EXPERIMENTAL INVESTIGATION OF MOLTEN SALT TORREFACTION AND THE DEVELOPMENT OF A LAB-SCALE TORREFACTION METHODOLOGY

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Experimental Investigation of Molten Salt Torrefaction and the
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MASTER OF SCIENCE

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ABSTRACT

A novel torrefaction methodology using molten salts as a means to reduce torrefaction temperatures was investigated. A lab-scale molten salt torrefaction methodology was developed to consistently torrify biomass; involving the development of a new torrefaction apparatus and investigation of key variables such as residence time, torrefaction temperature, salt-to-biomass ratio, and biomass particle size. Subsequently, this methodology was used to evaluate the effect of temperature and determine which component of the salt blend is the most influential on torrefaction levels. Temperatures ranging from 180 °C to 240 °C and salt blends with lithium nitrate, sodium nitrate, and potassium nitrate content ranging from 20 wt%-40 wt%, 0 wt%-20 wt%, and 50 wt%-70 wt% respectively were investigated. Molten nitrate salts do have the potential to reduce torrefaction temperatures up to 65 °C, while the torrefaction level of the biomass improves with increasing torrefaction temperatures and lithium nitrate content.

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1. INTRODUCTION

Torrefaction is a mild heat pre-treatment process of biomass in an inert environment. Traditionally the input energy required for biomass torrefaction is provided by combusting part of the raw biomass feedstock or fossil fuels [4,5]. Doing such reduces the overall yield and the amount of fossil fuels displaced by using torrefied biomass. Solar energy is a renewable energy source capable of supplying the input energy required to drive the torrefaction process without decreasing the yield. However, one drawback hindering the use of solar as an energy source is the location differences between solar and biomass resources. This location disconnect makes it difficult to consistently obtain temperatures necessary for torrefaction in regions with plentiful biomass resources. Thus, to use solar energy to torrify biomass, there is a need to develop a lower temperature torrefaction process. This research study is based on the hypothesis that by torrefying biomass in a molten salt bath, similar levels of torrefaction can be achieved at temperatures significantly lower than required for traditional torrefaction methods. This is a new, novel method of torrefaction and is, to the author's knowledge, one of the first studies on torrefaction in molten salts. As such, there are a number of unknowns this study helps to clarify through the development and use of a consistent and successful molten salt torrefaction methodology. Continued success of this process could lead to a new way of integrating two significant renewable resources, solar energy and biomass resources.

The research conducted to develop a lab scale molten salt torrefaction methodology and investigate the effect of altering the content of each component salt within the molten salt blend is detailed in the 5 remaining sections. The second section provides a look at traditional and alternate torrefaction methodologies, the latter of which aim to reduce torrefaction temperatures and integrate solar energy. Additionally, an insight into why torrefaction temperatures need to be reduced to effectively incorporate solar energy will be provided as well as a recent work with higher temperature biomass conversion processes successfully using molten salts to reduce reaction temperatures. The third section provides some context and lays out the objectives designed to develop and a lab-scale molten salt torrefaction methodology and evaluate the effect of the component salts on the torrefaction process. The fourth section includes methodology that will be used to meet the objectives in regards to the equipment and materials that were used, the processes undertaken to torrify biomass, the design of experiments to investigate key torrefaction variables and issues that arose with the torrefaction process as well as investigating salt composition and temperature variation, and the metrics used to characterize the torrefaction level of the biomass. The fifth section details the results of this research. It looks at torrefaction levels obtained through the molten salt torrefaction procedure and traditional methods as a way to determine how successful the developed methodology is and areas where it can be improved. Additionally, the results of varying the salt blend composition and torrefaction temperatures is detailed in this section. The sixth section recaps the results of this research and offers some recommendations for future research on molten salt torrefaction.

2. LITERATURE REVIEW

2.1. Biomass as an Energy Fuel

According to the United States Energy Information Administration, in 2018, North Dakota's energy dependency was heavily centered on fossil fuels; roughly 66 % of the state's energy was derived from coal and less than 26 %, roughly 140 trillion BTU's, came from renewable resources, primarily wind [6]. North Dakota has the potential to increase its renewable energy fraction by tapping into a significant renewable resource available within the state: biomass. The significant agricultural production of North Dakota, contributing ~8 % of the annual crop production of the United States [7], yields high quantities of biomass residue, which could be used as a fuel. Since this residue is unfit for human consumption, using it for energy would not increase the competition between food and energy end-uses for biomass resources [8]. Biomass is an attractive source of renewable energy due to its carbon neutral nature and adaptability. When biomass is used as an energy fuel, 100 % of the carbon released into the atmosphere was recently removed through photosynthesis [4,9]. A number of processing techniques have been developed which allow biomass to be used in a wide variety of industries; ranging from electricity production to transportation [8,10,11].

Although biomass is an attractive fuel for its carbon neutrality, there are drawbacks to its use as an energy source. Compared to fossil fuels, biomass has a low energy density, is very hydrophilic, contains significantly more moisture, and is heterogeneous. These properties are undesirable and limit the use of biomass as an energy fuel. The low energy density of raw biomass reduces economic feasibility as it is expensive to harvest and transport. One hundred miles is generally the break-even point where harvest and transportation costs exceed the value of energy contained within raw biomass [11,12]. As a hydrophilic substance which naturally contains a significant level of moisture, biomass is highly susceptible to rotting; further reducing energy content and economic feasibility [4,9,11,13]. Physically, biomass is a very heterogeneous and fibrous material; requiring significant handling considerations. One such consideration is in regulating energy output due to the non-uniform combustion characteristics of raw biomass; non-uniform combustion is caused by its heterogeneity. Additionally, the fibrous nature of biomass increases the energy required to grind it to a usable size [4,9,11,13].

2.2. Traditional Torrefaction

Torrefaction is a thermochemical conversion process which reduces many of biomass's undesirable traits hindering its efficient use as a fuel source. The desired product of torrefaction is a coal-like char which contains approximately 70 % of the feedstock's mass but retains 90 % of the feedstock's energy. Product char is more energy dense, less hydrophilic, and less susceptible to bio-degradation than the raw biomass feedstock. As well, the char is less fibrous, more homogeneous, and a significantly cleaner burning fuel [14,15]. Improvements in the fuel properties of torrefied biomass are due to the thermal decomposition of hemicellulose and cellulose. Hemicellulose decomposes at temperatures between 190 °C and 320 °C while cellulose decomposes at temperatures between 280 °C and 400 °C [13,16]. The mass and energy lost by the feedstock are released as volatiles during decomposition. The released volatiles include compounds such as steam, alcohols, sugars, CO, CO_2, H_2, and CH_4 [17].

A variety of torrefaction conditions have been researched including torrefaction temperatures, residence times, and biomass species. Research on torrefaction temperatures ranges from 200 °C to 320 °C; however, recommended torrefaction temperatures are between 250 °C and 300 °C [9,16,18–21]. At torrefaction temperatures below 250 °C, little-to-no torrefaction occurs and temperatures greater than 300 °C decompose the feedstock too severely. The product char contains a significantly reduced fraction of the feedstock's original energy content [9,16,18–21].

For most biomass species, optimal energy yields are experienced at temperatures between 260 °C and 275 °C [11,19]. A number of studies have investigated a variety of residence times ranging from 15 minutes to 3 hours [15,16,21–23]. Depending on the species of biomass and torrefaction temperatures, a residence time between 20 and 60 minutes will sufficiently torrify the feedstock without wasting energy to keep the reactor at temperature after the torrefaction reaction has completed [13,15,16,19,21–23].

In reference to torrefaction, biomass species are separated into two categories: woody and non-woody. Woody biomass is more difficult to torrify than non-woody biomass. This is due to the hemicellulose content of both materials, which the torrefaction procedure decomposes. Non-woody biomass is easier to torrify because the hemicellulose content is significantly greater for woody biomass than non-woody biomass. Torrefaction of woody biomass requires higher temperatures and longer residence times to achieve similar torrefaction levels as non-woody biomass [4,18].

Traditionally, the energy needed to drive thermochemical biomass conversion processes, i.e. torrefaction, pyrolysis, and gasification, has been obtained through combustion of a portion of the feedstock or fossil fuels [4]. Combusting raw feedstock or fossil fuels to supply energy for torrefaction significantly reduces the overall energy yields and the amount of fossil fuels offset by biomass. One example of this is with the gasification of prairie grass. When a portion of the feedstock is used to supply the process energy, the theoretical maximum energy yield dropped significantly to only 65 % of the feedstock's initial energy [5].

2.2.1. Uses for Torrefied Biomass

One use for torrefied biomass is co-firing with coal in energy producing facilities [11]. Although raw biomass can be combusted with coal, torrefied biomass, which has fuel properties more similar to coal, requires fewer adjustments to existing facilities to incorporate it. Improved energy density, homogeneity, ease of grinding and reduced moisture content improves the economics of transport, storage, and integration with minimal alterations to current procedures [11]. Another use for torrefied biomass is as a preprocessed feedstock for pyrolysis and gasification; higher temperature, thermochemical biomass conversion processes [24,25]. Biomass gasification occurs at temperatures greater than 800 °C; producing non-condensable gasses, namely hydrogen and carbon monoxide, through the partial oxidation of the feedstock [9,26]. Pyrolysis occurs in an inert environment at temperatures between 450 °C and 900 °C. The main product from pyrolysis is bio-oil, a liquid fuel which can be further refined into more volatile fuels [27,28]. Both processes rely on rapid heating and decomposition of the solid biomass into liquid or gaseous forms. Using torrefied biomass as the feedstock for these processes improves their efficiency through a reduction in grinding energy and input energy [4,18,26]. The rapid heating requirement of pyrolytic and gasification requirements requires the feedstock to be ground to particles measuring only a few microns in size. Torrefied biomass is ground much easier than a raw feedstock due to the reduction of rigidity and the fibrous nature of raw biomass [9,13]. Through torrefaction, many undesirable components of raw biomass have already been removed from the feedstock. Prior removal of those components slightly reduces the needed input energy while also improving product purity and energy density [9,13,29]. The greatest improvements in efficiency are experienced when the energy needed to torrify the raw feedstock is obtained from the lower quality, waste heat that is unusable for the primary reaction [22].

2.3. Alternate Torrefaction Methods

A handful of torrefaction studies have investigated alternate methods of torrefaction as a means to improve the efficiency of the torrefaction process.

2.3.1. Solar Torrefaction

Solar energy is an attractive energy source for torrefaction. A couple of the limited research studies performed on solar torrefaction theorize that there is the potential for an upgrading effect on the energy content of the feedstock using solar energy [29,30]. This effect has not been studied for solar torrefaction, but has been studied and confirmed for pyrolysis and gasification. During high temperature thermal treatment, solar energy is stored within the feedstock as it is converted into bio-oil and biogas. The result is useable products containing up to 30 % more energy per unit mass than the raw feedstock [5,31]. In addition to upgrading the biomass's energy content, the use of solar energy improves the overall energy yield of the process. Traditional methods combust a portion of the feedstock to provide the input energy, whereas solar energy allows for 100 % of the feedstock to be torrefied [29,32].

Since the 1980's, a number of studies have examined using concentrated solar energy to produce the high-temperature process heat needed to drive thermal biomass treatment processes, specifically pyrolysis and gasification [28]. However, to the author's knowledge, only a limited number of studies have investigated harnessing solar energy for torrefaction. These studies are focused around the Mediterranean and in western sub-Saharan Africa [29,30,32,33]. Unlike the majority of the world, these areas have sufficient solar resources to achieve the temperatures necessary for torrefaction and have an adequate supply of biomass resources. These studies used concentrators of the parabolic trough, parabolic dish, and linear mirror designs [29,30,32,33]. The concentration ratio was reported for only the linear mirror; it had a concentration ratio of 20 [32]. Each design was able to reach a steady state operating temperature between 250 °C and 300 °C inside the torrefaction reactor. Various types of biomass were successfully torrefied using solar energy; including woods [33], hay [32], olive oil extraction residue [29], and ethanol plant residues [30]. Torrefaction levels were identical for biomass torrefied using solar energy and biomass torrefied using combustion to provide the input energy. These studies demonstrate that concentrated solar energy can be used to provide the process energy for torrefaction in regions where both solar and biomass resources are adequate [29,30,32,33].

A likely reason for the limited development of solar torrefaction procedures in the United States is the spatial disconnect between the biomass and solar resources; solar resources are not ample in areas with large reserves of waste biomass [28,34]. Figure 2.1 highlights the disconnect between solar and biomass resources among regions of the United States. Figure 2.1 (a) shows the annual daily average solar irradiance in the United States; regions highlighted in darker hues receive more solar irradiance. Figure 2.1 (b) shows the available waste biomass resources in the United States counties which are grey or yellow in color have very little biomass resources available while red and blue counties have abundant waste bio-resources available. The Southwest (dark red) receives significant amounts of solar energy each day, but biomass resources (mostly gray) are sparse across much of the region. On the other hand, the Midwest has ample waste biomass resources (mostly blue and red), but receives significantly lower levels of daily solar radiation (beige and yellow).

Another likely reason solar torrefaction has not become a prominent research topic is the fact that solar energy needs concentration to effectively reach temperatures high enough to torrify biomass [28,34]. At the present time, the costs associated with concentrating solar energy to the

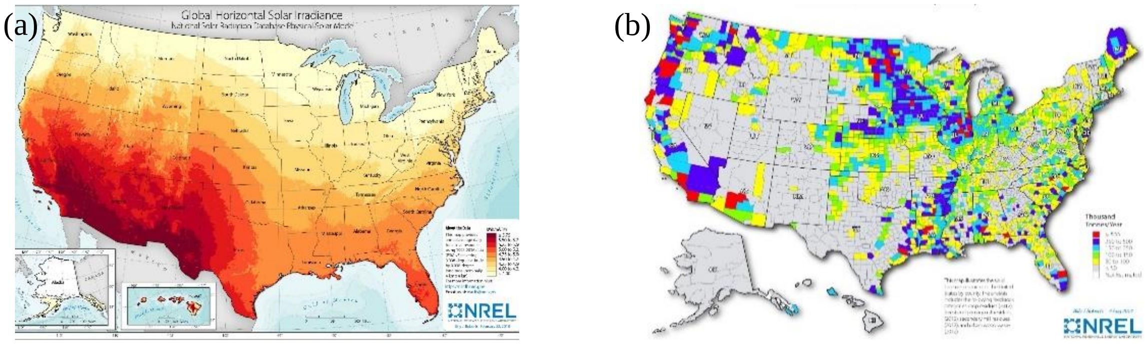

Figure 2.1: Map of (a) solar irradiance [1] and (b) waste biomass resources [2] in the United States

level needed for torrefaction outweighs its benefits. It is currently more economically feasible to combust a portion of the biomass to provide the input energy for torrefaction. Figure 2.2 relates the receiver temperature to the solar concentration ratio needed to achieve this temperature. To reach temperatures of 250 °C (red dot) and 300 °C (green dot), the upper and lower limit of the recommended temperatures for traditional torrefaction methods, the absolute minimum concentration ratio required to reach these temperatures is 10 and 15 respectively; these values were obtained using the Los Alamos National Laboratory’s plot digitizer. However, reducing torrefaction temperatures to 200 °C (blue dot) would reduce the minimum concentration ratio to only 5. Reducing the concentration ratio to only 5 would greatly improve the economic feasibility of solar torrefaction. Therefore, to efficiently and economically utilize solar torrefaction in the northern US, specifically the Midwest, a reduction in torrefaction temperatures is required.

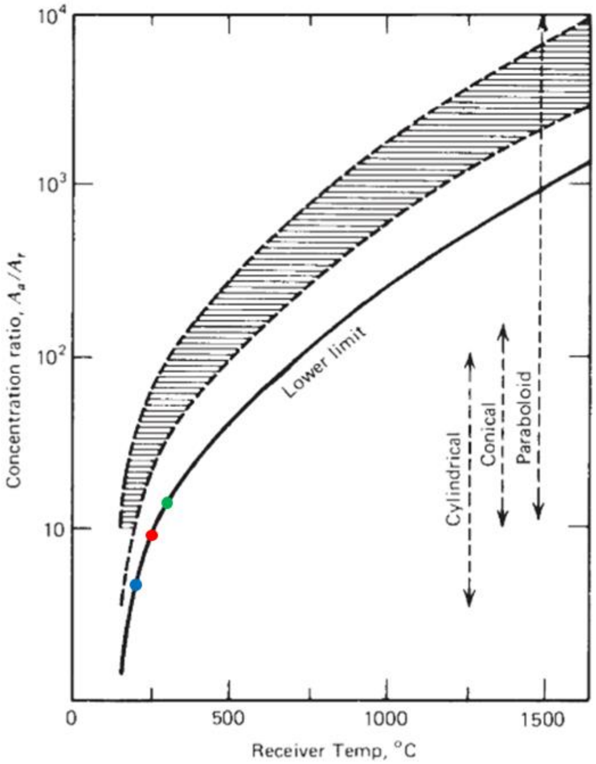

Figure 2.2: Relationship between receiver temperature and solar concentration ratio [3]

2.3.2. Hydro-Thermal Torrefaction

One technique which has shown promise in reducing torrefaction temperatures is wet torrefaction, alternately known as hydrothermal carbonization. At temperatures of 180 °C, researchers have been able to achieve levels of torrefaction similar to traditional methods at 250 °C while hydrothermal torrefaction at 260 °C results in torrefaction levels similar to 300 °C using traditional methods. [14,35,36]. Water contamination and high process pressures are two prominent challenges to overcome for commercialization of wet torrefaction [14]. Water requirements are significant for wet torrefaction; six-times the volume of water as biomass is required and the water is not reusable [14,36–38]. Wet torrefaction processes regularly experience pressures up to 22.1 MPa and occasionally reach pressures of 250 MPa. Pressures this great significant increase the cost of components in the facility [14] and require safety considerations when designing wet torrefaction reactors and commercial grade facilities [35,36,38,39].

2.4. Molten Salt Biomass Conversion Processes

The main hypothesis of the present work is that torrefaction temperatures can be reduced by utilizing a molten salt catalyst. Unlike wet torrefaction, molten salt torrefaction would occur at atmospheric conditions and the process catalyst would be reusable [14,40,41]. To the author’s knowledge, there is only one prior study on the use of molten salts for torrefaction. This study, focused primarily on pretreatment methods to improve the penetration of the molten salt into bamboo and leucaena during torrefaction. Additionally, the study investigated reducing torrefaction reaction times using a molten eutectic blend of potassium acetate and sodium acetate salts to improve heat transfer to the feedstock. This method was studied at a temperature of 300 °C. The study was successful in at least partially torrefying biomass in as little as 10 minutes. Using a scanning electron microscope, the researchers concluded that biomass torrefied in molten salts appeared to have decomposed from its raw state, indicating torrefaction has occurred.

However, the higher heating value, fixed carbon content, and other important properties related to using the torrefied biomass as a fuel are not reported [42].

The vast majority of research on using molten salt blends to catalyze thermochemical biomass conversion processes occurs with pyrolysis and gasification. Results indicate that alkali metal cations within the salt blends catalyze the process reactions while the higher thermal conductivity of salt blend improves heat transfer to the feedstock [31,40]. The use of a binary eutectic blend of sodium and potassium carbonates showed improved product yields and heat transfer to the feedstock at standard gasification temperatures [43]. Other studies have utilized a ternary eutectic blend of lithium, sodium, and potassium carbonate salts. These studies report increases in gasification reaction rates and biogas yields at temperatures 300 °C less than control studies performed under autothermal conditions [40,44]. Autothermal gasification occurs when the combustion of feedstock to provide the input energy occurs in the same reactor. Oxygen is introduced into the gasifier at a rate such that 20 %-30 % of the feedstock is combusted.

Pyrolysis studies have utilized an assortment of molten salt blends composed of various cations (sodium, lithium, zinc, iron, and potassium) and anions (nitrate, fluoride, chloride, and carbonate). Improved product yields, increased reaction rates, and increased energy yields at reduced temperatures were reported [45,46]. Similarly to gasification studies the addition of the lithium cation to the blends containing the potassium and sodium cations significantly improved the reaction rate and product yields [45,46]. The addition of the iron cation did little to influence reaction temperatures and rates [45]. However, the zinc and potassium chloride blend showed significantly improvements in the reaction rate and decreases in reaction temperatures over traditional methods. In fact, the results were identical to, but slightly better than, the lithium, sodium, and potassium carbonate salt blend [45,46].

Both pyrolysis and gasification process reactions occur more thoroughly and rapidly when lithium cations are present in the salt blends [40,44–46]. Previous research theorizes a couple of reasons that the addition of the lithium cation improves molten salt gasification and pyrolysis. One reason for the improvement with lithium is that lithium cations are more electronegative than the other alkali metal cations. This is due to lithium having less electrons and electron shields surrounding the nucleus of the atom, resulting in a shorter distance between the nucleus of the lithium cation and the molecules it is bonding to. The decreased distance increases the bond strength, and thus the catalytic effect [47]. A second theory is that the small size of the lithium ion allows it to move through smaller pores in the biomass and penetrate deeper into the biomass [45]. An additional benefit to of using a salt blend containing a lithium component is a significant reduction in the corrosive properties of the blend; corrosion rates of various stainless steel alloys drops to below 1 mm/year when lithium is included in the blend [48]. For the reasons presented above, it is believed that salt blends maximizing the lithium cation content will improve torrefaction levels by the greatest margin at a given temperature.

