The Effect of Chemical Storage Pretreatment of Loblolly Pine Bark on Pyrolysis Conversion

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Abstract

Bark is an undervalued but abundant and low-cost biomass feedstock available for thermochemical conversion into liquid fuels and biochar. But bark has a high ash (inorganic) and lignin content, restricting the conversion efficiency. This thesis focuses on the use of anerobic storage with low severity chemicals on pine bark to increase pyrolysis conversion. Treatments of loblolly pine bark included acid (0.1% and 1% sulfuric acid, w/w dry basis) and alkali (4% sodium hydroxide, w/w dry basis). Pretreated bark was then incubated anaerobically for 1 and 2 weeks, simulating an in-pile treatment at a refinery gate. Bark was pyrolyzed at 500°C by a microwave assisted fast pyrolysis reactor. Sulfuric acid treatments reduced alkali and alkaline earth metals (AAEM) from the bark and showed an increase in oil production over the native bark. Although oil production was not statistically significant, significant compositional changes of the bark were observed and influenced the quality of the pyrolysis products. Biochar was further analyzed for potential in the agricultural sector as a soil amendment and carbon sequester. Key performance indicators for the use of biochar as a solid fuel were also analyzed by proximate composition, thermal recalcitrance, combustion and energy characteristics, pH, and electrical conductivity. The 1% sulfuric acid treatment showed great improvement in key performance indicators therefore it can be successful in both soil amendment and solid fuel applications. The alkaline treatment significantly decreased both oil conversion and the key performance indicators, thus it is not a satisfactory pretreatment for pyrolysis conversion. Furthermore, a lower cost chemical drying process utilizing dimethyl ether (DME), was explored for compositional changes, pyrolysis yields, and biochar potentials. The DME treatment did not significantly change the initial materials composition.

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Dedication

To the 11 hours and 21 minutes of Lord of the Rings. To my family. I wouldn’t have gone this far without the encouragement and love from you all. Finally, in memory of Mama and Shelley.

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Chapter 1: Introduction

Motivation

Forest residues are currently considered a waste in the wood industry. Generally, forest residue is left to decompose in the forest, burnt for heat energy, or discarded in landfills. With the growing demand for alternative fuel sources, forest residues offer a plentiful low-cost feedstock for energy conversion. Forest residue can be separated into fractions; needles/leaves, bark, branches, and tops. The focus of this work is directed to the bark fraction. Bark is also accumulated in timber processing industries such as lumber and mill and paper and pulp. In the 1940's, newer bark removal technologies using hydraulics drew attention to the vast amount of bark. Little was known about the chemical composition of bark at the time, so research began to characterize and evaluate bark for utilization [1]. Since then, research activity on the utilization of bark has been conducted and has been evolving as new analytical techniques are developed. Currently, the use of biomass is heavily investigated as an alternative to fossil fuels, but bark is known for having high ash (inorganic) and lignin content and highly complex chemical makeup. These attributes hinder bark's ability for effective conversion into fuels.

The motivation of this work is exploring a way to valorize bark as a value-added product via pyrolysis. Bark is subjected to a combination of low severity chemical addition and anerobic storage time in hopes to remove ash and improve pyrolysis liquid yield. If the copious amount of bark produced could produce higher quantities of oil, the economic value will increase as well as provide renewable fuel. The quality of the products (char, oil, extractives) could also increase value and opportunities of bark as a renewable resource.

Review of Lignocellulosic Biomass

Renewable fuels made from lignocellulosic biomass have become a primary research area for the advancement of lower carbon emissions for power and transportation generation. Currently, renewable fuels from lignocellulosic biomass are difficult to produce in mass due to seasonal harvest and the high variations in chemical makeup and moisture contents between species. Lignocellulosic biomass can be broken into two types: herbaceous and woody biomass. Herbaceous biomass comes from plants that have nonwoody stem and will die back at the end of the growing season [2]. This type of biomass includes agricultural crops and grasses (i.e., bamboo, wheat straw, corn, etc.). Woody biomass includes trees and their associated parts: twigs, tops, needles, and leaves [3].

