanding this phenomenon, it can be safely concluded that

pyrolysis oil is not more volatile than ethanol.

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REFERENCES

1 "www.eia.gov" *U.S. Energy Information Administration energy consumption information*. Web. 17 April, 2013.

2 Moloodi, S. *Experimental Investigation of The Effects of Fuel Properties on Combustion Performance and Emissions of Biomass Fast Pyrolysis Liquid-Ethanol Blends in a Swirl Burner.* MS dissertation, University of Toronto, 2011.

3 Kuo, K.K., *Principles of Combustion*. 2005, New York: John Wiley & Sons.

4 Borman, G.L. and K.W. Ragland, *Combustion Engineering*. 1998, Singapore: McGraw-Hill.

5 Turns, S.R., *An Introduction to Combustion: Concepts and Applications*. 1996, New York: McGraw-Hill.

6 Law, C.K., *Combustion Physics*. 2006, New York: Cambridge University Press.

7 Williams, A., *Combustion of Liquid Fuel Sprays*. 1990, Boston: Butterworths.

8 Williams, A., *FUNDAMENTALS OF OIL COMBUSTION.* Progress in Energy and Combustion Science, 1976. **2**(3): p. 167-179

9 Onuma, Y. and M. Ogasawara. *Studies on the Structure of a Spray Combustion Flame*. in *Fifteenth Symposium (International) on Combustion*. 1975: The Combustion Institute.

10 Onuma, Y., M. Ogasawara, and T. Inoue. *Further Experiments on the Structure of a Spray Combustion Flame*. in *Sixteenth Symposium (International) on Combustion*. 1977: The Combustion Institute.

11 Burgoyne, J.H. and L. Cohen, *The Effect of Drop Size on Flame Propagation in Aerosols.* Proceedings of the Royal Society A, 1954. **225**: p. 375-392.

12 Lefebvre, A., *Atomization and Sprays*. 1988: Hemisphere Pub Combustion: An International Series.

13 Ashgriz, N., *Handbook of Atomization and Sprays.* 2011, New York: Springer.

14 Lefabvre, A., *Gas Turbine Combustion*. 1983, Washington: Hemisphere Pub. Corp.

15 LeFebvre, A.H., *Fuel Atomization, Droplet Evaporation, and Spray Combustion*, in *Fossil Fuel Combustion: A Source Book*, W. Bartok and A.F. Sarofim, Editors. 1991, John Wiley & Sons, Inc.: New York. p. 529-652.

16 Gupta, A.K., D.G. Lilley, and N. Syred, *Swirl Flows*. 1984, Turnbridge Wells: Abacus Press.

17 "www.epa.gov" *U.S. EPA information on exhaust sampling* Web. 17 April, 2013.

18 Longwell, J.P., *Interface Between Fuels and Combustion*, in *Fossil Fuel Combustion: A Source Book*, W. Bartok and A.F. Sarofim, Editors. 1991, John Wiley & Sons, Inc.: New York. p. 3-48.

19 Corporan, E., et al., *Emissions Characteristics of a Turbine Engine and Research Combustor Burning a Fischer-Tropsch Jet Fuel.* Energy & Fuels, 2007. **21**: p. 2615-2626.

20 Haynes, B.S., *Soot and Hydrocarbons in Combustion*, in *Fossil Fuel Combustion: A Source Book*, W. Bartok and A.F. Sarofim, Editors. 1991, John Wiley & Sons, Inc.: New York. p. 261-326.

21 Warnatz, J., U. Maas, and R.W. Dibble, *Combustion: Physical and Chemical Fundamentals, Modeling and Simulation, Experiments, Pollutant Formation*. 2001, New York: Springer.

22 Bowman, C.T., *Chemistry of Gaseous Pollutant Formation and Destruction*, in *Fossil Fuel Combustion: A Source Book*, W. Bartok and A.F. Sarofim, Editors. 1991, John Wiley & Sons, Inc.: New York. p. 529-652.

23 Brown, R.C., *Biorenewable Resources: Engineering New Products from Agriculture*. 2003, Ames, IA: Blackwell Publishing Co.

24 Roel J. M. Westerhof, Derk W. F. (Wim) Brilman, Wim P. M. van Swaaij, and Sacha R. A. Kersten*, Effect of Temperature in Fluidized Bed Fast Pyrolysis of Biomass: Oil Quality Assessment in Test Units.* Industrial & Engineering Chemistry Research, 2010. **49** (3), p. 1160-1168.