2.5. Low Melting Temperature Salt Blends

Prior to the start of this study, there was no published literature on torrefaction utilizing molten salts. The lack of precedence required the selection of a salt blend which met the following conditions:

1) Contain lithium cation
2) Melt below 150 °C
3) Thermally stable at temperatures up to 320 °C

It was desired for the blend to contain lithium, due to the reduced corrosive properties and positive results from higher temperature studies using molten salt blends containing the lithium cation. Of the blends previously used for pyrolysis and gasification studies, only the lithium, sodium, and potassium chloride and lithium, sodium, and potassium fluoride salt blends met this criteria [44,49–51]. Additionally, the selected salt blend needed to melt at temperatures significantly below traditional torrefaction temperatures. This ensures a completely liquid catalyst at process temperatures as low as 180 °C; the low end of the temperature range obtained with wet torrefaction [14,36]. A melt temperature of 150 °C was selected because it is well below this threshold; none of the previously used salt blends melted at or below 150 °C [44,49–51]. At a minimum, the molten salt blend needed to be thermally stable across all torrefaction temperatures generally researched; the upper limit of which is 320 °C. All of the previously used salt blends exceed this threshold and are thermally stable to at least 500 °C [44,49–51].

Since no previously used salt blend meets the requirements for torrefaction conditions, the salt selection process required expanding to new salts, outside the prior gasification and pyrolysis literature. One group of salt blends which meets the desired criteria are composed of lithium, sodium, and potassium nitrates. One blend composed of these salts that meets all three conditions is the ternary eutectic blend with respective compositions of 25.92 wt%, 20.01 wt%, and 54.07 wt% [52]; it contains the lithium cation, melts at 116 °C, and is thermally stable at temperatures up to 500 °C [52,53]. Twenty additional blends composed of these principal salts were identified which are thermally stable at high temperatures and melt below 160 °C. Table 2.1 details the four blends selected to expand the knowledge on how each salt component effects torrefaction levels. Of the blends selected, the lithium nitrate content varies from 20 wt% to 40 wt%, sodium nitrate content varies from 0 wt% to 20 wt% and potassium nitrate varies from 50 wt% to 70 wt% [54]. One benefit to using salt blends composed of lithium, sodium, and potassium nitrate is the mild toxicity of nitrate salts, especially compared to chloride and fluoride salts. Additionally, significant research has been conducted indicating these blends are compatible

Table 2.1: Selected salt blend compositions

Salt Blend	**2**	**3**	**4**	**5**
LiNO3 wt%	20	30	30	40
NaNO3 wt%	20	20	0	0
KNO3 wt%	60	50	70	60

with solar thermal energy production and storage. The high heat capacities of lithium, sodium, and potassium nitrate salt blends allows for the storage of thermal energy during daylight hours, and continued operation through the night [55,56].

2.6. Literature Summary

Biomass is an attractive energy source which has some drawbacks to its use as an energy fuel. Torrefaction is a proven procedure which improves the fuel properties and reduces the handling considerations necessary to integrate biomass necessary into existing procedures. Currently there are a couple alternate torrefaction methods. Hydrothermal torrefaction uses water under extreme pressure to lower torrefaction temperatures, solar torrefaction utilizes solar energy to drive the torrefaction procedure, reducing the need to combust a portion of the feedstock to drive the torrefaction procedure. Solar torrefaction is a promising concept because using solar energy to drive the torrefaction reaction allows 100 % of the feedstock to be torrefied and there is the potential to upgrade the total energy content of the biomass through the storage of solar energy. However, there is a disconnect between the location of solar and biomass resources in this country. By reducing torrefaction temperatures, solar energy becomes a more viable option to torrify biomass in northern climates where biomass resources are abundant but solar resources are not. Using molten salts as an improved heat transfer medium and catalyst has the potential to achieve this goal. Molten salts have successfully been used to improve reaction rates and product yields while also reducing the reaction temperatures of higher temperature biomass conversion processes. However, with only one study briefly touching on the topic of molten salt torrefaction, there is a large gap in the knowledge on this topic. The present study aims to fill in a portion of this gap by developing a successful lab scale torrefaction methodology, investigating variables which are key to torrefaction, and investigating the effect temperature and salt blend composition variation has on torrefaction levels.

3. RESEARCH OBJECTIVES

From the available literature there is little research conducted on the use of molten salts as a torrefaction catalyst. One study has been performed investigating the use of acetate salts as a catalytic medium [42]. However, there are no prior studies investigating torrefaction using nitrate salt blends. Nitrate salts are appealing as a torrefaction medium because they are commonly used to store solar energy due to their low melting point, energy storage capability, and thermal conductivity [55]. As well, there is no available literature detailing molten salts as a means of reducing torrefaction temperatures nor has methodology been developed to incorporate molten salts into the torrefaction procedure. Thus, there is a current gap in the knowledge that is limiting the potential for solar torrefaction of biomass in regions with good biomass resources.

The goal of this project is to investigate the hypothesis that torrefaction in molten salts can reduce the reaction temperature. As well, experimentally identify the key aspects of torrefaction in a molten salt, thereby fulling the current gas in the knowledge. The design and focus of each consecutive objective depends on the results obtained from the previously completed objective(s). To achieve the goals of the study, the research objectives are defined as:

1) Determine if molten nitrate salts reduce the torrefaction temperatures and identify the key parameters necessary to produce consistent and thoroughly torrefied biomass
2) Develop a methodology for successful lab-scale torrefaction in molten salts
3) Understand the effect temperature has on molten salt torrefaction levels
4) Identify which component of the salt blend has the most influence on torrefaction levels

4. EXPERIMENTAL MATERIALS AND METHODOLOGY

4.1. Exploratory Testing

Based on the literature of pyrolysis and gasification in molten salts [31,40,43,45] and on the methodology for traditional torrefaction in nitrogen, a number of milligram (small) scale screening tests were conducted to demonstrate proof of concept and identify key variables for molten salt torrefaction (Objective 1). Results from the milligram scale informed the design of the gram-scale screening tests. These gram-scale exploratory experiments were used to develop the experimental apparatus, testing methodology, and test torrefaction temperature, residence time, and salt-to-biomass ratios (Objective 2).

Table 4.1 shows the variables, constants, and characterization metrics for the milligram-scale and gram-scale screening tests. Throughout all of the exploratory scale tests, the same salt blend was utilized: the ternary eutectic lithium, sodium, and potassium nitrate salt blend. Milligram scale exploratory testing focused on investigating key torrefaction variables including the particle size of the biomass, the salt-to-biomass ratio, and the species of sweep gas used to purge the

Table 4.1: Exploratory testing variables and constants

Variables	Constants	Metrics
Milligram-scale		
Biomass Particle Size Salt-to-Biomass Ratio Sweep Gas Species	Torrefaction Temperature Residence Time Salt and Biomass Separation	Fixed Carbon Content (Proximate Analysis) Color Change
Gram-Scale Experimental Apparatus Experiments		
Salt Removal Process Experimental Apparatus Salt/Biomass Contact	Sweep Gas Species Biomass Particle Size Salt-to-Biomass Ratio Residence Time Torrefaction Temperature	Visual Inspection (Color Change) Fixed Carbon Content Higher Heating Value (Calorimetry)
Gram-Scale Torrefaction Variable Experiments		
Torrefaction Temperature Residence Time Salt-to-Biomass Ratio	Sweep Gas Species Biomass Particle Size Salt Removal Process Experimental Apparatus	Color Change Fixed Carbon Content Higher Heating Value

torrefaction environment. For this set of tests, the torrefaction temperature and residence time were identical and the method used to separate the salt and biomass post torrefaction was the same for each test carried out. Changes in torrefaction levels due to these variables was characterized by the exterior and cross-sectional appearance of the biomass particles and by the fixed carbon content of the torrefied biomass.

The first focus of the gram scale exploratory testing was on the development of an apparatus to improve contact between the molten salt and biomass, and develop a method to completely remove the salt from the biomass. Torrefaction conditions were kept constant throughout the development of the torrefaction apparatus and salt removal process. These include: sweep gas species, biomass particle size, salt-to-biomass ratio, residence time, and torrefaction temperature. Changes in the effectiveness of the torrefaction apparatuses and salt removal processes was conducted through visual inspection, the fixed carbon content and the HHV of the torrefied biomass. Visual inspection is used to identify how well the biomass and salt are interacting; biomass not in contact with the salt blend will not torrify and remain the color of raw biomass, while biomass in sufficient contact with the salt blend will darken significantly.

The second focus of the gram scale exploratory testing focused on investigating key torrefaction variables including torrefaction temperature, residence time, and revisiting the salt-to-biomass ratio. For this set of tests, the sweep gas species, biomass particle size, newly developed salt removal process and experimental apparatus used were all kept constant. Changes in torrefaction levels due to the variables tested were characterized by the color change of the biomass particles and the fixed carbon content of the torrefied biomass.

4.1.1. Milligram-Scale Exploratory Testing

Initial milligram-scale tests were conducted to explore the hypothesis of reduced torrefaction temperatures with the incorporation of molten salts and examine variables, that based on prior literature, were expected to be key variables for torrefaction in molten salts. As detailed in Table 4.2, the gram-scale exploratory tests investigated three variables: particle size, salt-to-biomass ratio, and sweep gas species. Particle sizes of 6×2 mm and 250-500 microns were studied to determine the degree of salt penetration into the biomass. Salt to biomass ratios of 10:1, 16:1 and 19:1 were investigated in this study. Air was also invested as a potential substitute to using nitrogen as the sweep gas species. The goal of this investigation was to identify if an inert purge is required for molten salt torrefaction; like it is for traditional torrefaction methods. Results from these tests were used to guide further procedural development at the gram-scale.

Table 4.2: Torrefaction variables for the milligram scale screening tests

Milligram Scale Tests	**1**	**2**	**3**	**4**	**5**
Particle Size	6 × 2 mm	6 × 2 mm	6 × 2 mm	250-500 µm	250-500 µm
Sweep Gas	Nitrogen	Nitrogen	Nitrogen	Nitrogen	Air
Salt - Biomass Ratio	10:1	16:1	19:1	19:1	19:1

4.1.1.1. Equipment and Materials

Milligram-scale testing was carried out using a Lindberg-Blue Automate Tube Furnace and a Perkin Elmer Pyris 1 TGA. The Automate tube furnace was used to melt together the component salts to develop a uniform salt blend and to dry the raw biomass and torrefied biomass after washing the salt blend away. The Pyris 1 was used to supply the input energy needed to drive the torrefaction reaction. Additional equipment used at the milligram scale was a Columbia International CIT-FW-40 high-speed rotary grinder; used to grind the biomass before sieving to the proper size and to grind the salt blend into a powder.

The biomass utilized for this study was pine, sourced as small pet bedding through Kaytee Pet Products. Pine was selected because it is a plentiful biomass residue often used as a feedstock and because woody biomass is more difficult to torrify than non-woody biomass [16,21,57]. The salt blend was a ternary eutectic blend of lithium nitrate, sodium nitrate, and potassium nitrate;

25.92 wt%, 20.01 wt%, and 54.07 wt% respectively [52]. Sodium and potassium nitrates were sourced through Alfa Aesar with purities of at least 98 % and 99 % respectively; lithium nitrate was sourced through Sigma Aldrich with a minimum purity of 95 %. Unless otherwise noted, Ultra-High-Purity nitrogen with a purity of 99.999 % was sourced through PRAXAIR and used to purge the oxygen from the torrefaction environment; creating an inert torrefaction environment.

4.1.1.2. Milligram-Scale Methodology

4.1.1.2.1. Pre-Torrefaction Processing

To create the salt blend used for torrefaction, the three component salts were heated to 350 °C as specified by Mantha et al.[52] and held at temperature for 5 hours to ensure uniformity throughout the blend. Once cooled, the salt was ground to a powder using the CIT-FW-40 rotary grinder. Due to the hydrophilic nature of the salts, the powder was stored in a dry nitrogen environment to reduce the absorption of moisture.

To prepare the biomass for torrefaction, it was sized and then dried. Two biomass particle sizes were prepared for the milligram-scale tests: a 6×2 mm strip and ground particles sieved to between 250 µm to 500 µm particles. The 6×2 mm strips were measured out and cut from the pet bedding using an X-ACTO knife. The strip thickness varied with the varying thicknesses of the pet bedding. The 250-500 µm particles were obtained by grinding the petting bedding with a high-speed rotary biomass grinder then the particles were sieved to between 250 µm and 500 µm. The feedstock is dried at 120 °C for two hours to remove excess moisture [58]. The dried biomass is stored in dry nitrogen environment to maintain low moisture levels for later use.

4.1.1.2.2. Torrefaction Procedure

The initial torrefaction procedure used at the milligram scale was guided by traditional torrefaction procedures outlined in the literature [9,15,16,21], with alterations made for incorporation of the salt blends. The salt and biomass were loaded into the crucible in layers, starting and ending with salt blend, and compacting to increase capacity and improve contact between the salt and biomass. The salt and biomass were heated in the Pyris 1 to 150 °C, 30 °C below the torrefaction temperature, and held at this temperature for 30-minutes. After 30 minutes had elapsed, the salt and biomass were heated to the torrefaction temperature at a rate of 5 °C/min to maintain a uniform temperature profile within the salt. For this study, a torrefaction temperature of 180 °C was utilized as it is well below traditional methods and matches the low temperature literature on hydrothermal torrefaction reports can be used to torrify biomass [14]. A residence time of two hours, double the maximum recommended time for traditional methods, was used to provide ample time for the biomass and salt to interact and torrify at the lower temperature.

4.1.1.2.3. Post-Torrefaction Processing

After torrefaction is complete, the salt blend and torrefied biomass is cooled to ambient. This encases the torrefied biomass in the solidified salt blend. Removal of the torrefied biomass from performed by dissolving the salt blend surrounding it in distilled water. The salt and biomass were submerged in 100 ml of water until all of the blend was visibly dissolved. The torrefied biomass soaked for an additional 10 minutes to as a precaution to ensure sufficient salt removal. It is then isolated and dried in the Automate tube furnace for 2 hours at 120 °C. Although less hydrophilic than raw biomass, the products torrefied biomass is also stored in dry nitrogen environment prior to analysis.

4.1.1.3. Torrefaction Controls

At this scale, torrefaction controls were conducted at 260 °C in an inert environment. A number of torrefaction studies report maximum energy yields at temperatures between 255 °C and 265 °C [11,16,19]. 260 °C is the middle of this temperature range. A two-hour residence time is used to reduce differences between the controls and molten salt torrefied biomass procedures. The pet bedding pine was prepared and stored in the same manner as it was for molten salt torrefaction.

Control torrefaction was performed using both particle sizes and sweep gas species for accurate comparison.

4.1.2. Gram-Scale Exploratory Testing

Using data obtained from the milligram-scale exploratory tests, a set of exploratory experiments were designed to develop a gram-scale molten salt torrefaction methodology to ensure consistent and thorough torrefaction. The experiments addressed two key issues for testing at the gram scale: consistent salt and biomass contact, and the removal of salt from the torrefied biomass. Three problems were identified which prevented good contact between the salt and biomass: 1) biomass floating to the surface of the salt blend; breaking the surface tension of the molten salt, 2) poor distribution of the biomass throughout the salt blend causing the biomass to clump together and creating pockets of biomass that the salt could not penetrate, and 3) biomass in direct contact with the inner crucible surfaces.

The development of a gram-scale experimental apparatus was required to improve salt and biomass contact by preventing the biomass from floating on the surface of the molten salt. At the milligram-scale, the surface tension of the molten salt, was sufficient to keep the biomass submerged because a narrower, deeper crucible was used. However, at the gram-scale, significant amounts of biomass floated to the surface of the molten salt and overcame the surface tension forces of the shallow and wide crucible used at this scale. Thus, a series of experiments were conducted to design an apparatus to prevent the biomass from floating. Figure 4.1 details the eight designs that were tested to prevent any biomass from floating.

The following is a description of each design tested:

a) Place a small layer of salt along the base of the crucible, layer 100 % of the biomass, load the remaining salt blend on top
b) Load 100 % of the biomass in the crucible, load 100 % of the remaining salt blend on top
c) Place a small layer of salt along the base of the crucible, sandwich 100 % of the biomass and 50 % of the remaining salt blend between two 70-mesh screens, load the remaining salt blend on top
d) Place a small layer of salt along the base of the crucible, sandwich 100 % of the biomass between two 70-mesh screens, load the remaining salt blend on top
e) Place a small layer of salt along the base of the crucible, layer 100 % of the biomass, load the remaining salt blend, place a stilted 70-mesh screen on top
f) Place a small layer of salt along the base of the crucible, layer 100 % of the biomass, place a stilted 70-mesh screen over the biomass, load the remaining salt blend on top
g) Place a small layer of salt along the base of the crucible, layer 100 % of the biomass next, load the remaining salt blend, place a weighted and a stilted 70-mesh screen on top
h) Place a small layer of salt along the base of the crucible, layer 100 % of the biomass next, load the remaining salt blend, place a weighted 70-mesh screen on top

Another key issue with the gram scale torrefaction procedure which surfaced during shakedown testing was poor salt and biomass contact. It was determined that there were two additional root causes preventing thorough salt and biomass contact. The first root cause was a portion of the biomass was in direct contact with the base and sides of the crucible instead of the salt blend. The second root cause was poor distribution of the biomass within the salt blend. During the torrefaction procedure, biomass would clump together forming pockets of tightly packed

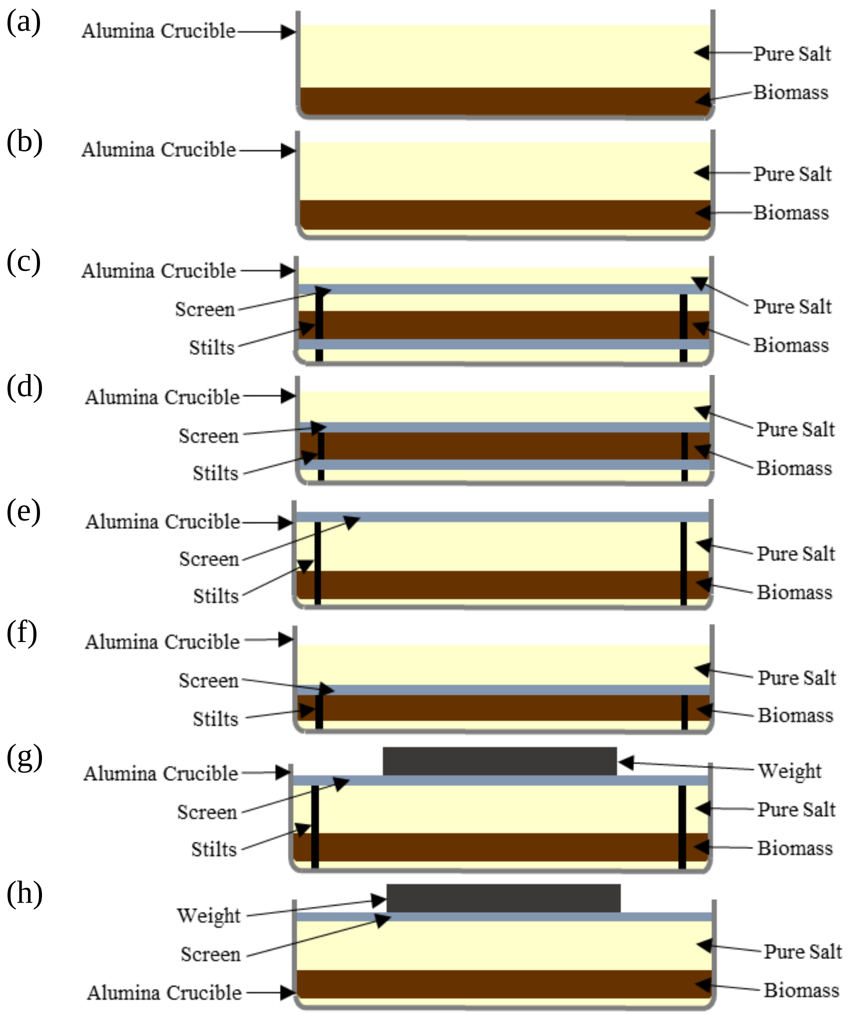

Figure 4.1: (a-e) Cross-sectional view of designs tested to prevent floating biomass

biomass particles. Volatiles given off during torrefaction would fill the small gaps in these pockets, preventing any salt from contacting the biomass inside these pockets. Four methods were tested to remedy this issue.