Benefits of woody biomass outnumbers herbaceous biomass though various means. Woody biomass has higher recalcitrance to microbial and enzymatic actions, can be harvest year-round, higher density, higher lignin content, and generally has lower pentose content for a more favorable conversion to ethanol [4]. In addition, herbaceous biomass contains more ash (up to 30% ash) than woody biomass (<0.5%) [5]. The physical properties of woody biomass (i.e., density, size, and shape) also exceeds herbaceous biomass as well as it's calorific value and chemical composition. The bulk density of woody biomass is roughly 250 kg/m^3 and a moisture content of 50% or higher wet basis whereas herbaceous biomass is 150-160 kg/m^3 and moisture content ranges from 18-30% (wet basis – w.b.). A method of increasing the energy properties of herbaceous biomass would be to blend with woody biomass, this can lower the energy consumption of having to grind and dry wood and increase the energy properties that herbaceous biomass lacks [3].

This review will describe the cell structure of lignocellulosic and woody biomass to understand the structural complexity, discuss delamination techniques, review some current methods of conversion, and discuss bark and potential utilization.

Lignocellulosic Composition

The plant cell structure is mainly composed of cellulose, hemicellulose, and lignin with small traces of pectin [6-8]. The cell wall is made up of several layers; the primary wall, secondary wall that is made up of three layers (S1, S2, and S3), and the middle lamella. The secondary wall differs from the primary wall due to the orientation of cellulose nano-fibrils. The middle lamella, mainly pectin, holds the neighboring cells together. The components work together to support nutrient transport in growth and gives strength for the plant to withstand the environmental stimuli such as wind, moisture, and physical disruption [7, 8].

Cellulose is the major component of the cell wall made of (1-4)-B-D-glucopyranose and other monosaccharides (fructose, galactose, cellulose, xyloglucans, and pectin). Hemicellulose consists of branched polymers made of monosaccharides, pentose sugars, hexoses sugars, L-arabinose and D-xylose, D-glucose, D-mannose, and D-galatose. Lignin is made of mostly insoluble phenyl propane units (monolignins) and gives support to the cell wall by filling the space between cellulose, hemicellulose, and pectin [6, 8-10]. Together, hemicellulose and lignin are a matrix of cellulose nano-fibrils cross-linked with hemicellulose polysaccharide chains that form p-hydroxyphenyl, guaiacyl, and syringyl units [6, 8]. Pectin has a makeup of rhamnogalacturonans I and II, pectinmethylesterase, homogalacturonan, and arabinogalactans [11].

Woody biomass

Wood formation is an ordered process of cell division, cell expansion, secondary wall deposition, lignification, and programmed cell death [12]. The center of the tree is the pith, surrounded by heartwood, a zone of inactive tissues that no longer move water is darker than the sapwood that surrounds it. Sapwood is also known as the secondary xylem. New wood is formed in the vascular cambium, or the interface with the bark. Annual rings are the repetitive light rings from earlywood in the beginning of the growing season and the denser dark rings of latewood [13]. The anatomy of a tree is depicted in Fig. 1.1.