25 Charles A. Mullen, Akwasi A. Boateng, Neil M. Goldberg, Isabel M. Lima, David A. Laird, Kevin B. Hicks, *Bio-oil and bio-char production from corn cobs and stover by fast pyrolysis*, Biomass and Bioenergy, 2010. **34** (1), p. 67-74.

26 David A. Laird, *The Charcoal Vision: A Win–Win–Win Scenario for Simultaneously Producing Bioenergy, Permanently Sequestering Carbon, while Improving Soil and Water Quality* Agronomy Journal 2008. **100** (1), p. 178-181.

27 Johannes Lehmann, *Black is the new green*, Nature 2006. **442** (10), p. 624-626.

28 Linghong Zhang, Chunbao (Charles) Xu, Pascale Champagne*, Overview of recent advances in thermo-chemical conversion of biomass,* Energy Conversion and Management, 2010. **51** (5), p. 969-982.

29 Perlack, Robert D., *Biomass as feedstock for a bioenergy and bioproducts industry: the technical feasibility of a billion-ton annual supply*. Oak Ridge National Lab, TN, 2005

30 Chiaramonti, David, Anja Oasmaa, and Yrjö Solantausta. *Power generation using fast pyrolysis liquids from biomass,*Renewable and Sustainable Energy Reviews 2007. **11** (6), p. 1056-1086.

31 Huffman, D.R., A.J. Vogiatzis, and D.A. Clarke, *Combustion of Bio-Oil*, in *Bio-Oil Production and Utilization*, A.V. Gridgwater and E. Hogan, Editors. 1996, CPL Press. p. 227-235.

32 Preto, F., P.E.G. Gogolek, and J.K.L. Wong, *Nozzle Testing and Development for Bio-Oil Combustion*, in *Science in Thermal and Chemical Biomass Conversion*, A.V. Bridgwater and D.G.B. Boocock, Editors. 2006, CPL Press. p. 1480-1490.

33 VanDeKamp, W.L. and J.P. Smart, *Atomisation and Combustion of Slow Pyrolysis Oils*, in *Advances In Thermochemical Conversion*, A.V. Bridgwater, Editor. 1994, Blackie Academic & Professional. p. 1265-1274.

34 Gust, S., *Combustion Experiences of Flash Pyrolysis Fuel in Intermediate Size Boilers*, in *Developments in Thermochemical Biomass Conversion*, A.V. Bridgwater and D.G.B. Boocock, Editors. 1997, Blackie Academic & Professional. p. 481-488.

35   Gust, S., *Combustion of Pyrolysis Liquids*, in *Biomass Gasification and Pyrolysis, State of the Art and Future Prospects*, M. Kalschmitt and A.V. Bridgwater, Editors. 1997, CPL Press. p. 498-503.

36   Shihadeh, A., et al. *Combustion Characterization of Wood-Derived Flash Pyrolysis Oils in Industrial-Scale Turbulent Diffusion Flames*. in *Proceedings of Biomass Pyrolysis Oil Properties and Combustion Meeting*. 1994. Estes Park, CO.

37   Oasmaa, A. and S. Czernik, *Fuel Oil Quality of Biomass Pyrolysis Oils*, in *Biomass: A Growth Opportunity in Green Energy and Value-Added Products*, R.P. Overend and E. Chornet, Editors. 1999, Elsevier. p. 1247-1252.

38   Oasmaa, A. and S. Czernik, *Fuel Oil Quality of Biomass Pyrolysis Oils - State of the Art for End Users.* Energy & Fuels, 1999. **13**: p. 914-921.

39   Oasmaa, A. and D. Meier, *Analysis, Characterisation and Test Methods of Fast Pyrolysis Liquids*, in *Biomass: A Growth Opportunity in Green Energy and Value-Added Products*, R.P. Overend and E. Chornet, Editors. 1999, Elsevier. p. 1229-1234.

40   Oasmaa, A., et al., *Norms and Standards for Pyrolysis Liquids. End-User Requirements and Specifications.* Energy & Fuels, 2005. **19**(5): p. 2155–2163.

41   Oasmaa, A. and D. Meier, *Characterisation, analysis, norms & standards. *, in *Fast Pyrolysis of Biomass: A Handbook*, A.V. Bridgwater, Editor. 2005, CPL Press: Newbury, UK.