A cross-sectional view of each method is provided in Figure 4.2:

I. Thicken the pure salt layer pure along the base of the crucible
II. Place a 70-mesh screen between the biomass and base salt layer
III. Thoroughly blend biomass and salt powder prior to loading the crucible
IV. Agitate the contents of the crucible during torrefaction by connecting a mechanism to a screen; moving the screen up and down motion for 30 seconds every five minutes

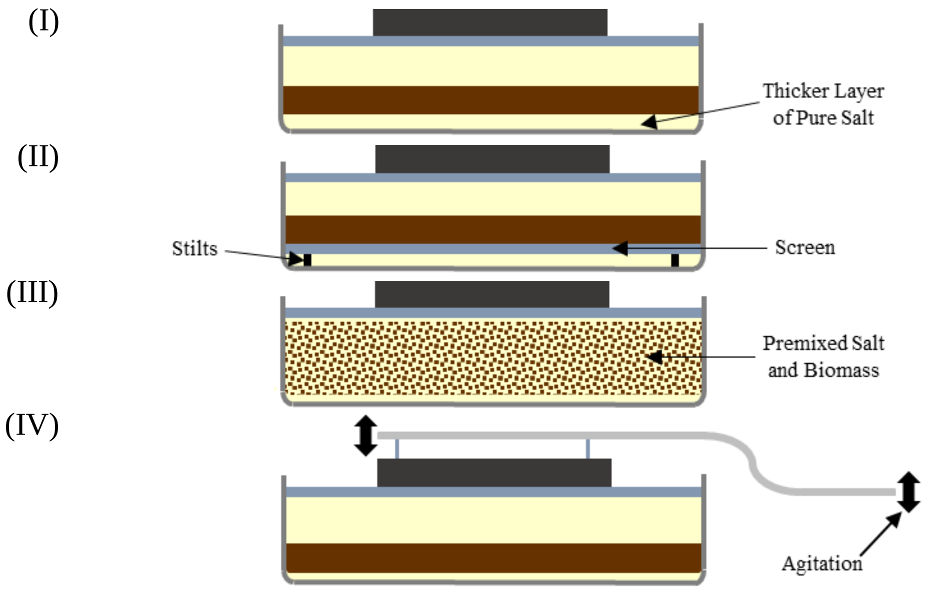

Figure 4.2: Cross-sectional view of the methods tested to (I, II) prevent biomass contact with the crucible and (III, IV) improve biomass distribution

An additional key issue was discovered was the incomplete separation of the salt blend and torrefied biomass. Employing the same wash methodology used at the gram-scale resulted in significant quantities of salt remaining in the torrefied biomass; discovered as residue in the bomb of the Parr 6200 calorimeter being used to determine the higher heating value of the torrefied biomass. Salt blend remaining in the torrefied biomass absorbs a significant quantity of heat when the biomass is combusted; resulting in an artificially low higher heating value. Additionally, the combustion of biomass, containing nitrate salts, has the potential to be an environmental concern; combustion of biomass produces enough heat to decompose the nitrate salts used to create the salt blends; releasing nitrous oxides into the atmosphere. A series of tests investigating multiple wash conditions were conducted to develop a method which completely separates the salt and biomass. The wash conditions tested are detailed in Table 4.3; including agitation of the wash water, wash water temperature, number of wash cycles, and whether it is best to dry the samples between each wash cycle, or after all washes are complete.

Variables tested during the large-scale exploration of molten salt torrefaction are detailed in Table 4.4. Temperatures of 180 °C, 200 °C, and 225 °C; Residence times of 1, 2, and 3 hours; and salt to biomass ratios of 10:1, 15:1, 20:1, and 60:1 were investigated in this study. Various temperatures were tested to determine a temperature at which molten salt torrefaction produces torrefaction levels similar to biomass torrefied at 275 °C using traditional methods. 275 °C is the midpoint of 250 °C to 300 °C; the recommended range of torrefaction temperatures for traditional methods. Variation of the residence time is used to determine whether the originally employed two-hour residence time is too short or too long, or if it is the correct length of time for thorough torrefaction. With the small-scale torrefaction method, a salt to biomass ratio of 20:1 was required to ensure thorough salt and biomass contact and to fully immerse the biomass in the salt blend. Various salt to biomass ratios were investigated to determine if 20 times the biomass mass in salt is required for thorough torrefaction, or if a greater quantity of salt is needed; a salt to biomass ratio of 60:1 takes this to the extreme.

Table 4.3: Conditions tested for complete removal of the salt blend

Test	**1**	**2**		**3**				**4**				**5**				**6**			
		a	**b**	**a**	**b**	**c**	**d**	**a**	**b**	**c**	**d**	**a**	**b**	**c**	**d**	**a**	**b**	**c**	**d**
Agitation (Y or N)	N	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
Water Temp (°C)	25	25	80	25	25	80	80	25	25	80	80	25	25	80	80	25	25	80	80
Wash Cycles	1	1	1	2	2	2	2	3	3	3	3	4	4	4	4	5	5	5	5
Dry Between Cycles	N/A	N/A	N/A	Y	N	Y	N	Y	N	Y	N	Y	N	Y	N	Y	N	Y	N

Table 4.4: Torrefaction conditions for the gram scale screening tests

Gram Scale Tests	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Torrefaction Temp (°C)	180	180	180	200	200	200	180	225	225	225
Residence Time (h)	1	2	3	1	2	3	2	2	2	2
Salt - Biomass Ratio	20:1	20:1	20:1	20:1	20:1	20:1	60:1	10:1	15:1	20:1

4.1.2.1. Equipment and Materials

Gram-scale exploratory testing was carried out using an Across International STF1200 tube furnace. All processes occurring at an elevated temperature were carried out in an STF1200 tube furnace: melting the component salts together to create a uniform salt blend, drying the raw biomass and torrefied biomass after washing, and the torrefaction process. Additional equipment used at the gram scale was a Columbia International CIT-FW-40 high-speed rotary grinder. It was used to grind the biomass up before sieving to the proper size. A Bodum Bistro rotary coffee grinder was used to grind the salt blend into a powder.

Further research on molten salt torrefaction warranted the need to track the specific species of biomass used for further studies. Ponderosa pine, sourced through Valley Hardwoods in Dilworth MN, allowed the specific species of biomass to be tracked; it was used in place of the pet bedding pine used previously. Ponderosa pine was selected because there is prior published literature on torrefaction of a number of pine species from the same family of pine [4,21,59]. The salt blend used for this study is the same ternary eutectic blend of lithium nitrate, sodium nitrate, and potassium nitrate used at the milligram scale; sourced through Sigma Aldrich and Alfa Aesar. Ultra-High Purity nitrogen sourced through PRAXAIR provided an inert torrefaction environment.

4.1.2.2. Gram-Scale Methodology

4.1.2.2.1. Pre-Torrefaction Processing

The salt blend was prepared by heating the three component salts in the STF1200 to 350 °C and holding the temperature for 5 hours. The Bodum coffee grinder, modified to handle the excess loads applied by the salt blend, was used to reduce the salt blend from a solid brick to a powder. The salt blend powder was subsequently stored in a dry nitrogen environment to prevent moisture absorption until needed for torrefaction.

Ponderosa pine was ground using the CIT-FW-40 high-speed, rotary biomass grinder and sieved to between 250 µm and 500 µm. This particle size was used because results at the gram scale showed the salt blend could fully penetrate this biomass particle size, more thorough torrefaction levels. Once properly sized, the feedstock is dried in the STF1200 for two hours at 120 °C [58] and stored in a dry nitrogen environment prior to torrefaction.

4.1.2.2.2. Torrefaction Procedure

Data collected from the milligram scale torrefaction exploration guided the development of a set of experiments to further refine the molten salt torrefaction procedure to be used at the gram-scale. Salt and biomass were loaded into the crucible the manner specific to the design being tested; the manner in which the crucibles are loaded for each design are depicted in Figures 4.1 and 4.2. The design and loading methodology which performed the best were subsequently used to test key torrefaction variables. Many of the torrefaction conditions used at the milligram-scale were retained at the gram scale. Similarly to the milligram scale testing, at the gram scale, the salt and biomass were heated in the STF1200 to 150 °C, 30 °C below the torrefaction temperature, and held at this temperature for 30-minutes. After 30 minutes had elapsed, the salt and biomass were heated to the torrefaction temperature at a rate of 1 °C/min to maintain a uniform temperature profile throughout the salt. Additionally, a salt to biomass ratio of 20:1, torrefaction temperature of 180 °C, and residence time of two hours was utilized as baselines for gram scale exploration; similarly, to the milligram scale. Results from the gram scale dictate a salt to biomass ratio of at least 19:1 for good torrefaction results. While testing key torrefaction variables, the salt to biomass ratio, torrefaction temperatures, and residence times varied according to Table 4.4.

4.1.2.2.3. Post Torrefaction Processing

Part of the gram scale exploration involved testing at this scale involved developing a preprocessing methodology which would fully separate the salt blend and biomass. After torrefaction, the contents of the crucible were allowed to cool to ambient; solidifying the salt blend. 800ml of distilled water was used for all wash cycles which were carried out over a two-hour period. Agitation of the wash water was accomplished by stirring the water at 800RPM, sufficient to prevent the biomass from settling, using a VWR combination hot plate and magnetic stir plate; also used for heating the wash water to 80 °C. Drying was conducted in the STF1200 tube furnace over a two-hour period of time at 120 °C hours and stored in a dry nitrogen environment to maintain the low moisture content. The conditions tested to develop this methodology are outlined in Table 4.3. The best set of conditions for removal of the salt blend from the biomass were subsequently employed as the wash method utilized for testing key torrefaction variables and future testing.

4.1.2.3. Torrefaction Controls

Ponderosa pine torrefied as a control samples, was prepared in the same manner as described in the preprocessing methods section. Control samples were torrefied at 180 °C, 225 °C, 260 °C, and 275 °C for two hours in an inert environment. 180 °C and 225 °C control temperatures directly correlate to the lowest and highest temperatures investigated for molten salt torrefaction. 275 °C is the target torrefaction temperature for the baseline tests to meet, and 260 °C is in the middle of reported torrefaction temperatures which maximize the energy yield of the torrefied products. Torrefaction was carried out in a similar manner to molten salt torrefaction to minimize the differences between how each is prepared. The biomass was heated to 30 °C below torrefaction temperature and held for two hours. The temperature was increased at a rate of 1 °C/min to the torrefaction temperature and held at temperature for two hours.

4.2. Salt Blend Composition and Temperature Variation

Using the gram-scale torrefaction methodology developed through the exploratory tests, a series of experiments were conducted to determine the relationship between torrefaction levels, torrefaction temperature, and the composition of the salt blend. There was specific interest in which component salt had the most influence on torrefaction levels, which was the second most influential, and which was the least influential.

Three torrefaction temperatures of 210 °C, 225 °C, and 240 °C were investigated as part of this study. Previous work determined torrefaction at 225 °C in the ternary eutectic nitrate salt blend is a good baseline torrefaction temperature, producing slightly better torrefaction levels then traditional methods at a torrefaction temperature of 275 °C. The 50 °C reduction in torrefaction temperature observed using molten nitrate salts led to the belief that a smaller temperature range would be needed for molten salt torrefaction to accurately represent torrefaction levels produced using traditional methods between 250 °C and 300 °C. For this study, a 30 °C range in torrefaction temperatures, 210 °C-240 °C was investigated; 15 °C warmer and 15 °C cooler than the baseline temperature.

The salt blends studied for influence on torrefaction levels are detailed in Table 4.5. Four salt blends were studied along with the ternary eutectic salt blend used in previous work. An experimental study conducted by Hector Carveth investigated the melting temperatures of various lithium nitrate, sodium nitrate, and potassium nitrate salt blends. The four additional salt blends were selected based on Carveth's results to all have a melting temperature below 150 °C. The sodium content is constant at 20 wt% among salt blends 1, 2, and 3. Changes in torrefaction level will relate to the lithium nitrate and potassium nitrate content which vary inversely of each other by 10 wt% from 20-30 wt% and 50-60 wt% respectively. Additionally, between salt blends 1 and 5 the potassium nitrate content is constant; relating changes in torrefaction level to varying lithium nitrate and sodium nitrate content. Between blends 3 and 4 the lithium nitrate content is constant; changes in torrefaction level will be related to varying the content of sodium nitrate and potassium

Table 4.5: Salt blend compositions

Salt Blend	**1**	**2**	**3**	**4**	**5**
LiNO3 wt%	25.92	20	30	30	40
NaNO3 wt%	20.01	20	20	0	0
KNO3 wt%	54.07	60	50	70	60

nitrate. Salt blends 1, 2, and 4 maximize the content of sodium nitrate, lithium nitrate, and potassium nitrate respectively.

The results obtained from this set of experiments are used to determine which component salt has the greatest effect on torrefaction levels. Results from molten salt pyrolysis and gasification studies indicate that increasing the lithium nitrate content of the salt blend will have a significant positive effect on torrefaction levels. However, it is not known how varying any of the blends will affect torrefaction levels due to the novelty of molten salt torrefaction.

4.2.1. Equipment and Materials

Equipment used to prepare and torrify the biomass includes an Across International STF-1200 Tube Furnace, a Columbia International CIT-FW-40 rotary biomass grinder, a Bodum Bistro rotary coffee grinder, and a VWR combination hot plate and magnetic stir plate. The STF-1200 is used to dry the feedstock, dry the torrefied biomass after washing, supply the input energy needed to drive the torrefaction reaction, and create the salt blends. The CIT-FW-40 grinder is used to break down the raw feedstock before sieving to the proper particle size. And the Bodum coffee grinder is used to reduce the salt blend to a powder once it solidifies. The VWR hot/stir pate agitates the wash water while separating the salt blend and torrefied biomass.

Ponderosa pine, sourced through Valley Hardwoods, was used as the feedstock for this study. The lithium nitrate, sodium nitrate, and potassium nitrate used to create the various salt blends were sourced through Sigma Aldrich and Alfa Aesar. Ultra-high purity nitrogen, sourced from PRAXAIR provided an inert torrefaction environment.

4.2.2. Methodology

4.2.2.1. Pre-Torrefaction Processing

The salt blends and feedstock were prepared for torrefaction in a similar manner to feedstock and salt blend used throughout the gram-scale exploratory testing. Each salt blend was created by heating the component salts to 350 °C for 5 hours and grinding the solidified blend to a powder using the modified Bodum bistro coffee grinder. The ponderosa pine used for this study was ground up using the CIT-FW-40 biomass grinder and subsequently sieved to a particle size between 250 µm and 500 µm. Once sized, the raw biomass was dried at 120 °C for 2 hours. A dry nitrogen environment is used for storage of both the biomass and salt powder for later use.

4.2.2.2. Torrefaction Procedure

The torrefaction methodology used for this study was developed through the exploration experiments described in the previous sections. The contents of the crucible are loaded in the manner depicted in Figure 4.3. The bottom layer is pure salt; preventing biomass contact with the crucible base during torrefaction. The remaining salt blend, except for five grams, is thoroughly mixed with the biomass prior to loading the crucible. The five reserved grams of salt form the top layer; preventing biomass from contacting the weighted screen used to prevent floating. The weighted screen is a 70-mesh screen weighted to 87.4 g used to keep all of the biomass submerged throughout the torrefaction procedure. Determined from exploratory test results, a salt to biomass ratio of 20:1 was used. This ratio is achieved using 60 grams of salt blend and 3 grams of raw, dried biomass.

Torrefaction was carried out at temperatures of 210 °C, 225 °C, and 240 °C. Heating the salt and biomass to torrefaction involved first heating to 30 °C below the torrefaction temperature and holding for 30 minutes to fully melt the salt blend and bring everything into thermal equilibrium. After 30 minutes, heating to the torrefaction temperature occurred at a rate of 1 °C/min. A residence time of two-hours was used for all salt blends and temperatures studied.

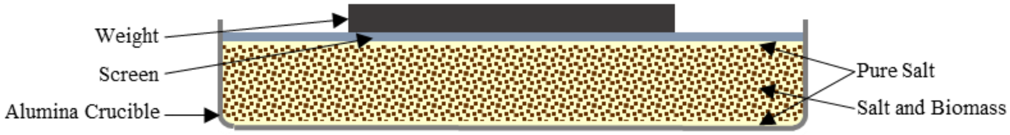

Figure 4.3: Cross-sectional view of a crucible loaded for torrefaction

4.2.2.3. Post-Torrefaction Processing

Post torrefaction, the samples are cooled to ambient, solidifying the salt blend. The samples are subsequently washed in distilled water to separate the torrefied biomass and salt blend. Three, two-hour wash cycles using 800ml of room temperature distilled water are needed to fully remove the salt from the biomass. Wash water is agitated for the duration of each wash using a VWR hot/stir plate at a speed of 800RPM. Following each wash cycle, a 125-mesh sieve is used to separate the torrefied biomass and wastewater. After washing, the torrefied biomass is dried in the STF-1200 tube furnace at 120 °C for two hours to remove excess moisture. The samples are subsequently stored in a dry nitrogen environment to maintain a low moisture content until they are analyzed.

4.3. Material Property Characterization of Torrefaction Samples

Sample color, fixed carbon content (%FC), and higher heating value (HHV) are the metrics used to define the torrefaction levels of the biomass produced using molten salt torrefaction. At the milligram scale, sample color and fixed carbon content were used to characterize the torrefied biomass. Sample sizes were on the order of 10^2 times smaller than the minimum amount needed to test the HHV. At the gram scale, all three metrics were used to characterize the torrefied biomass produced during the gram scale exploratory tests and the investigation of temperature and salt blend composition effects.

4.3.1. Sample Color

As referenced by Acharya et al. and Cellatoğlu et al. torrefaction results in the color of biomass turning a dark shade of brown; indicating carbonization of the biomass through hemicellulose and cellulose decomposition. As torrefaction levels increase, the shade of brown darkens, even to the point of turning black, indicating more complete decomposition of the hemicellulose and cellulose [29,38]. Two methods will be used to classify the color change of the biomass, visual inspection and the mean gray value of images taken of the torrefied biomass. The mean grey value is a method to quantify the color change biomass experiences through torrefaction. The gray value of each pixel ranges from 0 to 256; a value of zero correlates to a jet-black pixel and 256 correlates to pure white. The mean gray value is the average of the gray values of all the pixels in a selected area. The gray value of an RGB pixel is calculated using Eq. (1) [60].

$$gray = \frac{red+blue+green}{3} \tag{1}$$

4.3.2. Fixed Carbon

The fixed carbon content of a sample is the amount of combustible carbon contained within it and is a good indicator of the amount of energy within the sample. The fixed carbon content and the energy contained within a sample vary proportionally to each other [61]. The fixed carbon content of a sample is determined through proximate analysis which is also used to determine the moisture, volatile, and ash content of a sample. Proximate analysis was performed using thermogravimetric analysis as outlined by García et al. and Mayoral et al. [58,62]. A Perkin Elmer Pyris 1 TGA and Perkin Elmer STA8000 were used to perform thermogravimetric proximate analysis throughout this study. The Pyris 1 was used to conduct proximate analysis during exploratory testing while the STA8000 was used to conduct proximate analysis during gram-scale exploratory testing to determine the effect of key variables on the torrefaction procedure and throughout the temperature and salt blend composition study.

Figure 4.4 is a plot of the weight loss vs temperature for raw ponderosa pine undergoing thermogravimetric proximate analysis. The difference in mass between points A and B, points B and C, and points C and D is the mass of the moisture, volatiles, and fixed carbon within the sample respectively; the mass reading at point D is the mass of ash remaining after the other components have been released. The volatile content, fixed carbon content, and ash content are all calculated

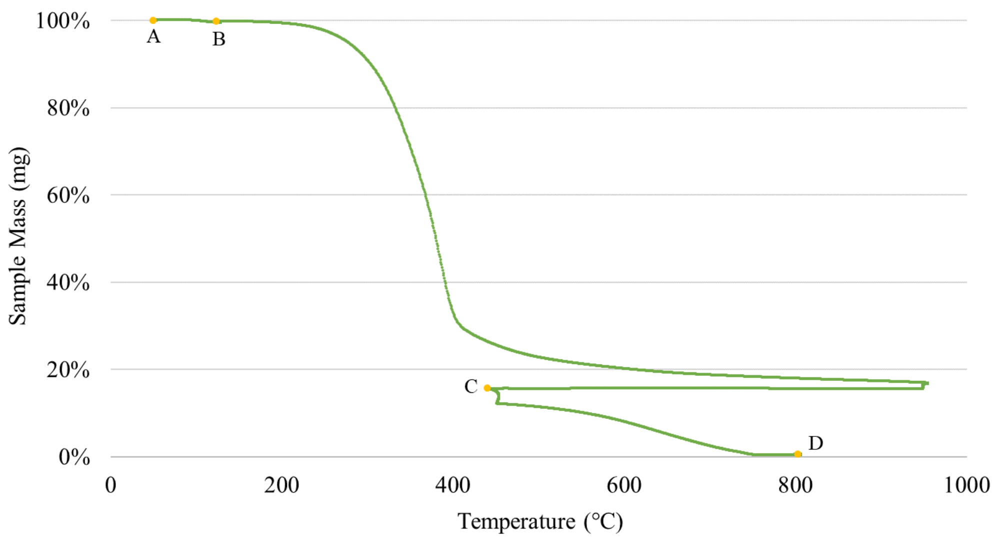

Figure 4.4: Weight percent vs temperature curve for proximate analysis detailing the (A) initial weight, (B) weight after moisture removal, (C) weight after volatile release and (D) final weight after the combustion of all combustible material

on a dry basis after the moisture in the biomass has been evaporated. The fixed carbon content is calculated using Eq. (2)

$$\%FC = \frac{w_C - w_D}{w_B} \tag{2}$$

Where: w_B is the weigh measurement at point B, w_C is the weigh measurement at point C, and w_D is the weight measurement at point D

4.3.3. Higher Heating Value

The higher heating value (HHV) is the energy content of a sample assuming the latent heat of vaporization of the water within the sample is recoverable. It is the method commonly used in literature to report the energy content of torrefied biomass. The HHV was obtained through calorimetry using a Parr 6200 Isoperibol, bomb type, calorimeter following the manufacturer's guidelines and procedures.