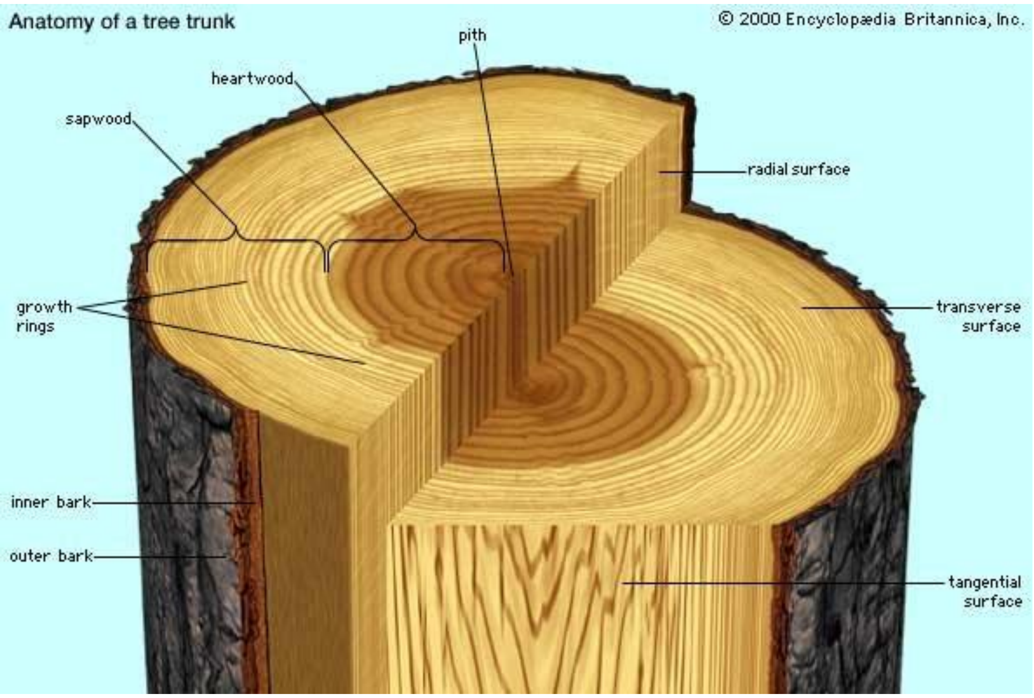

Figure 1.1. The anatomy of a tree trunk. Encyclopedia Britannica

Wood is a complex biomass with a heterogeneous macro and micro-scale makeup in a 3D network polymer composed of tracheids (Fig. 1.2). These hollow fibrous cells interconnected to each other, and the cell walls have sub-layers of numerous microfibrils [14].

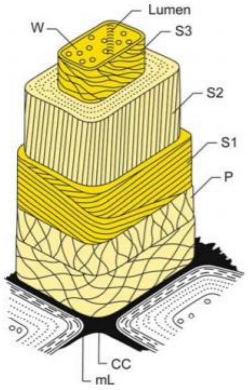

Figure 1.2 Schematic description of tracheid cell wall structure in black spruce wood: W = thin warty layer in cell lumins, S3, S3, S1 = secondary wall layers, P = primary wall, mL = middle lamella, and CC = cell corner [6].

Hardwood and softwood have different characteristics. In general, softwood has a chemical makeup of 42% cellulose, 27% hemicellulose, 28% lignin, and 3% extractives whereas hardwood have 44%, 28%, 24% and 4% respectively [9, 13]. Examples of hardwood trees include species such as beech, maple, ash, and oak; softwoods include pine, fur, and cedar. Softwood has cells whereas hardwood has irregularity of large tracheids among the regular cells as seen in Fig 1.3 [13, 14]. Tracheids support the mass of the tree and transport water and mineral salts from the roots aligned longitudinally to the trunk. The longitudinal direction allows for the transport of fluids in addition to supporting the structure. Ray cells bring radial movement of water and minerals between the tracheids. Pits provide the transfer of moisture between the tracheids, containing cellulose membranes acting as valves to control the transport of moisture in response to internal pressure.