42   Tzanetakis, T., Moloodi S., Farra N., Nguyen B., Thomson M.J., *Spray combustion and particulate matter emissions of a wood derived fast pyrolysis liquid-ethanol blend in a pilot stabilized swirl burner*. Energy & Fuels, 2011 **25** (4): p. 1405-1422.

43   Hallett W.L.H., Clark N.A., *A model for the evaporation of biomass pyrolysis oil droplets*, Fuel, 2006 **85** (4), p. 532-544.

44   Garcia-Perez, M., et al., *Spray Characterization of a Softwood Bark vacuum Pyrolysis Oil*, in *Science in Thermal and Chemical Biomass Conversion*, A.V. Bridgwater and D.G.B. Boocock, Editors. 2006, CPL Press. p. 1468-1479.

45   Wiemer, H.-J., et al., *Spray Characteristics for the Gasification of Pyrolysis Oil Slurries*, in *Science in Thermal and Chemical Biomass Conversion*, A.V. Bridgwater and D.G.B. Boocock, Editors. 2006, CPL Press. p. 1559-1564.

46   Chiaramonti, D., et al. *Sprays of biomass pyrolysis oil emulsions: Modeling and experimental investigation. Preliminary results and modeling*. 14th European Biomass Conference. Paris: Blackie Academic Press. 2005.

47   Wissmiller, D. *Pyrolysis oil combustion characteristics and exhaust emissions in a swirl-stabilized combustor*. PhD Diss., Iowa State University, 2010.

48   Kyto, M., P. Martin, and S. Gust, *Development of Combustors for Pyrolysis Liquids*, in *Pyrolysis and Gasification of Biomass and Waste*, A.V. Bridgwater, Editor. 2003, CPL Press. p. 187-190.

49   Oasmaa, A., M. Kyto, and K. Sipila, *Pyrolysis Oil Combustion Tests in an Industrial Boiler*, in *Progress in Thermochemical Biomass Conversion*, A.V. Bridgwater, Editor. 2001, Blackwell Science Ltd. p. 1468-1481.

50   Rossi, C., et al., *Combustion Tests of Bio-Oils Derived From Biomass Slow Pyrolysis*, in *Advances In Thermochemical Conversion*, A.V. Bridgwater, Editor. 1994, Blackie Academic & Professional. p. 1205-1213.

51   VanDeKamp, W.L. and J.P. Smart, *Evaluation of the Combustion Characteristic of Pyrolytic Oil Derived from Biomass*, in *Proceedings of Energy from Biomass Contractors' Meeting*. 1991: Florence, Italy.

52   Solantausta, Y., et al., *Low Boiler Emissions with a Cost Competitive Liquid Biofuel*, in *2nd World Conference and Technology Exhibition on Biomass for Energy, Industry and Climate Protection Rome*. 2004: Rome, Italy.

53   Wickboldt, P., R. Strenziok, and U. Hansen, *Investigation of Flame Characteristics and Emission of Pyrolysis Oil in a Modified Flame Tunnel*, in *Biomass: A Growth Opportunity in Green Energy and Value-Added Products*, R.P. Overend and E. Chornet, Editors. 1999, Elsevier. p. 1241-1246.

54   Huffman, D.R., A.J. Vogiatzis, and A.V. Bridgwater, *The Characterization of Fast Pyrolysis Bio-Oils*, in *Advances in Thermochemical Conversion of Biomass*, A.V. Bridgwater, Editor. 1994, Blackie Academic & Professional: Glasgow. p. 1095-1102.

55   Tzanetakis, T., Farra, N., Moloodi, S., Lamont, W., McGrath, A., & Thomson, M. J. *Spray combustion characteristics and gaseous emissions of a wood derived fast pyrolysis liquid-ethanol blend in a pilot stabilized swirl burner*. Energy & Fuels, 2010 **24** (10): p. 5331-5348.

56   Tzanetakis, T. *Spray combustion characteristics and emissions of a wood derived fast pyrolysis liquid-ethanol blend in a pilot stabilized swirl burner*. Mechanical and Industrial Engineering, University of Toronto, PhD Thesis 2011.

57   Stamatov, V., et al., *Origin of NOx Emission from Bio-Oil Flames*, in *Science in Thermal and Chemical Biomass Conversion*, A.V. Bridgwater and D.G.B. Boocock, Editors. 2006, CPL Press. p. 1504-1510.