4.3.4. Statistical Analysis

Statistical analysis was performed to calculate the uncertainty in the data collected while investigating the effect of temperature and salt blend composition on torrefaction levels. For each data point, enough torrefied biomass was produced to allow for three fixed carbon and two HHV measurements. Uncertainty calculations were made following methods outlined by Robert Moffat using pooled variance to determine small sample uncertainties [63].

Each salt blend was used as the domain within which the variances were pooled to estimate the overall variance if the number of samples were to increase, as shown by Eq. (3).

$$s_{pooled}^2 = \frac{(n_{210}-1)s_{210}^2+(n_{225}-1)s_{225}^2+(n_{240}-1)s_{240}^2}{(n_{210}-1)+(n_{225}-1)+(n_{240}-1)} \tag{3}$$

Where: s_i^2 is the variance in the average fixed carbon or higher heating value at each temperature, i, and n_i is the number of measurements taken to obtain the average value. Calculation of the pooled standard deviation is shown by Eq. (4).

$$s_{pooled} = \sqrt{s_{pooled}^2} \tag{4}$$

Using the pooled standard deviation, the precision index for the average measurement at temperature, i, (p_i) is calculated using the student t variable with 95 % confidence, associated with the degrees of freedom of the pooled variance, as shown by Eq. (5).

$$p_i = \frac{s_{pooled} * t(0.95, j)}{\sqrt{n_i}} \tag{5}$$

Where: j is the degrees of freedom of the pooled variables; which is equal to the number of variances pooled together. For this study, j equals three as the variance in the average data collected at each of the three temperatures are pooled together for each salt blend tested.

The bias uncertainty, B_i, in the fixed carbon content was calculated using sequential perturbation. The bias uncertainty, reported by the manufacturer, in the weight readings collected at points B, C, and D by the STA 8000 were propagated through Eq (2) to calculate the bias in the fixed carbon content. The bias uncertainty in the HHV was determined through experimentation. The HHV for benzoic acid, the standard for the Parr 6200 calorimeter, was calculated 10 times and averaged. The difference between this average and the accepted HHV for benzoic acid is the bias uncertainty in the HHV measurements.

The total uncertainty (U_i) in both the HHV and fixed carbon was calculated with Eq. (6).

$$U = \sqrt{p_i^2 + B_i^2} \tag{6}$$

5. RESULTS AND DISCUSSION

5.1. Exploratory Testing

To investigate the hypothesis that molten nitrate salts will catalyze the torrefaction reaction and reduce torrefaction temperatures, exploratory testing at the milligram and gram scale was conducted (Objective 2). These results guided the development of a lab-scale torrefaction methodology used to test key torrefaction variables and conditions.

5.1.1. Milligram-Scale Exploratory Testing

Testing at the milligram scale was designed to test the hypothesis that molten salts will reduce torrefaction temperatures, and investigate the effect of varying particle sizes, sweep gas species, and salt to biomass ratios. Characterization of the torrefaction levels was accomplished through visual appearance and the fixed carbon percent obtained through proximate analysis.

The hypothesis that torrefaction temperatures could be reduced by using a molten salt catalyst was visually confirmed with the initial milligram scale experiment. Figures 5.1 and 5.2 show images and the corresponding mean gray values, of raw biomass and biomass torrefied at 180 °C and 260 °C in nitrogen and biomass torrefied at 180 °C in the eutectic molten salt at a salt-to-biomass ratio of 19:1 respectivley. In a nitrogent environment, the pine does not have significant visual indications of torrefaction. There is only a relativley small difference in the mean gray values of raw biomass (Fig. 5.1 (a)), 97.79, and the biomass torrefied at 180 °C (Fig. 5.1 (b)), 79.54. However, there is a signficiant difference in the mean gray values of raw biomass, 94.79, and that of the biomass torrefied in molten salt at 180 °C (Fig. 5.1 (d)), 31.48. The color of the pine torrefied in molten salts at 180 °C, with a mean gray value of 31.48, is closer to that of pine torrefied at 260 °C in nitrogen (Fig. 5.1 (c)), 27.05, than to the 180 °C nitrogen sample (Fig. 5.1 (b)), 79.54.

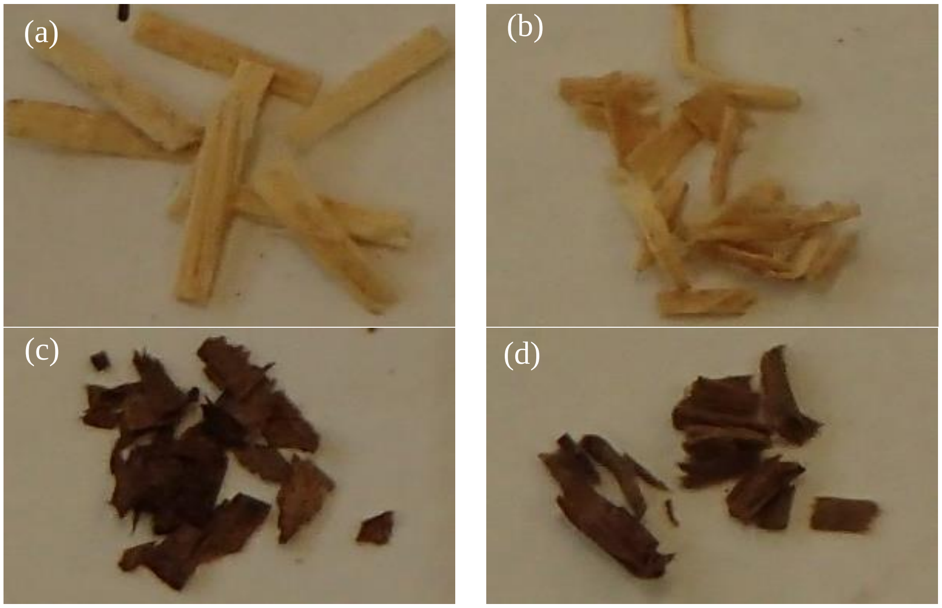

Figure 5.1: Images of (a) raw 6×2 mm pine and pine torrefied in nitrogen at (b) 180 °C and (c) 260 °C and (d) torrefied in molten salt at 180 °C.

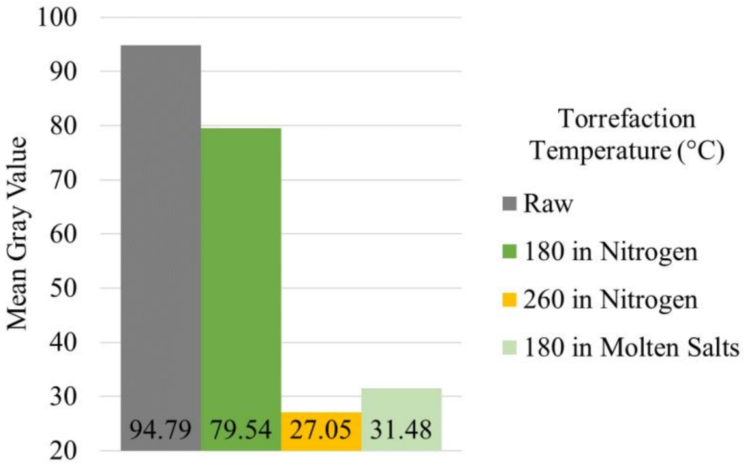

Figure 5.2: Mean gray values for (a) raw 6×2 mm pine and pine torrefied in nitrogen at (b) 180 °C and (c) 260 °C and (d) torrefied in molten salt at 180 °C.

After the initial proof-of-concept, the effect of the salt-to-biomass ratio was investigated for ratios of 10:1, 15:1, and 19:1 with the 6×2 mm particles. The results demonstrate the importance of the ratio for ensuring good contact between the salt and biomass. In locations on the particles where the pine was not in contact with the salt, for example where the particles were in contact with one another or in contact with the container wall, there was little-to-no change in the color of the biomass, indicating lower levels of torrefaction. At the lower salt-to-biomass ratios, there were more of these lower-torrefaction locations on the particles because there was less salt to encompass the biomass. However, at the high ratio (19:1), the biomass was more uniformly torrefied because there is more salt to interact with the biomass. Therefore, a ratio of 19:1 was used for the remainder of the milligram-scale experiments.

The effect of particle size was investigated by comparing the torrefaction of the 6×2 mm particles to particles ground and sieved to between 250-500 µm. The objective was to select a small enough particle size that ensured the salt could penetrate and torrify the full thickness of the particle. For the larger 6×2 mm particles, the salt did not penetrate through the full thickness. Figure 5.3 shows the outside (Fig. 5.3 (a) and (b)) and cross-section (Fig. 5.3 (d) and (e)) of 6×2 mm particles torrefied with a salt-to-biomass ratio of 10:1 and 19:1. The outside of the biomass appears torrefied (Fig. 5.3 (a) and (b)), but interior regions of the particle has less color change as shown by the cross-sectional view of the particles in Fig. 5.3 (d) and (e). Increasing the salt-to-biomass ratio improved the ability of the salt to permeate the 6×2 mm biomass particles. With a salt-to-biomass ratio of 10:1 (Fig. 5.3 (d)) more of the cross-sectional of the biomass is the color of raw biomass, than when a ratio of 19:1 (Fig. 5.3 (e)) is used. With larger portions of the biomass the color of raw biomass, the samples torrefied using a 10:1 ratio are less torrefied than when a 19:1 ratio is used. Visual inspections of the 250-500 µm particles (Fig. 5.3 (c) and (f)) indicated that the color was consistent through the entire thickness; salt penetrated and torrefied the entire

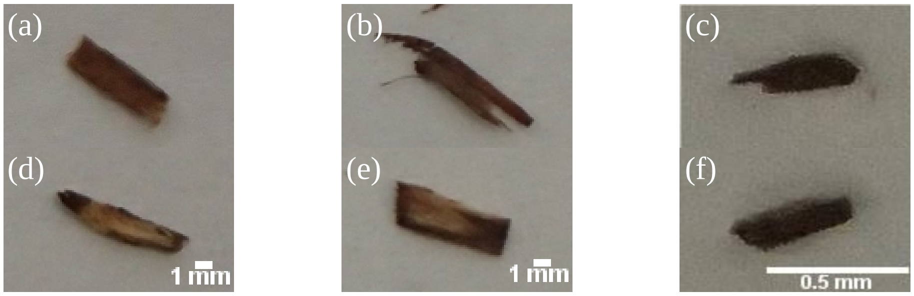

Figure 5.3: Exterior and cross-sectional views of 6×2 mm particles torrefied in (a,d) 10:1 and (b,e) 19:1 salt-biomass ratios and (c,f) 250-500 µm particles torrefied using a 19:1 ratio

particle (Fig. 5.3 (f)). Thus, a salt-to-biomass ratio of 19:1 and particle size between 250 µm and 500 µm were used for subsequent tests.

Using a particle size of 250-500 µm to ensure complete torrefaction of the biomass, pine was torrefied in molten salts with a salt to biomass ratio of 19:1 and a temperature of 180 °C to obtain the fixed carbon content for molten salt torrefaction. Figure 5.4 provides the %FC for raw pine, pine torrefied in nitrogen and air at 180 °C and 260 °C, and pine torrefied at 180 °C in molten salts with a nitrogen and air purge. When nitrogen is used as the purge gas, the fixed carbon percent for pine torrefied in the molten salts at 180 °C is 19.1 %; ~47 % greater than pine torrefied at the same temperature in nitrogen. The fixed carbon percent for pine torrefied in nitrogen at 180 °C is relatively unchanged from raw pine, ~13 %; indicating that the molten salt catalyst is a key reason for torrefaction experienced at 180 °C. Additionally, the fixed carbon percent for pine torrefied in molten salts is ~15 % greater than pine torrefied at 260 °C, 16.6 % (Fig. 5.4 (a)). The improved fixed carbon percent indicates a greater level of torrefaction is achieved in molten salts at 180 °C than in a nitrogen environment at 260 °C; success at reducing torrefaction temperatures by more than 80 °C.

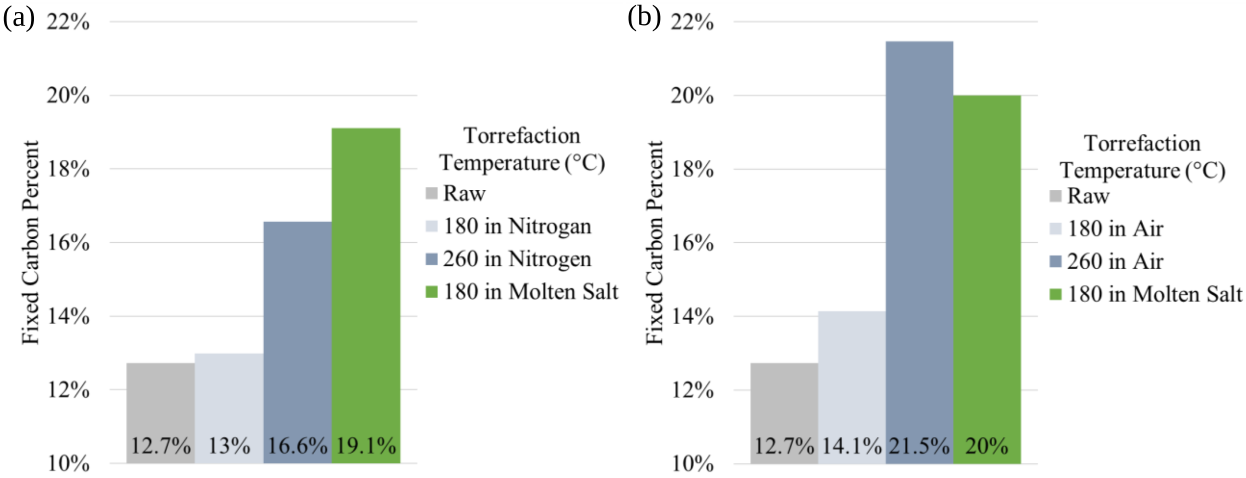

Figure 5.4: Fixed carbon for pine torrefied with (a) nitrogen and (b) air purge

The effect of using an air purge was investigated to determine if it could be used to replace nitrogen as the purge for molten salt torrefaction. Figure 5.4 (b) presents the fixed carbon for raw pine and pine torrefied in molten salts and traditional methods using an air purge. At 260 °C, pine torrefied using an air purge (Fig. 5.5 (c)) is a noticeably darker color than its counterpart torrefied with a nitrogen purge (Fig. 5.5 (a)). However, for biomass torrefied in molten salts (Fig. 5.5 (b) and (d)), the appearance of the biomass is identical whether an air purge or nitrogen purge is used. The fixed carbon percent of the samples torrefied directly in air increased significantly, for example at 260 °C the fixed carbon percent is ~30 % greater when using air as the purge gas; 16.6 % with a nitrogen purge and 21.8 % with an air purge. This increase in fixed carbon is due to the partial combustion of a portion of the biomass, releasing volatiles that would not have been released using a nitrogen purge [64]. Although the fixed carbon increases, the partial combustion of the biomass significantly reduces the overall energy yield; counteracting any benefit from releasing more volatiles. However, the fixed carbon percent of the biomass torrefied in molten salts is much less sensitive to the purge gas species. The fixed carbon content is only ~6 % greater

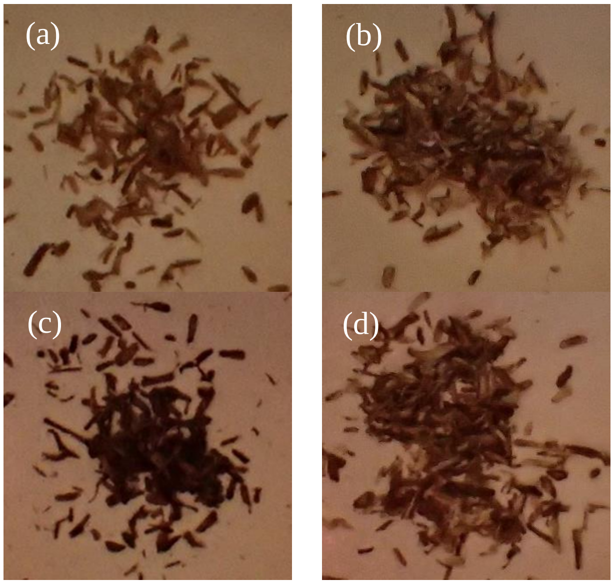

Figure 5.5: Images of 250-500 µm pine torrefied in nitrogen at (a) 260 °C and (b) 180 °C in molten salt; and torrefied in air at (c) 260 °C and (d) 180 °C in molten salt

at 20 % using air as a torrefaction purge. This lower sensitivity to purge gas species could be beneficial because it indicates that air, rather than high purity nitrogen, could be used as the purge gas. For plant-scale torrefaction, this switch could result in significant energy savings due to the high energy requirement, relative to air, associated with producing high-purity nitrogen.

Valuable knowledge was gained as a result of the milligram scale molten salt torrefaction experimentation. First, the use of molten salts does reduce torrefaction temperatures. Visually, pine torrefied in molten salts appeared to be torrefied to a similar level as pine torrefied using traditional methods at temperatures 80 °C greater. Additionally, evaluation of the fixed carbon shows a ~15 % improvement when torrefying in molten salts at 80 °C cooler than traditional methods; confirming lower temperatures are needed to torrify biomass in molten salts. Key variables were also investigated at the milligram scale which shaped the scope of the work performed at the gram scale. Using a 19:1 salt to biomass ratio improved penetration into the biomass and reduced contact between other biomass particles and the crucible walls. Because of this, a salt to biomass ratio of 20:1, similar to 19:1 and an even multiple of ten, was used as the baseline ratio for gram scale torrefaction. Additionally, biomass sized between 250 and 500 µm will be used going forward as the molten salt blend is able to permeate into the entire particle. Although results indicate air has the potential to replace nitrogen as the purge gas with molten salt torrefaction, an inert environment is used at the gram scale to retain similarity with traditional torrefaction methods.

5.1.2. Gram-Scale Exploratory Testing

5.1.2.1. Torrefaction Experimental Apparatus and Procedure

Preliminary tests at the gram scale identified three issues which resulted in poor contact between the salt and biomass: 1) biomass floating to the surface of the salt blend; breaking the surface tension of the molten salt, 2) poor distribution of the biomass throughout the salt blend

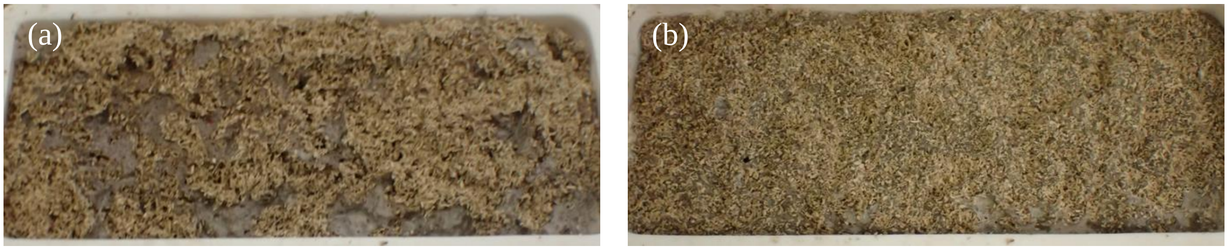

Figure 5.6: Untorrefied biomass due to (a) floating and (b) poor biomass distribution. (a) is a view of the top surface of the biomass, (b) is at an intermediate cross-section

causing the biomass to clump together and creating pockets of biomass that the salt could not penetrate, and 3) biomass in direct contact with the inner crucible surfaces. Figure 5.6 presents post torrefaction photographs of untorrefied biomass due to issues 1 (a) and 2 (b). 5.6 (a) is a top view of floating biomass after cooling to ambient and the small amount of salt that was unable to drain through the biomass as it lifted up. 5.6 (b) is a cross section view of a pocket of biomass which occupied an entire layer of the crucible; this image was obtained by lifting the solidified upper layer of salt to reveal this pocket of untorrefied biomass.