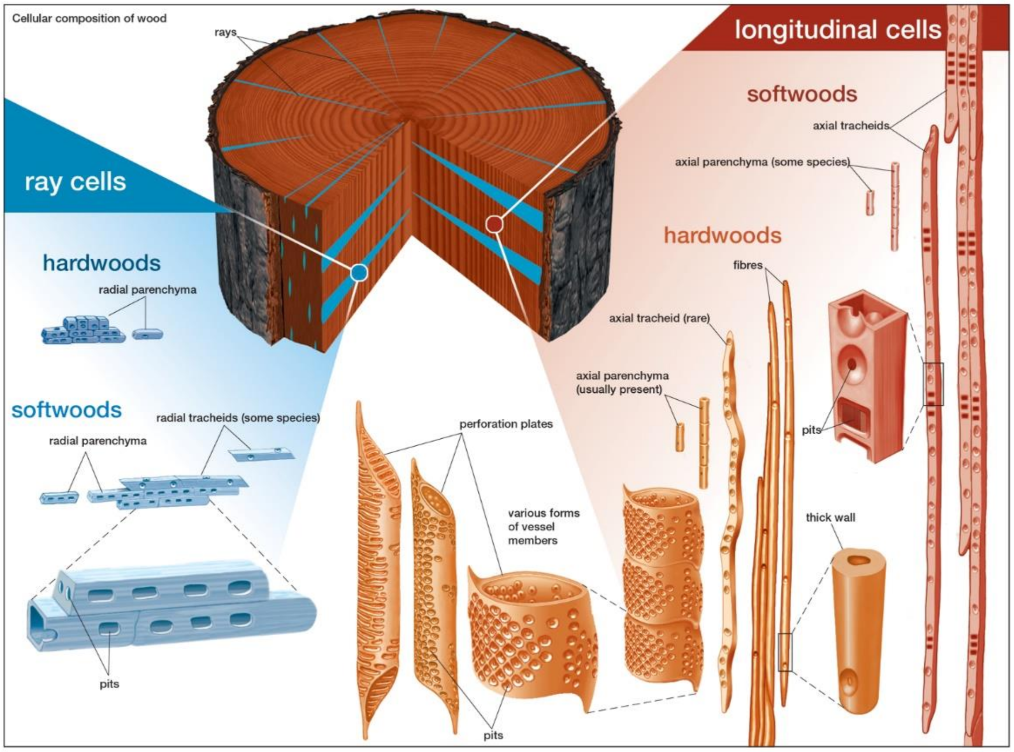

Figure 1.3 Types of cells present in hardwood and softwood. Encyclopedia Britannica.

Forest Residue and Potentials

The use of woody biomass in 2010 worldwide, was around 9% of the total primary energy consumption and 65% of the renewable energy consumption [15]. Additionally, if 10% of the woody biomass (forest residues, wood processing, and agricultural sector) was used for energy at a 50% conversion efficiency there would be a generation of 3.1 trillion tonnes of oil equivalent energy [9]. The use of all resources in woody biomass, predicted by modeling for 2050, the total world energy production by woody biomass could be 10-40% [15]. Finland has used woody biomass to achieve a 38% proportion of renewable energy by 2020 that was reached in 2014 by increasing the energy generation of forest chips and forest industry by-products, bark producing 7.9 million m^3 or 49,4 TJ in 2019 [16]. In the United States in 2019, 5% of the total primary energy was biomass created, and of that 46% was derived from woody biomass [17].

Forest residue is the biproduct from tree harvesting (Fig 1.4). This contains the needles, leaves, bark, tops, and branches that are removed from the log before transportation.

Figure 1.4. Tree felling and the forest residue pile up.

Needles show to have chemical and fibrous properties comparable to wood substrate. The buildup of needles littering on the forest floor fuel wildfires and release greenhouse pollutants. Burning needles release carbon monoxide, hydrogen, light volatiles, and organic vapors. Pine needles, bark, and trees are all constantly diverse in both the chemical makeup and potential uses [18].

Evaluation of various conifer needles has shown to be an important source for organic substances in biochemical and ecological functions. Essential oils from *Abies*, *Larix*, *Pseudotsuga*, *Tsuga*, *Picea, Chamaecyparis,* and *Pinus* species have mild antimicrobial properties that can inhibit the growth of both gram-positive and gram-negative bacteria and fungi. GC-MS of an essential oil collected from *Cedrus deodara* needles were evaluated for the chemical composition; terpenoids (78.66%) and aromatic compounds (16.13%). Literature also showed *C. deodara* needles are a natural antioxidant and antimicrobial agent in food processing and inhibit tumor proliferation [18, 19].

Leaves are being studied for becoming solid biofuel due to the increase in need for leaf removal in cities and green areas. Leaves are characterized by increased content of ash largely accumulated from air pollution captured during growing seasons. Trees are specifically grown in cities to absorb pollutants through their leaves to improve air quality. Management of urban trees has need for improvement. Currently the leaves are composted for soil substrates but there are other optimization techniques that can be explored. Mudryk et al. indicated that leaves are a possible means to produce quality biofuels in combustion processes by milling or pelletizing methods [20].

Bark (secondary phloem and cork) surrounds the exterior of the tree and makes up 10-20% of the volume of a tree [21]. Bark is detached from wood mainly at the cambium zone or on either side of the phloem and xylem differencing zone where new wood is formed by the expansion of new cells [13]. The primary cell walls of willow barks cambium layer have a polysaccharide content of approximately 30% cellulose, 30% hemicellulose, 35% pectin, and 5% polysaccharide-modifying protein [22].

Bark has shown to have beneficial and valuable compounds locked within its structure (Figure 1.5). Salicylin, found in willow bark, can be used as an anti-inflammatory, antipyretic, and analgesic [16, 23]. *Picea abies* bark has an industrial application for tannin production [24]. Other extractives include suberin, lignin, lignans, phenolic acids, and cellulose [25]. Suberin is a polyester biopolymer that is found in plant tissues that can act as an absorbent of carcinogens and antimutagens [26, 27]. Bark also contains compounds used in resins, foam materials, wooden panels, and building insulation [28, 29]. The bark waste after the extraction of industrial tannins from *Acacia mangium* can be used to prepare activated carbon [30].