58   Stamatov, V., D. Honnery, and J. Soria, *Combustion properties of slow pyrolysis bio-oil produced from indigenous Australian species.* Renewable Energy, 2006. **31**(13): p. 2108-2121.

59   Andrews, R.G., et al., *Results of Industrial Gas Turbine Tests Using a Biomass-Derived Fuel*, in *Making a Business from Biomass in Energy, Evironment, Chemicals, Fibers, and Materials*, R.P. Overend and E. Chornet, Editors. 1997, Pergamon. p. 425-435.

60   Andrews, R., et al. *Firing Fast Pyrolysis Oil in Turbines*. in *Biomass Pyrolysis Oil Properties and Combustion Meeting*. 1994. Estes Park, CO.

61   Andrews, R.G., S. Zukowski, and P.C. Patnaik, *Feasibility of Firing and Industrial Gas Turbine Using a Bio-Mass Derived Fuel*, in *Developments in Thermochemical Biomass Conversion*, A.V. Bridgwater and D.G.B. Boocock, Editors. 1997, Blackie Academic & Professional. p. 495-506.

62   Strenziok, R., U. Hansen, and H. Kunstner, *Combustion of Bio-Oil in a Gas Turbine*, in *Progress in Thermochemical Biomass Conversion*, A.V. Bridgwater, Editor. 2001, Blackwell Science Ltd. p. 1452-1458.

63   Kasper, J.M., G.B. Jasas, and R.L. Trauth, *Use of Pyrolysis Derived Fuel in a Gas Turbine Engine.* ASME Paper, 1983. **83-GT-96**.

64   Lopez Juste, G. and J.J. Salva Monfort, *Preliminary test on combustion of wood derived fast pyrolysis oils in a gas turbine combustor.* Biomass and Bioenergy, 2000. **19**(2): p. 119-128.

65   Solantausta, Y., et al., *Wood Pyrolysis Liquid as Fuel in a Diesel Power Plant.* Bioresource Technology, 1993. **46**(1-2): p. 177-88.

66   Solantausta, Y., et al. *Preliminary Tests with Wood-Derived Pyrolysis Liquid as Fuel in a Stationary Diesel Engine*. in *Biomass Pyrolysis Liquid Properties and Bomsution Meeting*. 1994. Estes Park, CO.

67   Shihadeh, A. and S. Hochgreb, *Diesel engine combustion of biomass pyrolysis oils.* Energy and Fuels, 2000. **14**(2): p. 260-274.

68   Shihadeh, A. and S. Hochgreb, *Impact of Biomass Pyrolysis Oil Process Conditions on Ignition Delay in Compression Ignition Engines.* Energy & Fuels, 2002. **16**: p. 552-561.

69   Gros, S. *Pyrolysis Liquid as Diesel Fuel*. in *Seminar on Power Production from Biomass II*. 1995. Espoo, Finland.

70   Jay, D., et al. *Wood Pyrolysis Oil for Diesel Engines*. in *1995 Fall Technical Conference*. 1995. Milwaukee, WI: ASME.

71   Calabria, R., F. Chiariello, and P. Massoli, *Combustion fundamentals of pyrolysis oil based fuels.* Experimental Thermal and Fluid Science, 2007. **31**: p. 413–420.

72   D'Alessio, J., et al., *Thermo-Optical Investigation of Burning Biomass Pyrolysis Oil Droplets*, in *27th Symposium (International) on Combustion/The Combustion Institute*. 1998.

73   Shaddix, C.R. and S.P. Huey, *Combustion Characteristics of Fast Pyrolysis Oils Derived From Hybrid Poplar*, in *Developments in Thermochemical Biomass Conversion*, A.V. Bridgwater and D.G.B. Boocock, Editors. 1997, Blackie Academic & Professional. p. 465-480.

74   Shaddix, C.R. and P.J. Tennison, *Effects of char content and simple additives on biomass pyrolysis oil droplet combustion.* Proceedings of the 1998 27th International Symposium on Combustion, 1998. **2**: p. 1907-1914.

75   Wornat, M.J., B.G. Porter, and N.Y.C. Yang, *Single droplet combustion of biomass pyrolysis oils.* Energy & Fuels, 1994. **8**(5): p. 1131-1142.

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