As outlined in section 4.1.2, eight experimental apparatuses were designed and tested to prevent the biomass from floating to the surface. The majority of the eight experimental apparatuses developed did not work as intended. These designs include designs (a) – (c), (e), and (f). Designs (d) and (g) reduced floating biomass, but did not completely prevent it. However, design (h), a modified design (g), did prevent the biomass from floating on top of the molten salt. In design (d) the mass of the screens used to sandwich the biomass was not enough to completely overcome the buoyancy forces of the biomass. These forces would lift the entire apparatus to the surface and a small amount of the biomass would break the surface of the molten salt. Additionally, sandwiching all of the biomass between the two screens inhibited penetration of the molten salt into the layer of biomass. Design (g) utilized a 117.4 g weight atop the screen to keep the biomass submerged. However, due to the volume shrinkage of the salt powder upon melting, the stilts which were designed to stabilize the weighted screen and prevent it from compacting all biomass at the bottom of the crucible, held the screen above the surface of the molten salt. With the screen held above the surface, a small portion of the biomass floated to the surface. Design (h) was the only design which prevented floating throughout the entire torrefaction process. It was developed by removing the stilts used in design (g) and reducing the weight to 87.4 g. This design allowed the screen and weight to be neutrally buoyant in the molten salt with 3 g of ponderosa pine.

Two methods, (I and II) were tested to reduce contact with the interior surfaces of the crucible. In method I, to increase the buffer between the biomass and a surface, a layer of pure salt was placed between the biomass and the crucible bottom and between the biomass and the top screen. This method proved effective. It visibly reduced the number of biomass particles with untorrefied regions. This indicates a significant reduction in the amount of the biomass contacting anything but salt blend. Method II utilized a screen held a short distance above the base of the crucible; allowing only salt to be in direct contact with the crucible base. However, it was ineffective because contact between the biomass and this screen visibly reduced torrefaction levels; portions of the biomass particles remained the color of raw biomass.

Two methods (III and IV) were developed to improve the distribution of biomass throughout the salt. Method III premixed the salt and biomass prior to torrefaction while method IV broke up the pockets of biomass by agitating the salt and biomass. Both were successful and prevented the formation of untorrefied biomass pockets within the salt blend. No pockets of untorrefied biomass were visually detected after torrefaction using either method. Additionally, the quantitative results were similar for both methods. Figure 5.7 shows the HHV of ponderosa pine torrefied using methods III (Fig. 5.7 (a)) and IV (Fig 5.7 (b)) at 180 °C in salt-to-biomass measurements were taken. The difference in HHV between methods III and IV are within the

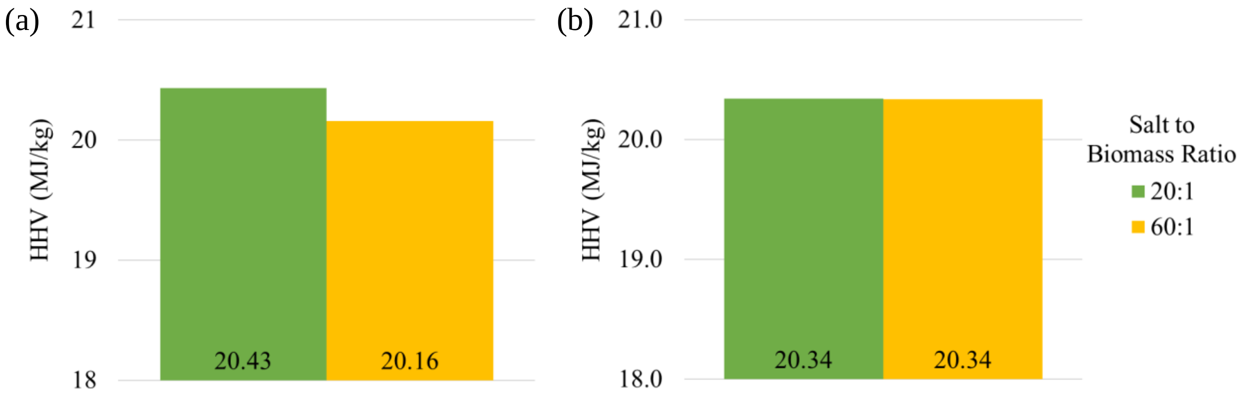

Figure 5.7: HHV for (a) premixed salt and biomass and (b) agitation during torrefaction at salt-to-biomass ratios of 20:1 and 60:1

measured bias of each other. Method III is the simpler of the two solutions and is a passive solution. For these reasons, it was used in subsequent experiments.

Combining the results discussed in this section, Figure 5.8 is a cross sectional schematic detailing how crucibles are loaded for subsequent torrefaction. This methodology incorporates methods I and III, and design h; ensuring thorough and consistent salt-to-biomass contact. The salt and biomass are premixed prior to loading the crucible. To load the crucible, a layer of pure salt is placed along the base of the crucible then a layer of premixed salt and biomass, then a layer of pure salt, and lastly a weighted screen is set atop the crucible contents to prevent floating. This experimental apparatus and loading procedures were used for all subsequent tests.

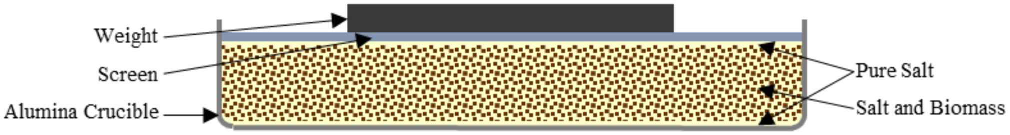

Figure 5.8: Cross sectional of the torrefaction apparatus

5.1.2.2. Salt Removal Procedure

Another issue identified and tested during preliminary gram scale testing is the incomplete removal of the salt blend from the biomass after torrefaction. As discussed in the methodology section, the salt was dissolved in water to remove it from the biomass. Stagnate and agitated water were tested; both were able to dissolve the salt. However, with stagnate water, it takes approximately 8 hours to visibly dissolve the salt blend; two washes of four hours each. It is hypothesized that during the wash cycle with stagnate water, the water immediately surrounding the solid salt and biomass becomes saturated with dissolved salt, thus reducing the driving potential for dissolving more of the salt and slowing the rate at which the salt dissolved. Agitating the wash water, it is hypothesized, maintains low-salinity water near the solid salt which promoted more rapid dissolving. Washing with agitated water visibly dissolved the salt blend within 30 minutes. To shorten the timeframe of testing, agitation was used in subsequent tests.

The number of washes, the temperature of the wash water, and drying the biomass between each wash were also tested. Figure 5.9 shows the HHV for ponderosa pine torrefied in molten salts using multiple wash cycles and water temperatures. Without the presence of the molten salt inside the biomass, combustion energy is transferred to the calorimeter's water jacket; an increase in temperature is detected by the calorimeter and used to calculate the HHV. The presence of residual salt within the samples results in an artificially low HHV measurement because a portion of the combustion energy is absorbed by the melting of the salt instead of transferring to the calorimeter's

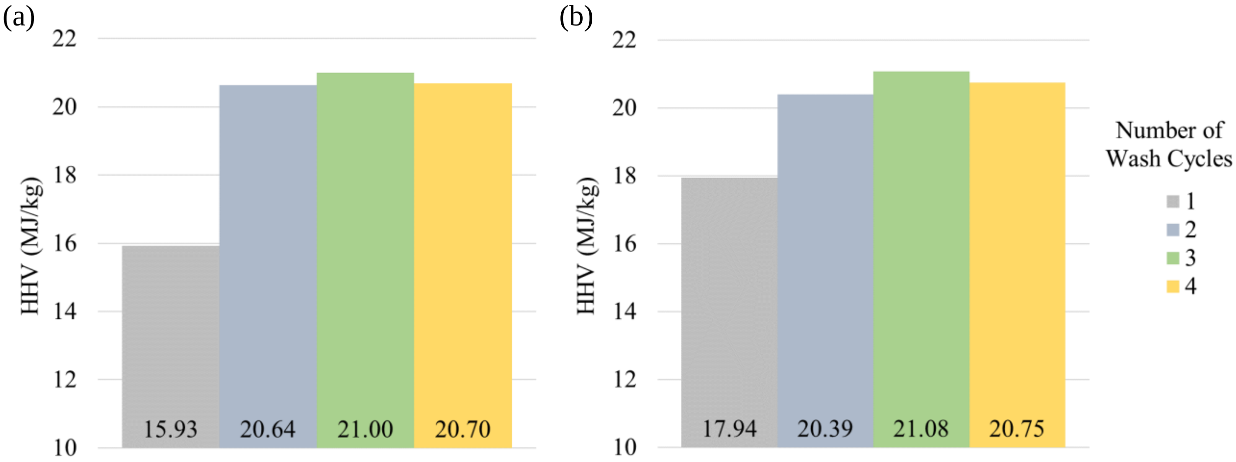

Figure 5.9: HHV for ponderosa pine following washes in (a) room temperature and (b) 80 °C water

water jacket. For a single wash cycle, using 80 °C water improved removal of the salt blend from the biomass over using room temperature water as demonstrated by the HHV obtained with 80 °C (18 MJ/kg) than with room temperature water (16 MJ/kg). However, a single wash cycle did not fully dissolve the salt within the biomass. At least two wash cycles were required to fully remove the salt blend regardless of water temperature and resulted in statistically similar HHV regardless of water temperature. Using more than two wash cycles, regardless of the water temperature, did not significantly improve the HHV. However, to conservatively ensure completely salt remove, torrefaction samples produced from subsequent tests underwent three wash cycles. There was no difference in the HHV's whether drying occurred between wash cycles or after completing all wash cycles.

5.1.2.3. Key Torrefaction Variable Investigation

The last set of gram-scale exploratory investigations examined three key variables: residence time, torrefaction temperature, and salt-to-biomass ratio, to develop a baseline laboratory torrefaction methodology. Figures 5.10 (a) and (b) show how the fixed carbon and HHV, respectively, change with residence time. Ponderosa pine was torrefied for 1, 2 and 3 hours at 180 °C and 200 °C in molten salt with a salt-to-biomass ratio of 20:1. A residence time of one-

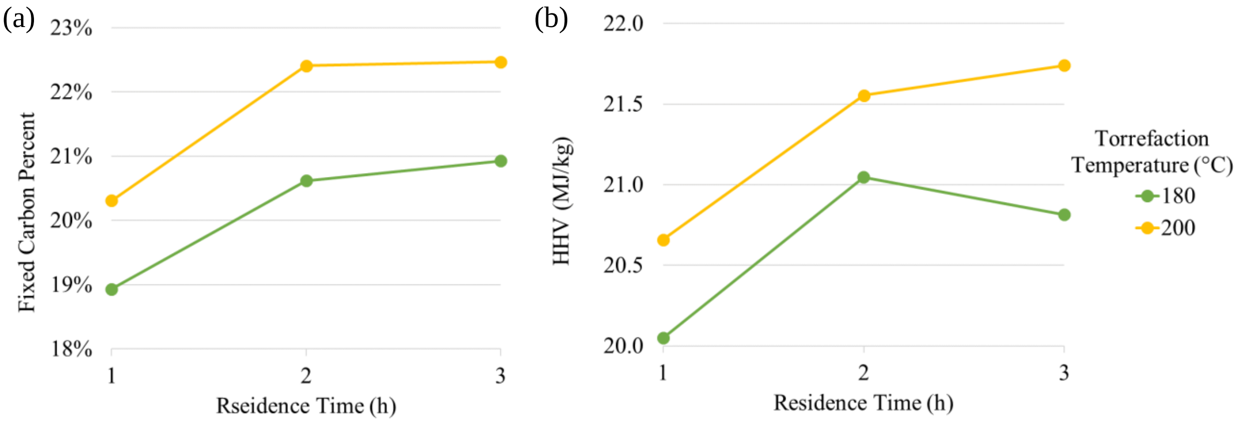

Figure 5.10: (a) %FC and (b) HHV for ponderosa pine torrefied at 180 °C and 200 °C as a function of residence time

hour does not provide enough time to fully torrify biomass, while three hours is excessively long. From a one-hour torrefaction time to a two-hour torrefaction time, there is a noticeable increase in the HHV and fixed carbon at both torrefaction temperatures. For example, for biomass torrefied at 180 °C, the fixed carbon percent increases from 18.9 % at one-hour, to 20.6 % at a two-hour residence time. Additionally, the HHV increases from 20.1 MJ/kg at one-hour, to 21.1 MJ/kg at a two-hour residence time. Conversely, the rate of change for the fixed carbon and HHV between two and three hours is minimal. The use of a three-hour residence time at 180 °C results in a 1 % increase in fixed carbon content to 20.9 % and a 1 % decrease in the HHV to 20.8 MJ.kg. Likewise, at 200 °C a less than 1 % difference in the fixed carbon percent and HHV are noted. Thus, a residence time of two hours will continue to be used with subsequent tests.

Figure 5.11 (a) and (b) compares the HHV and %FC respectively for ponderosa pine torrefied in molten salts with a ratio of 20:1 at 180 °C, 200 °C, and 225 °C, and biomass torrefied using traditional methods at 275 °C. Using 180 °C as the baseline, an increase in torrefaction temperatures to 200 °C resulted in a 9 % improvement in fixed carbon and 2 % improvement in HHV. Increasing the torrefaction temperature to 225 °C improved torrefaction levels significantly; fixed carbon increased by 43 % from 20.6 % at 180 °C to 29.4 % and the HHV increased by 12 % from 21.05 MJ/kg at 180 °C to 23.66 MJ/kg. The goal of investigating torrefaction temperatures

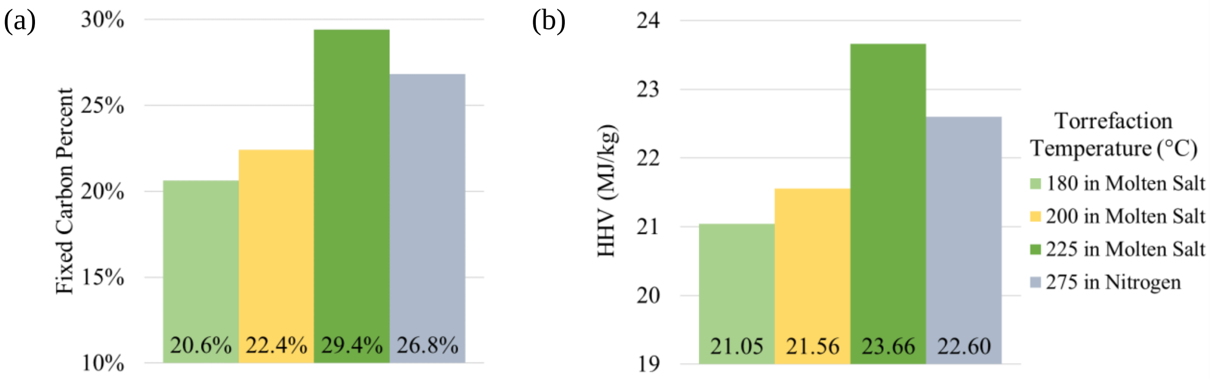

Figure 5.11: (a) %FC and (b) HHV for ponderosa pine torrefied for 2 hours

was to find a temperature at which torrefaction levels would meet or exceed torrefaction levels produced using traditional methods at 275 °C, an average temperature for traditional torrefaction. At this temperature, the fixed carbon content and HHV for traditionally torrefied ponderosa pine is 26.8 % and 22.60 MJ/kg, respectively. Thus, 225 °C was selected as the baseline torrefaction temperature for the testing and development of molten salt torrefaction conditions and methods.

With methods in place to improve salt and biomass contact, the salt to biomass ratio was revisited. Figure 5.12 shows the HHV and fixed carbon content of pine torrefied using a 20:1 and 60:1 salt to biomass ratio at 180 °C (a and b); and pine torrefied in a 10:1, and 20:1 ratio at 225 °C (c and d). At 180ºC, increasing the salt to biomass ratio to 60:1 had little effect on torrefaction levels. The HHV decreased slightly from 20.43 MJ/kg to 20.34 MJ/kg while the fixed carbon increased slightly from 20.6 % to 21.1 %. At 225 °C, it was determined that the salt and biomass ratio should stay at 20:1. Reducing salt-to-biomass ratio to 10:1 reduced the fixed carbon content

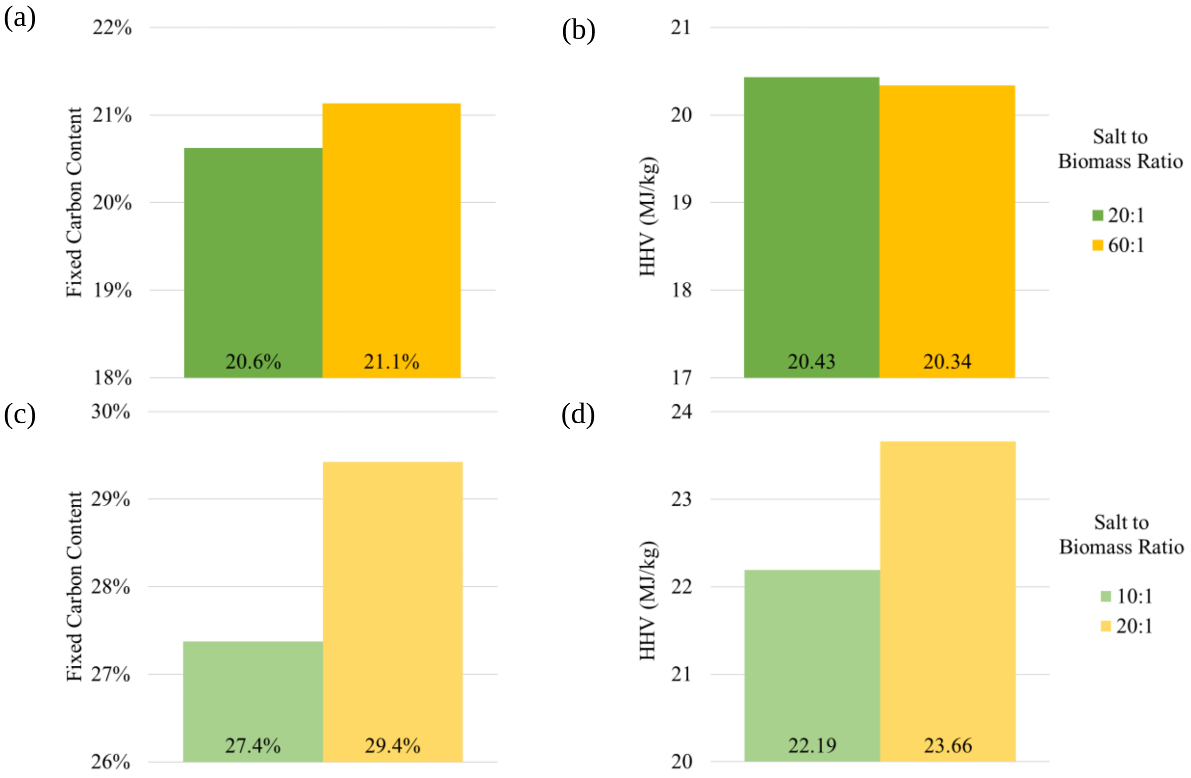

Figure 5.12: (a) %FC and (b) HHV for ponderosa pine torrefied at 180 °C and (c) %FC and (d) HHV for ponderosa pine torrefied at 225 °C

from 29.4 % to 27.4 %, a 7 % loss. As well, the HHV was reduced by over 6 % from 23.66 MJ/kg to 22.19 MJ/kg. Therefore, a salt to biomass ratio of 20:1 was used to ensure good contact between the salt and biomass, and to limit excessive salt usage.

The results obtained through the gram scale exploratory testing shaped the lab-scale torrefaction procedure and baseline conditions used to test various aspects of molten salt torrefaction, specifically torrefaction temperature and salt blend composition. Measures were developed to ensure consistent salt and biomass contact through the prevention of floating biomass, reducing biomass contacting the inner surfaces of the crucible, and preventing pockets of untorrefied biomass from forming. Baseline conditions for further testing and optimization of the molten salt torrefaction procedure were established through exploration testing. The baseline conditions for molten salt torrefaction determined via the exploratory testing with the ternary eutectic salt composition include a biomass particle size between 250 µm and 500 µm, a salt to biomass ratio of 20:1, torrefaction temperature of 225 °C, and a residence time of 2 hours.

5.2. Salt Blend Composition and Temperature Variation

Using the lab scale torrefaction methodology developed through exploration tests, a set of experiments were developed to investigate the effect of temperature and salt blend composition on torrefaction levels. Characterization of torrefaction levels was accomplished using the fixed carbon percent, the higher heating value, and visual appearance as quantified by the mean gray value.

5.2.1. Temperature Variation

Three torrefaction temperatures were investigated to further understand the effect temperature variation has on torrefaction levels in molten salt. This investigation observed torrefaction levels produced using the baseline temperature of 225 °C, determined during the gram-scale exploratory testing, and temperatures of 210 °C and 240 °C. All three temperatures were investigated with the five different salt blends. The fixed carbon content, higher heating value, and visual characteristics of the biomass, quantified using the mean gray value, were used to quantify torrefaction levels of the biomass.

At all torrefaction temperatures and with all the salt blends, the visual appearance and corresponding mean gray values indicate the pine has torrefied from its raw state. An example of this is presented in Figures 5.13 and 5.14 which provide images and the corresponding mean gray values, respectively, for raw ponderosa pine and ponderosa pine torrefied in a ternary eutectic salt blend at 210 °C, 225 °C, and 240 °C respectively. At all temperatures, the pine torrefied in the molten salt blend is visibly darker than raw pine and has reduced mean gray values. Raw pine (Fig 5.13 (a)) has a significantly higher mean gray value, 85.69, than the pine torrefied in molten salts, 44.15-34.65 (Fig. 5.14). Additionally, pine torrefied at higher temperatures is a darker color

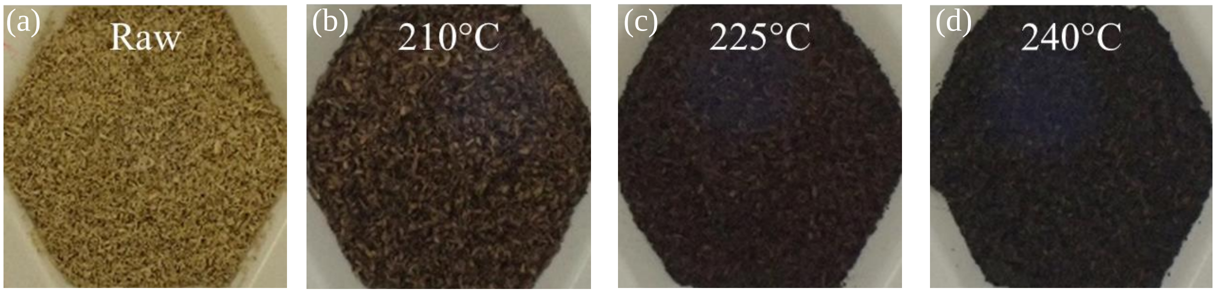

Figure 5.13: Ponderosa pine (a) raw and torrefied in the ternary eutectic salt blend at (b) 210 °C, (c) 225 °C, (d) 240 °C

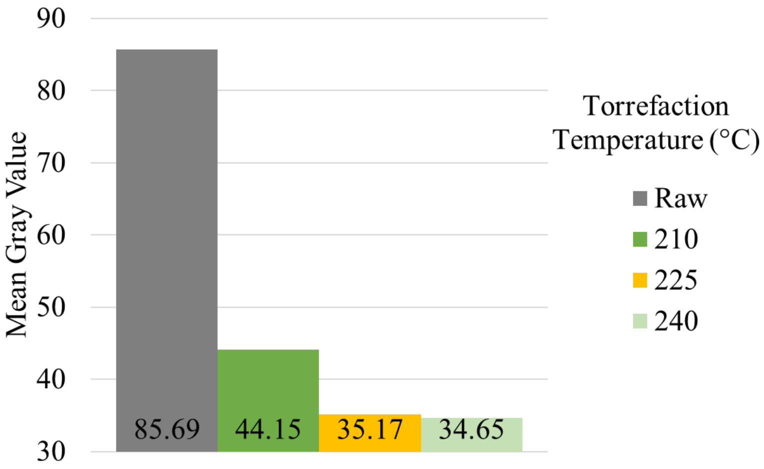

Figure 5.14: Mean gray value for pine torrefied in the ternary eutectic salt blend at 210 °C, 225 °C, and 240 °C

than pine torrefied at lower temperatures. Pine torrefied at 240 °C in molten salts (Fig. 5.13 (d)) is significantly darker than pine torrefied at 210 °C (Fig. 5.13 (b)). Pine torrefied at 240 °C has a mean gray value of 34.65, much lower than the mean gray value of 44.15 for pine torrefied at 210 °C. These trends in the visual appearance of the torrefied biomass is observed in all salt blend compositions.

The HHV and fixed carbon content confirm that torrefaction of the pine has occurred at all three torrefaction temperatures in the salt blends. Additionally, the data confirms that levels of torrefaction, as measured by an increase in HHV and fixed carbon percent, increases as temperature increases. An example of the fixed carbon and HHV results are presented in Figures 5.15 (a) and (b), respectively, for the ternary eutectic salt blend. Torrefaction at 210 °C resulted in an increase in fixed carbon content from 15.1 ± 0.55 % for raw biomass to 22.9 ± 0.79 %. However, the HHV remained statistically unchanged: 20.33 ± 0.24 MJ/kg for the raw versus 20.48 ± 0.2 MJ/kg for 210 °C. Torrefaction temperatures of 225 °C and 240 °C showed greater improvements in the fixed carbon percent and HHV. At 240 °C, the fixed carbon and HHV are 36.5 ± 0.79 % and 24.24 ± 0.26 MJ/kg. These values represent a 142 % increase in the fixed carbon

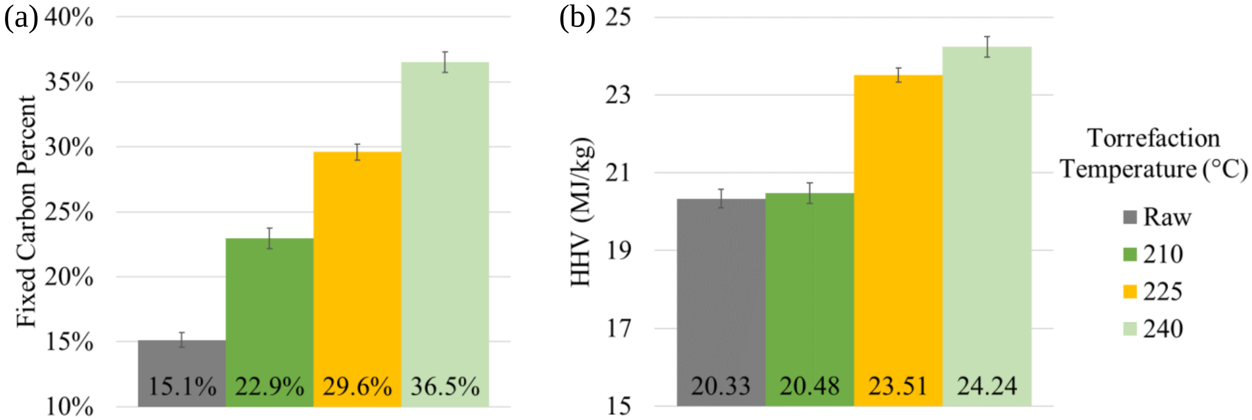

Figure 5.15: (a) Fixed carbon content and (b) HHV for raw and torrefied for ponderosa pine in the ternary eutectic blend at 210 °C, 225 °C, and 240 °C. Uncertainty is calculated with 95 % confidence.

content and 19 % increase in HHV relative to raw biomass. Thus, similar to traditional torrefaction methods, increasing the torrefaction temperature results in increased torrefaction levels.

Torrefaction in molten salts also results in a greater rate of increase in torrefaction levels relative to changes in temperature than for biomass torrefied using traditional methods. An example of this is presented in Figures 5.16 (a) and (b) which present the fixed carbon and HHV of biomass for pine torrefied in the ternary eutectic salt blend and pine torrefied using traditional methods as a function of temperature. Figure 5.16 (a) shows that for biomass torrefied in molten salts, the fixed carbon vs temperature curve from 210 °C-240 °C is steeper than the fixed carbon curve for traditionally torrefied biomass between 210 °C and 275 °C. For example, between 210 °C and 225 °C, molten salt torrefaction increases the fixed carbon content by 6.7 %, an average increase of ~0.45 % per degree Celsius. Over the same temperature step, traditional torrefaction methods only increased the fixed carbon content by 2.5 %, an increase of ~0.17 % per degree Celsius. Additionally, the HHV vs temperature curve for biomass torrefied in molten salts is steeper than for biomass torrefied using traditional methods (Fig. 5.16 (b)). For example, between 210 °C and 225 °C, molten salt torrefaction increases the fixed carbon content by 3.03 MJ/kg, an

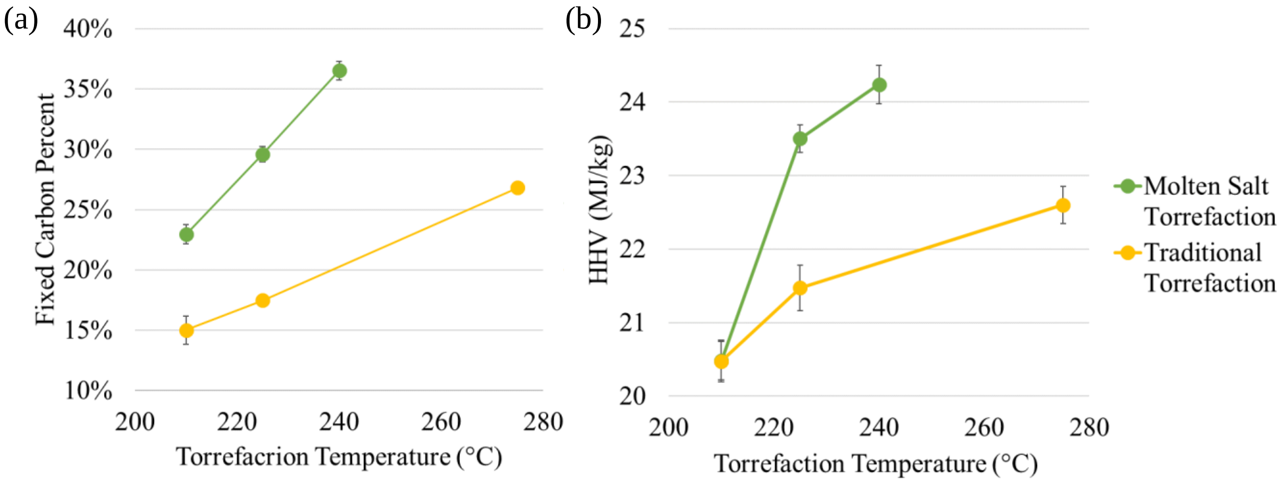

Figure 5.16: (a) Fixed carbon and (b) HHV for pine torrefied at 210 °C and 240 °C in the ternary eutectic salt blend, and 225 °C and 275 °C using traditional methods. Uncertainty is calculated with 95 % confidence.

average increase of 0.202 MJ/kg per degree Celsius. Over the same temperature step, traditional torrefaction methods only increased the fixed carbon content by 0.99 MJ/kg, an average increase of 0.066 MJ/kg per degree Celsius.

5.2.2. Salt Blend Composition

Based on research conducted using molten salts with gasification and pyrolysis, it was expected that lithium would have the greatest effect on torrefaction levels. However, there is no conclusive evidence as to how sodium or potassium content would affect torrefaction levels. To gain an understanding as to how each salt blend composition effects torrefaction levels, five salt blends were investigated. Lithium nitrate composition ranges from 20 wt% to 40 wt%, sodium nitrate composition ranges from 0 wt% to 20 wt% and potassium nitrate composition ranges from 50 wt% to 70 wt%. All compositions were tested at 210, 225, and 240 °C.

The results from torrefying pine in the five salt blends were used to determine which salt type is the most influential in changing the torrefaction level of biomass. The results indicate that lithium nitrate was the most influential, followed by sodium nitrate, and lastly potassium nitrate. This ranking was determined by observing three trends in the date that are summarized in Table 5.1. The first two trends relate to changes in lithium content relative to the other two salts. When the lithium nitrate content increases, which necessitates a decrease in either potassium nitrate (row 1 of Table 5.1) or sodium nitrate (row 2), the level of torrefaction increases. The third trend is that when the lithium content is constant, and the sodium nitrate content increases at the expense

Table 5.1: A summary of the trends between the effect of changing the salt content on the torrefaction level. A dash indicates that the salt content is held constant. An arrow indicates that the salt content increases (up arrow) or decreases (down arrow)

Lithium Nitrate	**Sodium Nitrate**	**Potassium Nitrate**	**Torrefaction Level**
⬆	—	⬇	⬆
⬆	⬇	—	⬆
—	⬆	⬇	⬆

of potassium nitrate, the torrefaction level increases. These trends are observed at the three torrefaction temperatures. However, the trends are most clearly observed in the visual data (mean gray scale value) at a torrefaction temperature of 225 ºC and in the fixed carbon content and HHV data at a torrefaction temperature of 240ºC. Thus, in this section, these are the torrefaction temperatures discussed for each data type. All of the data on varying salt composition and temperature is available in appendix A.

The first trend involves increasing the lithium nitrate, holding the sodium nitrate constant, and decreasing the potassium nitrate content of the salt blend. As shown visually by Fig. 5.17, this change in salt blend composition improves the torrefaction levels of the biomass. Figure 5.17 provides a visual of biomass torrefied at 225 °C in blends 1, 2, and 3, while Figure 5.18 provides the corresponding mean gray value. Figure 5.19 provides the HHV and fixed carbon content for biomass torrefied in these salt blends respectively. Salt blends 1, 2, and 3 all contain 20 wt% sodium nitrate content and varying lithium nitrate and potassium nitrate contents. Salt blend 2 contains 20 wt% lithium nitrate and 60 wt% potassium nitrate and the biomass torrefied in it appears the least torrefied (Fig. 5.17 (a)) and has the highest mean gray value, 39.38 (Fig. 5.18). Additionally, biomass torrefied in salt blend 2 has the lowest fixed carbon content and HHV of the three salt blends at 28.2 ± 0.82 % (Fig. 5.19 (a)) and 22.77 ± 0.40 MJ/kg (Fig. 5.19 (b)) respectively.

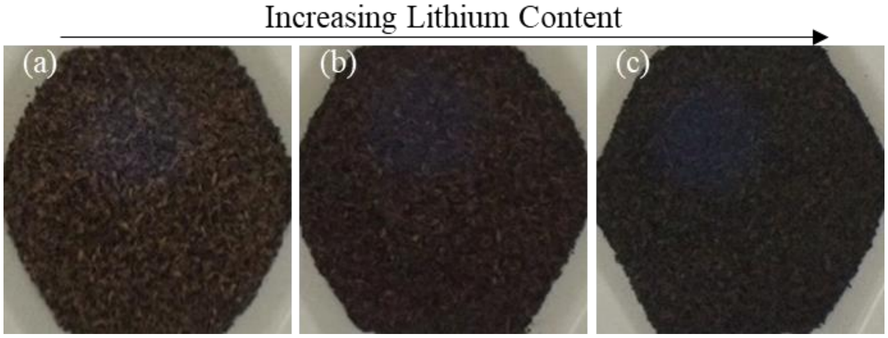

Figure 5.17: Ponderosa pine torrefied at 225 °C in salt blends (a) 2, (b) 1, (c) 3, (d) 5. In all blends the sodium nitrate content is the same. Thus, an increase in lithium nitrate corresponds to a decrease in potassium nitrate.

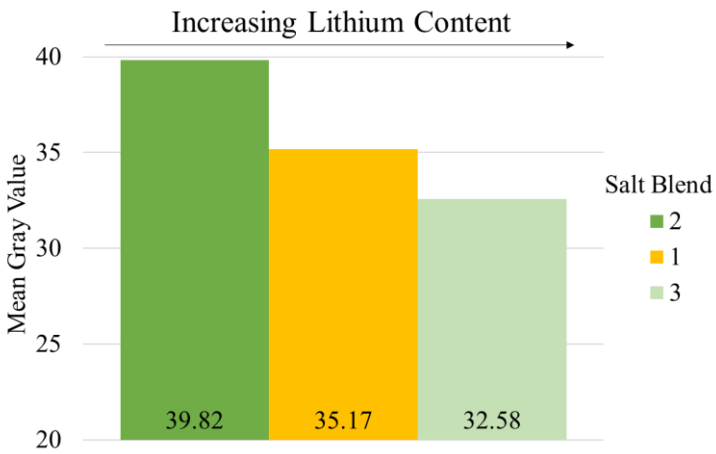

Figure 5.18: Mean gray values for ponderosa pine torrefied at 225 °C in salt blends 1, 2, 3. In all blends the sodium nitrate content is the same. Thus, an increase in lithium nitrate corresponds to a decrease in potassium nitrate. Uncertainty is calculated with 95 % confidence.

With salt blend 3, which contains lithium nitrate and potassium nitrate compositions of 30 wt% and 50 wt% respectively, the biomass visually appears more torrefied (Fig. 5.17 (c)) and has a gray value of 34.38, confirming the visual observation that increased lithium content resulted in darker torrefied biomass. Biomass torrefied in blend 3 has the greatest fixed carbon content and HHV of the three blends; 44.4 ± 0.98 % (Fig. 5.19 (a)) and 24.89 ± 0.16 MJ/kg (Fig. 5.19 (b)) respectively. Thus, the HHV and fixed carbon values for biomass torrefied in the salt blends confirmed the

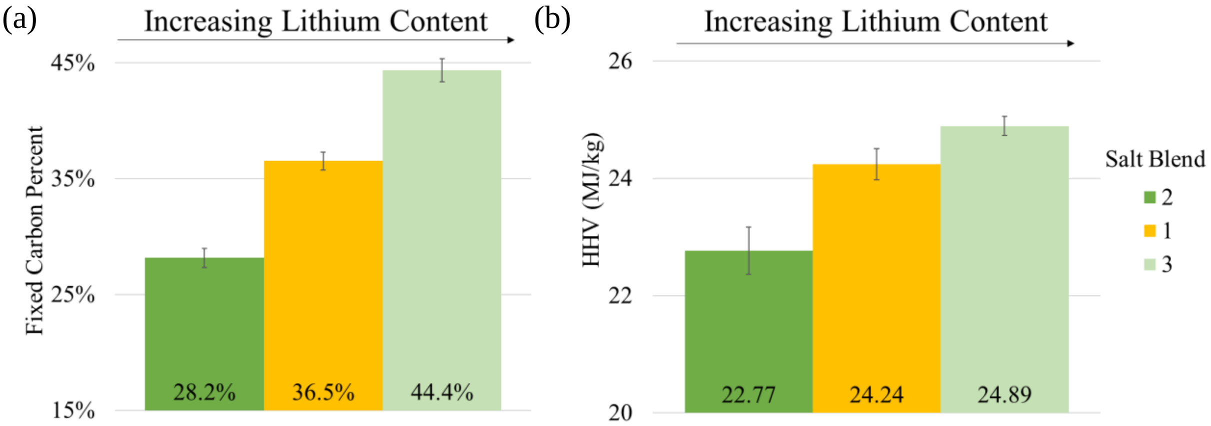

Figure 5.19: (a) Fixed carbon content and (b) HHV for ponderosa pine torrefied at 240 °C in salt blends 1, 2, and 3. In all blends the sodium nitrate content is the same. Thus, an increase in lithium nitrate corresponds to a decrease in potassium nitrate. Uncertainty is calculated with 95 % confidence.

visual observations that increasing lithium at the cost of decreasing potassium nitrate improves torrefaction levels.

The second trend involves increasing the lithium nitrate, decreasing the sodium nitrate, and holding constant the potassium nitrate content of the salt blend. As shown visually by Fig. 5.20 (a) and Fig. 5.20 (b), this change in salt blend composition improves the torrefaction levels of the biomass. Figures 5.20 (a) and (b) provide a visual of biomass torrefied at 225 °C in blends 2, and 5, while Figure 5.20 (c) provides the corresponding mean gray value. The HHV and fixed carbon content for biomass torrefied in these salt blends are provided in Figures 5.21 (a) and (b) respectively. Both salt blends 2 and 5 contain 60 wt% potassium nitrate content and varying lithium nitrate and sodium nitrate contents. Salt blend 2 contains 20 wt% lithium nitrate and 20 wt% sodium nitrate and the biomass torrefied in it appears less torrefied (Fig. 5.20 (a)) and has a higher mean gray value, 39.38 (Fig. 5.20 (c)) than blend 5. Additionally, the fixed carbon content and HHV of biomass torrefied in salt blend 2 is significantly lower than blend 5 at 28.2 ± 0.82 % (Fig. 5.21 (a)) and 22.77 ± 0.40 MJ/kg (Fig. 5.21 (b)) respectively. The biomass torrefied in salt blend 5 (Fig. 5.20 (b)), which contains lithium nitrate and sodium nitrate compositions of 40 wt%

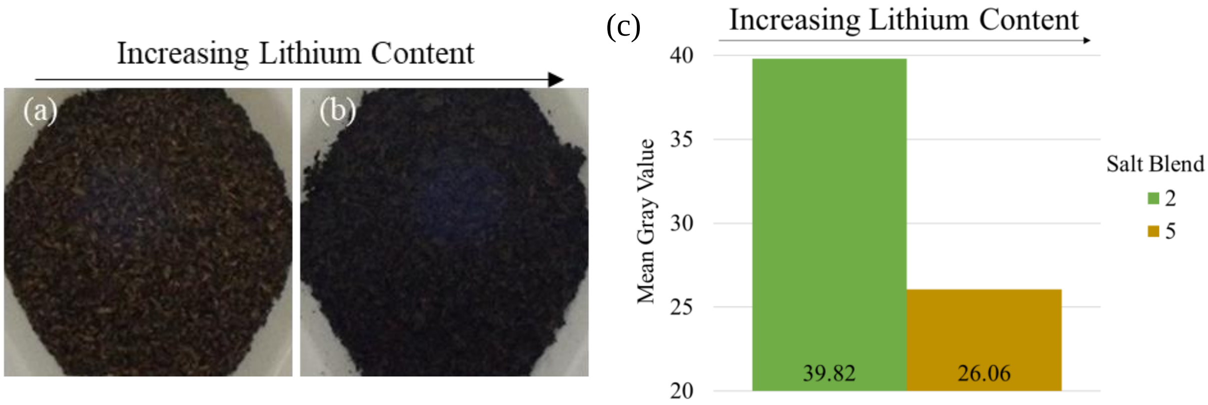

Figure 5.20: Ponderosa pine torrefied at 225 °C in salt blends (a) 2, and (b) 5; and (c) the corresponding mean gray values. In both blends the potassium nitrate content is the same. Thus, an increase in lithium corresponds to a decrease in sodium nitrate. Uncertainty is calculated with 95 % confidence.

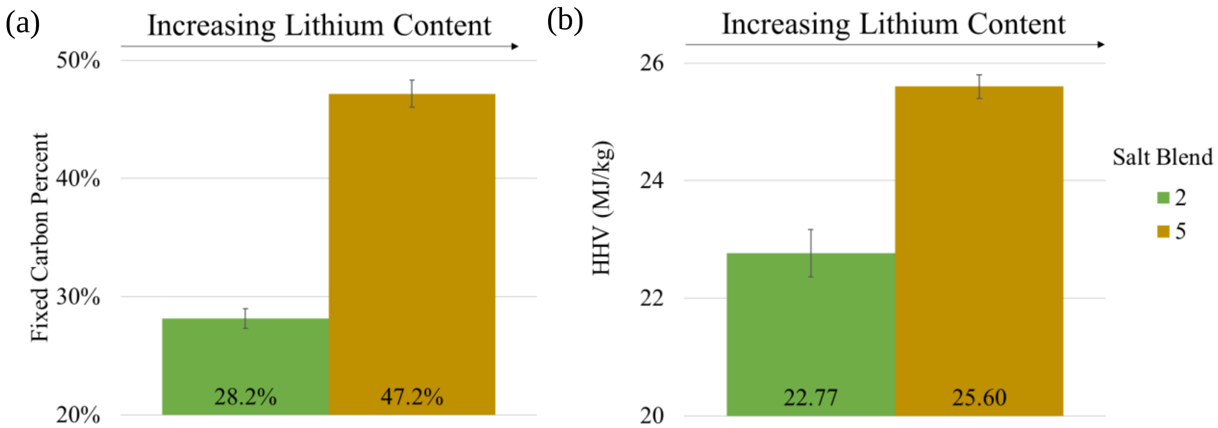

Figure 5.21: (a) Fixed carbon content and (b) HHV for ponderosa pine torrefied at 240 °C in salt blends 2 and 5. In both blends the potassium nitrate content is the same. Thus, an increase in lithium corresponds to a decrease in sodium nitrate. Uncertainty is calculated with 95 % confidence.

and 0 wt% respectively, visually appears to be significantly more torrefied than blend 2 and has a gray value of 26.06. Biomass torrefied in blend 5 has a greater fixed carbon content and HHV than blend 2; 47.2 ± 1.14 % (Fig. 5.21 (a)) and 25.60 ± 0.20 MJ/kg (Fig. 5.21 (b)) respectively. Thus, the HHV and fixed carbon values for biomass torrefied in salt blends 2 and 5 confirmed the visual observation that increasing lithium at the cost of sodium nitrate results in improved torrefaction levels.

The third trend involves holding the lithium nitrate constant, increasing the sodium nitrate, and decreasing the potassium nitrate content of the salt blend. As shown visually by Fig. 5.22 (a) and Fig. 5.22 (b), this change in salt blend composition improves the torrefaction levels of the biomass. Figures 5.22 (a) and (b) provide a visual of biomass torrefied at 225 °C in blends 2, and 5, while Figure 5.22 (c) provides the corresponding mean gray value. The HHV and fixed carbon content for biomass torrefied in these two salt blends are provided in Figures 5.23 (a) and (b) respectively. Both salt blends, 2 and 5, contain 30 wt% lithium nitrate content and varying sodium nitrate and potassium nitrate contents. Salt blend 4 contains 0 wt% sodium nitrate and 70 wt% potassium nitrate and the biomass torrefied in it appears less torrefied (Fig. 5.22 (a)) and has a

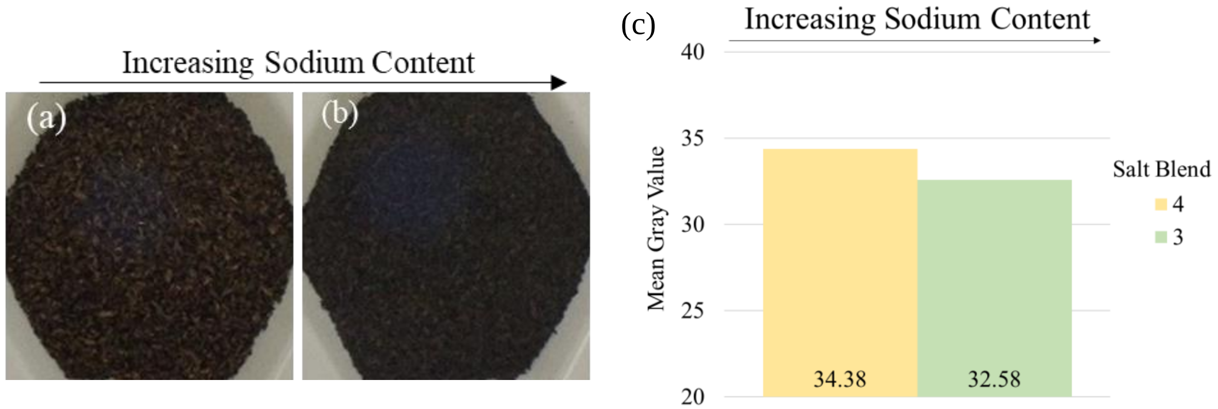

Figure 5.22: Ponderosa pine torrefied at 225 °C in salt blends (a) 4, and (b) 3; and (c) the corresponding mean gray values. In both blends the lithium nitrate content is the same. Thus, an increase in sodium corresponds to a decrease in potassium nitrate. Uncertainty is calculated with 95 % confidence.

higher mean gray value, 34.38 (Fig. 5.22 (c)) than blend 5. Additionally, the fixed carbon content and HHV of biomass torrefied in salt blend 4 is significantly lower than blend 5 at 35.5 ± 1.45 % (Fig. 5.23 (a)) and 23.37 ± 0.16 MJ/kg (Fig. 5.23 (b)) respectively. The biomass torrefied in salt blend 3 (Fig. 5.22 (b)), which contains sodium nitrate and potassium nitrate compositions of 20 wt% and 50 wt% respectively, visually appears to be more torrefied than blend 4 and has a gray value of 32.58. Biomass torrefied in blend 3 has a greater fixed carbon content and HHV than

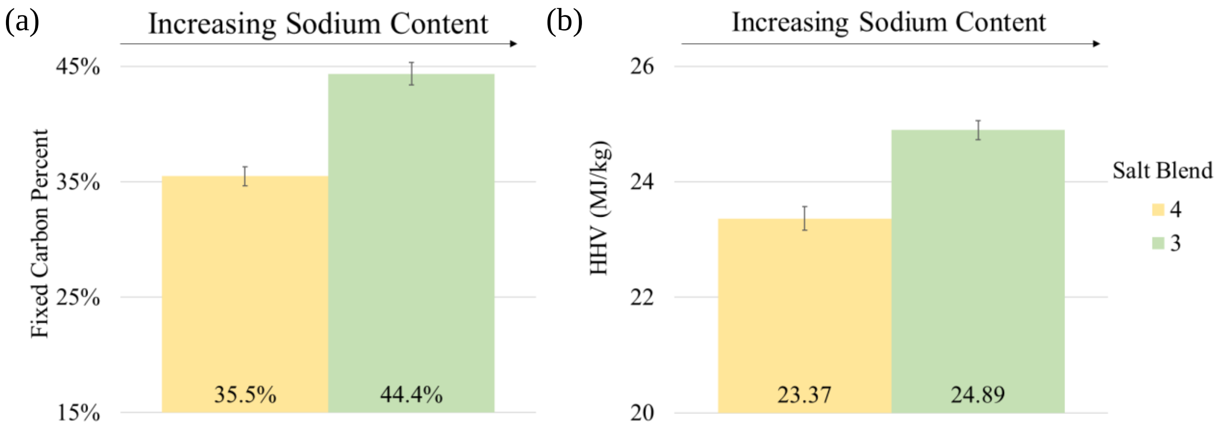

Figure 5.23: (a) Fixed carbon content and (b) HHV for ponderosa pine torrefied at 240 °C in salt blends 3 and 4. In both blends the lithium nitrate content is the same. Thus, an increase in sodium corresponds to a decrease in potassium nitrate. Uncertainty is calculated with 95 % confidence.

blend 4; 44.4 ± 0.98 % (Fig. 5.23 (a)) and 24.89 ± 0.16 MJ/kg (Fig. 5.23 (b)) respectively. Thus, the HHV and fixed carbon values for biomass torrefied salt blends 3 and 4 confirmed the visual observation that increasing sodium at the cost of potassium nitrate results in improved torrefaction levels.

In summary, increasing the content of lithium nitrate improved torrefaction levels regardless of which other salt it is replacing in the salt blend. Increases in sodium nitrate sodium nitrate did not improve torrefaction levels if the salt it was replacing is lithium nitrate, but improves torrefaction levels when replacing some of the potassium nitrate in the blend. From this, it can be concluded that lithium nitrate is the most influential component of the salt blend; producing the greatest effect on the torrefaction levels when its amount is altered in the blend. The second most influential salt blend is sodium nitrate. It improves the torrefaction levels if it reduced potassium nitrate content but decreases the torrefaction levels when it replaces lithium nitrate. The least influential component is potassium nitrate. Any increase in potassium nitrate reduced torrefaction levels at all temperatures because to increase the potassium nitrate content requires a decrease in one of the more active salt types. Thus, it is hypothesized that the greatest torrefaction levels at a given temperature will maximize the lithium nitrate and sodium nitrate contents, prioritizing lithium content over sodium content, and minimizing the amount of potassium nitrate in the salt blend.

With lithium being the component salt with the most influence on torrefaction levels, blends which maximize lithium content can be used to further reduce torrefaction temperatures. An example of this compares the torrefaction levels of biomass torrefied using traditional methods to biomass torrefied using blends 2 and 5. Figures 5.24 and 5.25 provide the fixed carbon and HHV for biomass torrefied in salt blend 2 at 225 °C and 240 °C, blend 5 at 210 °C, and using traditional methods at 275 °C. Pine torrefied in salt blend 2 at 225 °C has a fixed carbon content and HHV is less than pine torrefied at 275 °C using traditional methods. However, at 240 °C, pine torrefied in blend 2 has a fixed carbon content and HHV slightly greater than traditionally torrefied pine at 275 °C. Torrefaction in blend 2 at a temperature close to, but less than then 240 °C, produces torrefaction levels similar to traditional methods at 275 °C, a reduction of at least 35 °C. However, using salt blend 5, at a torrefaction temperature of 210 °C, torrefied biomass has a fixed carbon

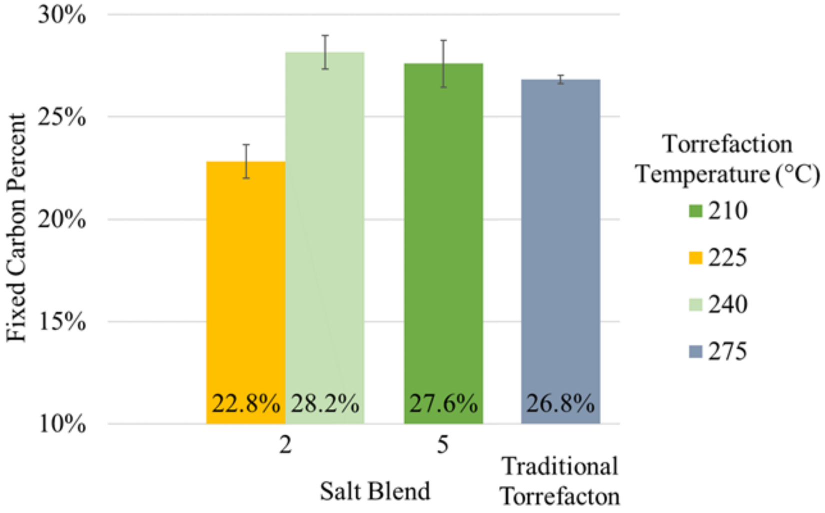

Figure 5.24: Fixed Carbon for pine torrefied in salt blends 2 and 5 and using traditional methods at 275 °C. Uncertainty is calculated with 95 % confidence.

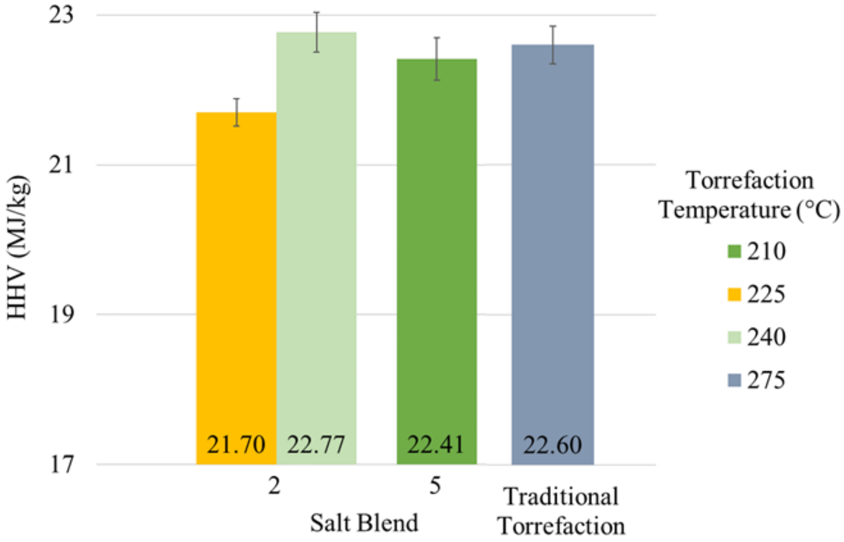

Figure 5.25: HHV for pine torrefied in salt blends 2 and 5 and using traditional methods at 275 °C. Uncertainty is calculated with 95 % confidence.

content (27.6 ± 1.14 %) and HHV (22.41 ± 0.20 MJ/kg) statistically identical to biomass torrefied using traditional methods at 275 °C (26.8 ± 0.20 % and 22.60 ± 0.25 MJ/kg respectively); a significant reduction in torrefaction temperature, 65 °C. Torrefaction in blend 5 achieves the same level of torrefaction as traditional methods at 275 °C, a 30 °C reduction over blend 2. Therefore, the use of a salt blend with greater lithium content can be used to reach identical torrefaction levels as a low lithium salt blend, at significantly reduced temperatures.

The results obtained through testing the effect of the salt blend and torrefaction temperature confirm that torrefaction in molten salts can be used to significantly reduce torrefaction temperatures. At temperatures as low as 210 °C, high lithium salt blends can achieve torrefaction levels identical to traditional methods at 275 °C. Additionally, these results show that similarly to traditional torrefaction, torrefaction levels improve with increasing temperature. However, smaller increases in temperature are needed to improve torrefaction levels by a similar margin, i.e. torrefaction in molten salts is more sensitive to temperature variation than traditional torrefaction methods. The main take away from these results is how torrefaction levels change with altering salt compositions. Lithium nitrate is the most influential component salt, sodium nitrate is the next most influential component salt, and potassium nitrate is the least influential salt on torrefaction levels. Additionally, using a salt blend with high lithium nitrate composition significantly reduces torrefaction temperatures.

6. CONCLUSIONS AND RECOMMENDATIONS

6.1. Conclusions

This thesis has shown confirmation of the hypothesis that molten salts can reduce torrefaction temperatures. A reduction in temperature by as much as 65 °C was achieved without affecting the biomass's level of torrefaction. Torrefying ponderosa pine at 210 °C in a 40 wt% lithium nitrate and 60 wt% potassium nitrate salt blend, the fixed carbon content and HHV were statistically indifferent from ponderosa pine torrefied at 275 °C using traditional methods; ~27 % and ~22.5 MJ/kg respectively.

This study developed a successful molten salt torrefaction methodology to achieve consistent torrefaction. The baseline methodology utilizes the ternary eutectic nitrate salt blend, biomass particles between 250 µm and 500 µm, a salt-to-biomass ratio of 20:1, a torrefaction temperature of 225 °C, a residence time of 2 hours, and a high purity nitrogen environment. A lab-scale torrefaction apparatus and loading methodology was developed to maintain consistent contact between the salt and biomass during torrefaction. This methodology uses a weighted screen to keep the biomass completely submerged in the molten salt, premixing of the salt and biomass before loading the crucibles, and a buffer layer of pure salt to separate the biomass from the weighted screen and crucible. Additionally, a washing methodology was developed utilizing three, two-hour wash cycles to fully separate the salt and biomass after torrefaction.

Using this lab-scale methodology, research was conducted to investigate the effect of temperature and salt blend composition on torrefaction levels. Five salt blends with lithium, sodium, and potassium nitrate compositions varying from 20 wt% to 40 wt%, 0 wt% to 20 wt%, and 50 wt% to 70 wt% respectively were investigated along with temperatures of 210 °C, 225 °C, and 240 °C. This research determined that regardless of the salt blend used, increasing the torrefaction temperature improved the level of torrefaction of the biomass; resulting in a greater fixed carbon content and higher heating value. Additionally, it was determined that lithium nitrate is the most influential, sodium nitrate is the second most influential, and potassium nitrate is the least influential of the salts on torrefaction levels. All of the salt blends tested were successful in reducing torrefaction temperatures when compared to traditional torrefaction methods; salt blends with the highest lithium nitrate content reduced torrefaction temperatures by the greatest amount.

6.2. Future Recommendations

This work has provided the basis through which a further understanding of molten salt torrefaction can be developed. Further work should focus on the purge gas species, prediction of the salt blend composition, reuse of the salt blend, a cost analysis of the process, and development of a solar reactor for molten salt torrefaction.

For traditional torrefaction methods, an inert environment is necessary to prevent the biomass from combusting. In an oxidative environment, partial combustion of the biomass occurs through the torrefaction procedure; reducing the total energy content of the products [64]. However, with molten salt torrefaction, the biomass is completely submerged in the molten salt blend and not in direct contact with the environment. Results from this study indicate that molten salt torrefaction is not as sensitive to an oxidative torrefaction environment as traditional torrefaction method. If combustion of the biomass does not occur in an oxidative environment, the cost and energy associated with producing the nitrogen needed to create an inert environment are saved; improving the efficiency and feasibility of molten salt torrefaction. Further work needs to be performed to confirm if this can be taken advantage of.

In this research, five salt blends were investigated to determine which component salt was the most influential on torrefaction levels; determining lithium nitrate is the most influential component and sodium nitrate is the second most influential. The composition of the blends tested were obtained from an experimental study to determine the eutectic composition of this three-component system. However, the actual eutectic composition was determined through modeling of the Gibbs energy of the system [52]. Using the Gibbs energy method, a model could be developed to determine the composition of salt blends which melt at a given temperature. This would be useful to obtain the maximum lithium and sodium nitrate content (prioritizing the lithium nitrate content) salt blend which can be used with a given torrefaction temperature.

The current torrefaction methodology dissolves the entire salt blend to separate it from the biomass, a method should be developed to remove the salt blend while the blend is still molten. This would leave the majority of the blend to be reused without further processing and require less energy to remove the rest of the salt blend from the wash water to reuse it. This would also reduce the amount of water needed to remove all of the salt blend from the biomass. Additionally, confirmation is needed on reusing the salt blend for subsequent torrefaction procedures. It has been shown that for gasification, the salt blend can be reused without any negative effects [44]. However, at a 20:1 salt to biomass ratio, the cost of torrefaction would far outweigh the benefits of molten salt torrefaction if the salt cannot be reused.

A cost and benefit analysis should be performed to optimize the economics of molten salt torrefaction; for example, salt blend composition vs torrefaction temperature. Although maximizing the lithium content of the salt blend produces greater levels of torrefaction at lower temperatures, the cost of the salt blend increases because lithium nitrate is the most expensive of the three component salts. However, as torrefaction temperatures are reduced the cost of the solar concentrator is reduced as well. A cost analysis of the system would be beneficial at simultaneously investigating the cost of the salt blend and solar concentrator vs the energy content of the torrefied biomass to determine the most economic salt blend and torrefaction temperature. Additional areas that could be considered in a cost vs benefit analysis include the salt to biomass ratio, residence time, reclamation of the salt blend and wash water.

Finally, the driving factor of the development of a molten salt torrefaction procedure was to take advantage of solar torrefaction using the reduced solar resources in areas of the country with ample biomass resources. This research has reduced torrefaction temperatures significantly, by at least 65 °C. With this information, the design and testing of a solar, molten salt torrefaction reactor would be a logical step to take in the future. However, as detailed previously, there are other aspects of the molten salt torrefaction procedure which need further attention prior to bringing the research full circle and designing a solar reactor for molten salt torrefaction.

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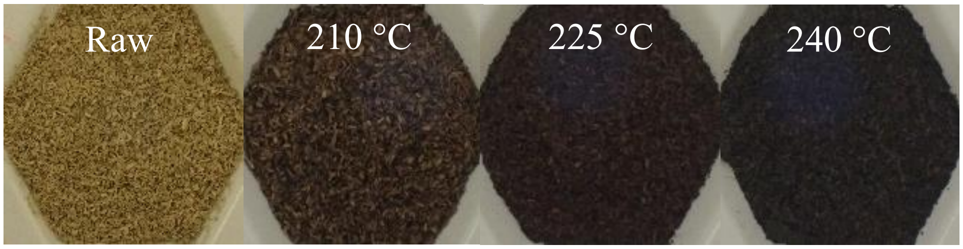
APPENDIX: SALT BLEND COMPOSITION DATA

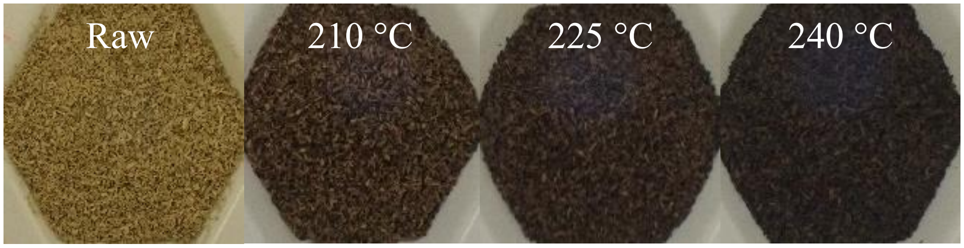
This appendix details all of the data collected through the investigation of temperature and salt blend composition effects on torrefaction levels. Included are images of the torrefied biomass, mean gray values for those images, the fixed carbon percent and the higher heating value of the biomass torrefied in the five salt blends at 210 °C, 225 °C, and 240 °C in addition to the controls. It was determined that the fixed carbon content and HHV for biomass torrefied at 225 °C in salt blend 4 and at 240 °C using traditional methods is not reliable. For this reason, at these data points, the fixed carbon and HHV data has been omitted.

(a)



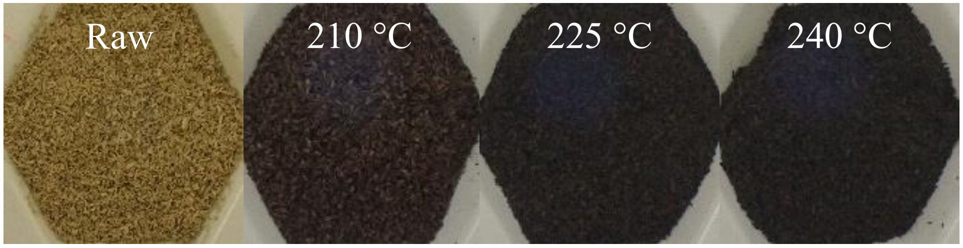
20.01 wt% $NaNO_3$, 25.92 wt% $LiNO_3$, 54.07 wt% KNO_3

(b)



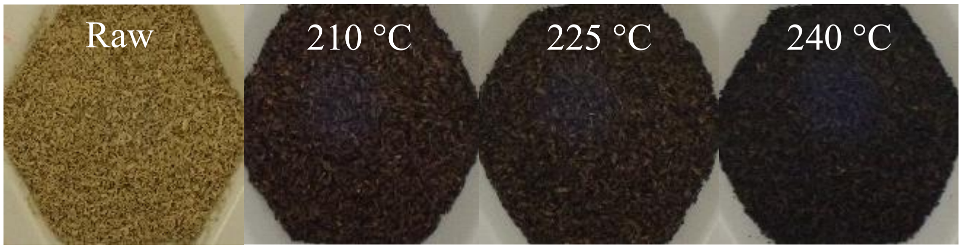
20 wt% $NaNO_3$, 20 wt% $LiNO_3$, 60 wt% KNO_3

(c)



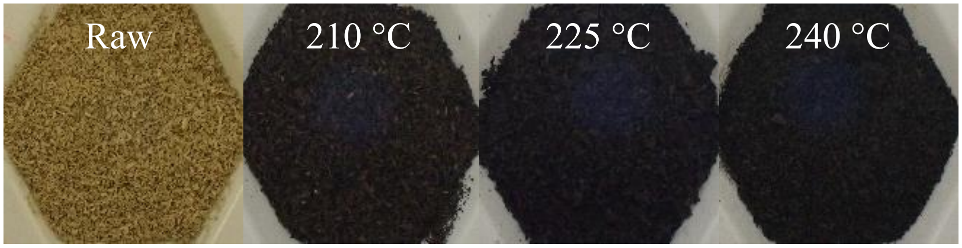
20 wt% $NaNO_3$, 30 wt% $LiNO_3$, 50 wt% KNO_3

(d)



0 wt% $NaNO_3$, 30 wt% $LiNO_3$, 70 wt% KNO_3

(e)



0 wt% $NaNO_3$, 40 wt% $LiNO_3$, 60 wt% KNO_3

Figure A.1: Images of raw ponderosa pine, and ponderosa pine torrefied at 210 °C, 225 °C, and 240 °C in (a) salt blend 1, (b) salt blend 2, (c) salt blend 3, (d) salt blend 4, and (e) salt blend 5

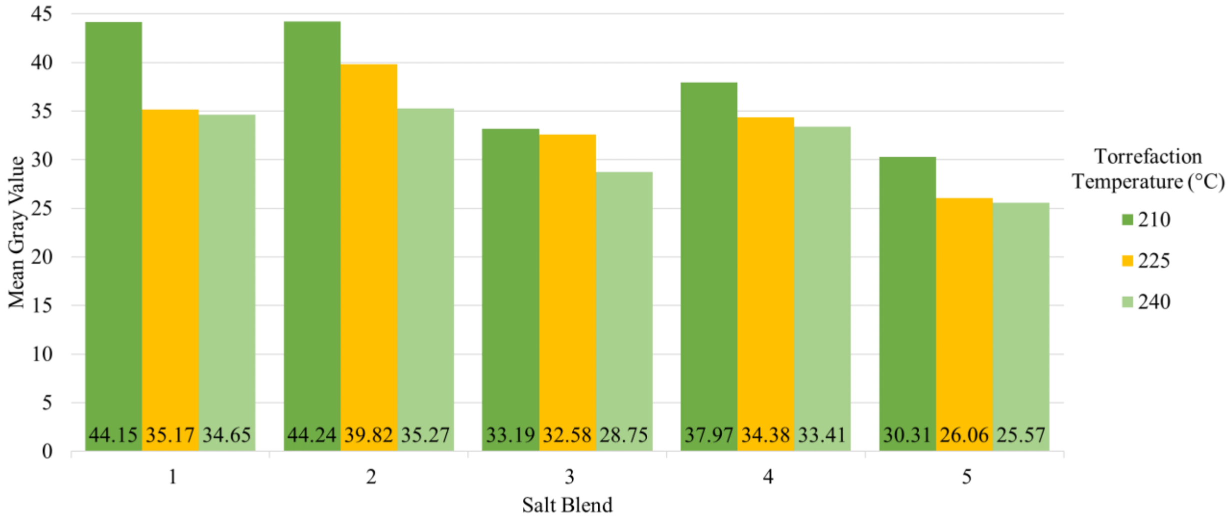


Figure A.2: Mean gray values for pine torrefied in each salt blend at 210 °C, 225 °C, and 240 °C

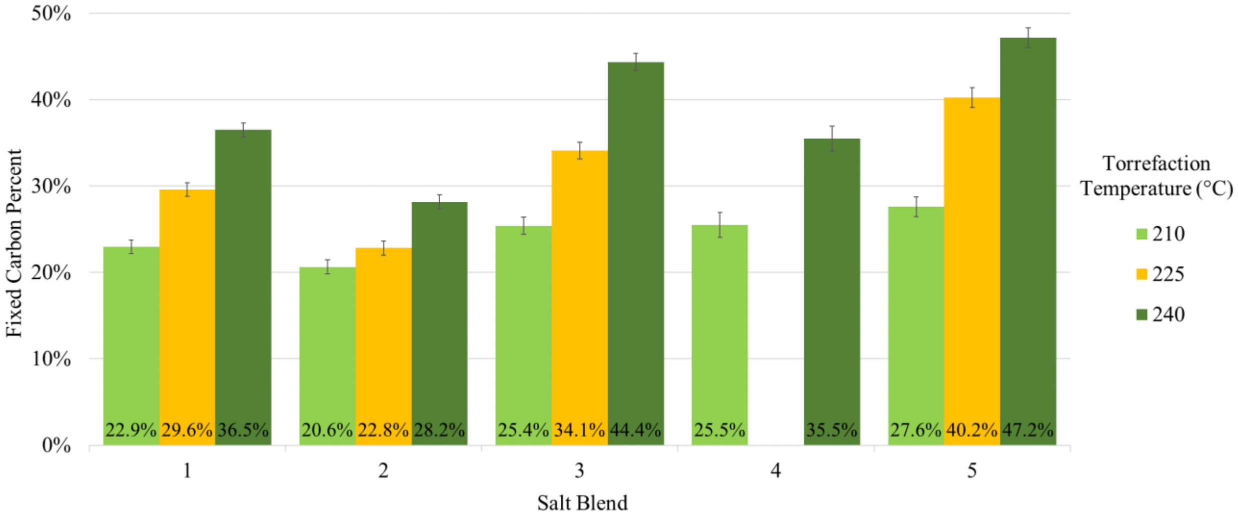


Figure A.3: Fixed carbon content for pine torrefied in each salt blend at 210 °C, 225 °C, and 240 °C. Uncertainty is calculated with 95 % confidence.

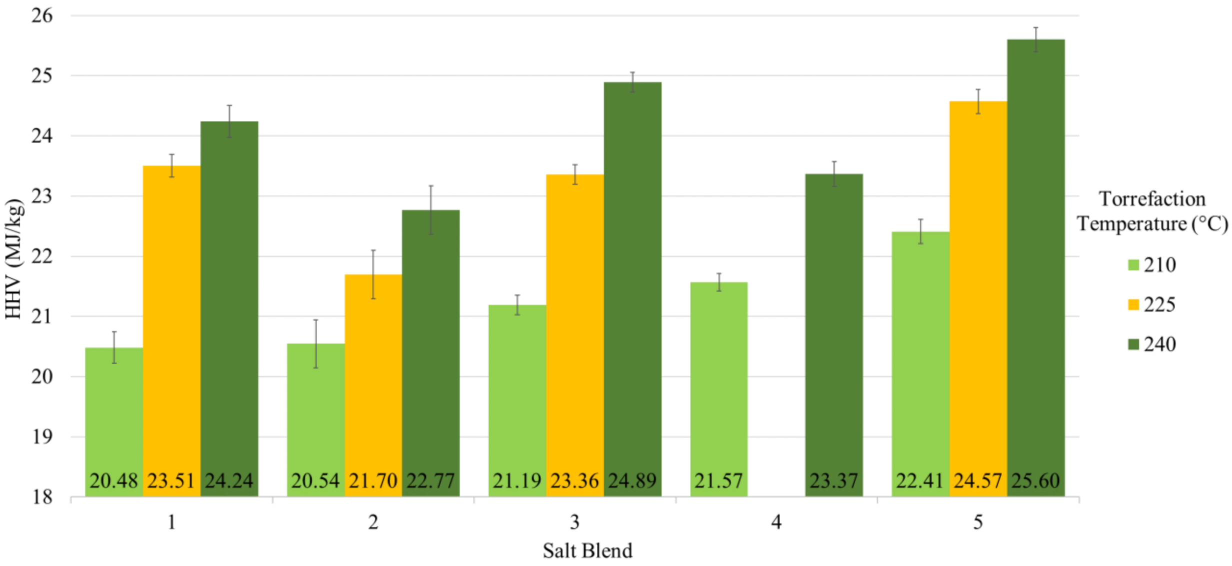


Figure A.4: Higher heating values for pine torrefied in each salt blend at 210 °C, 225 °C, and 240 °C. Uncertainty is calculated with 95 % confidence.

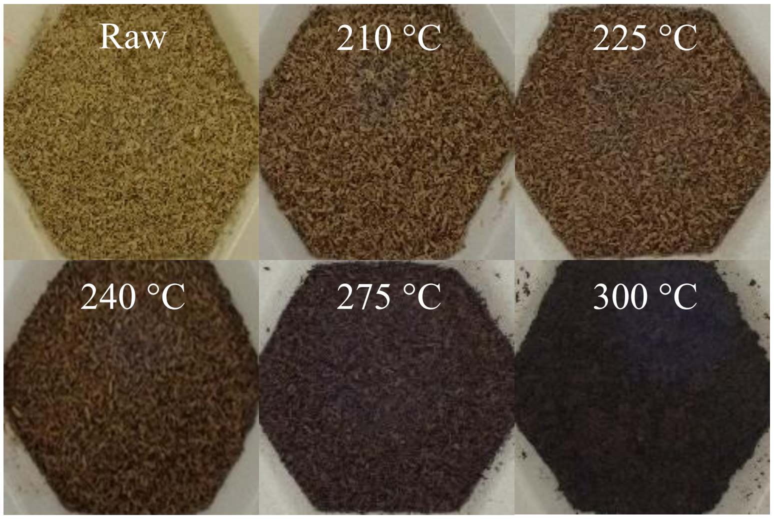


Figure A.5: Raw ponderosa pine and ponderosa pine torrefied using traditional methods at 210 °C, 225 °C, 240 °C, 275 °C, and 300 °C

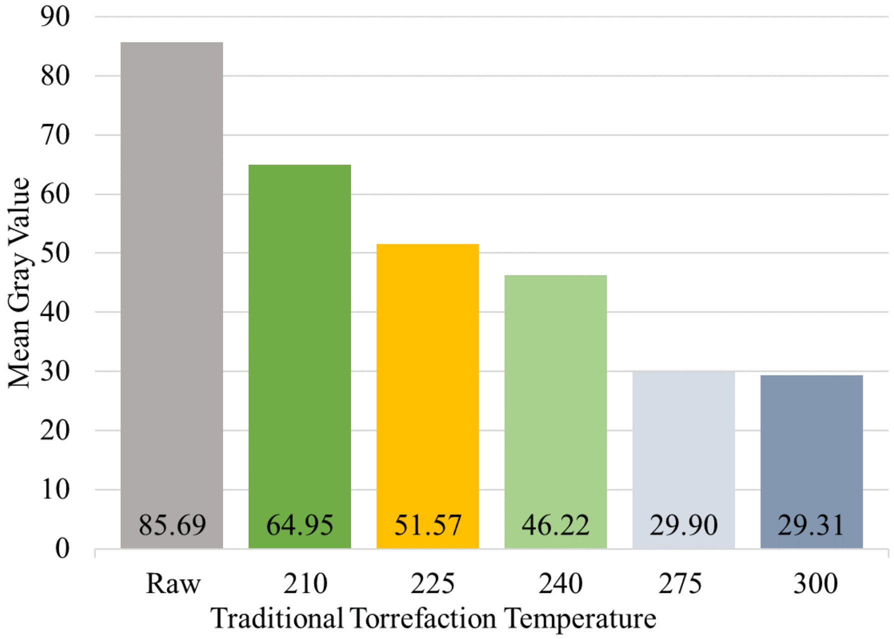


Figure A.6: Mean gray values for raw ponderosa pine and ponderosa pine torrefied using traditional methods at 210 °C, 225 °C, 240 °C, 275 °C, and 300 °C

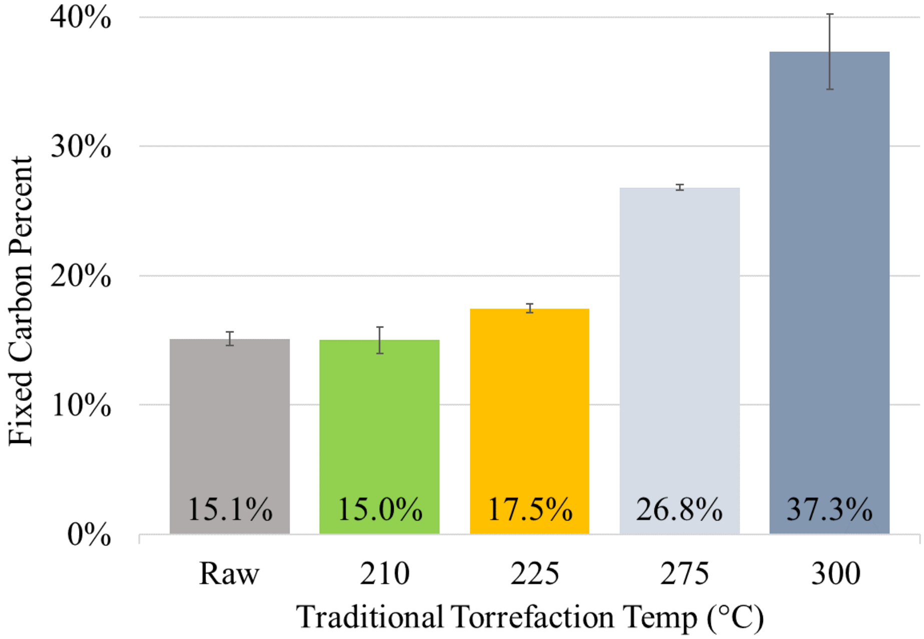


Figure A.7: Fixed carbon percent for raw ponderosa pine and ponderosa pine torrefied using traditional methods at 210 °C, 225 °C, 240 °C, 275 °C, and 300 °C. Uncertainty is calculated with 95 % confidence.

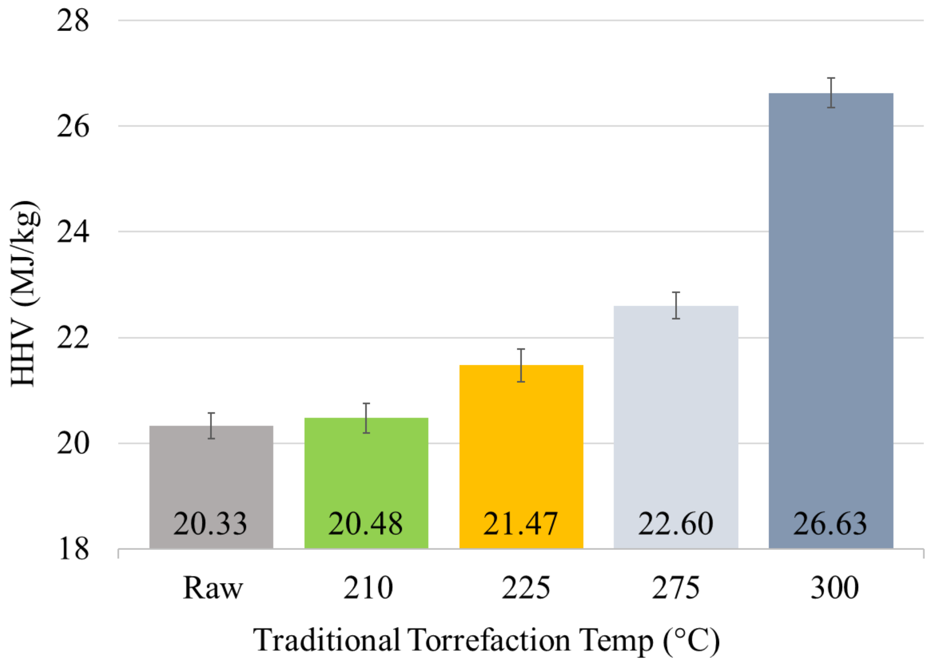


Figure A.8: Higher heating values for raw ponderosa pine and ponderosa pine torrefied using traditional methods at 210 °C, 225 °C, 240 °C, 275 °C, and 300 °C. Uncertainty is calculated with 95 % confidence.