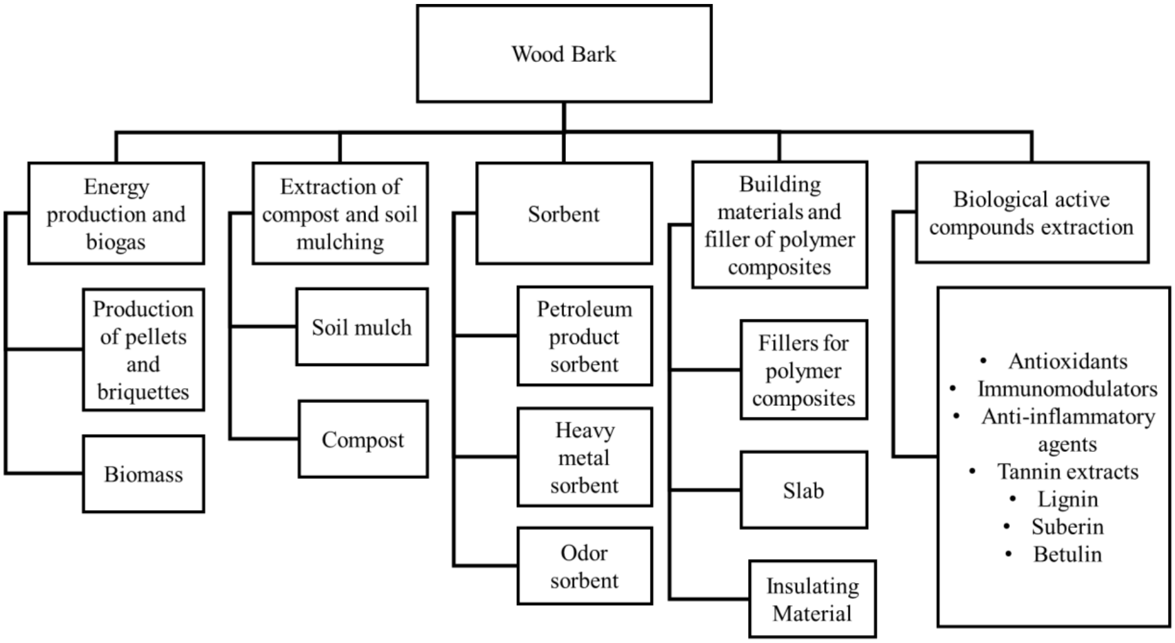

Figure 1.5 Opportunities of wood bark [31].

Bark production globally is estimated to be up to 400 million cubic meters per year [21]. In North America, 50 million tons of bark is the annual yield with 17 million m^3 produced in Canada [28]. Bark is mainly considered a waste stream. Accordingly, various research has gone into bark for extractions of compounds and avenues for conversion due to the excess volume, potential in growing economic value, and an alternate fuel source.

Assessments on Delamination

Bark delamination, or debarking, by mechanical and chemical means are to be able to improve the homogenous composition of white wood and increase the quality by minimizing wood loss [23, 32]. This processing can also create the side stream of bark as a value added biproduct. Different factors such as moisture content, harvest season, and the cultivation can all potentially affect the mechanical properties of the wood-bark interface. The residues from coniferous trees are in surplus in the debarking process [16]. Research is trying to unlock the potentials of bark but there are noticeable drawbacks. The fuel quality also has a strong dependency on the season of harvest, the temperature, moisture content, freshness, and dimensions of the logs [16, 23].

Chahal et al. are studying the wood-bark bond strength under different conditions to find effective and efficient debarking technologies [22, 23, 32]. They determined that the moisture content has a negative correlation with wood-bark bond strength. Removing bark from the whitewood will allow for a higher wood value and create a better product for biomass production. Other delamination methods use physical damage or separation. Mechanical debarking methods include drum, cradle, ring, frail, high pressure water jets, and compression [23]. Using chemicals, bacteria, or fungi for delaminating, called biodegradation, can also be considered as a pretreatment as well as improving delamination [33].

Pretreatments Currently Utilized on Woody Biomass

Variations in the plants chemical and structural makeup are dependent between species as well as the environment in which a plant grows. Different strategies will be needed to be applied in engineering woody biomass for reduced recalcitrance. Woody biomass has a higher recalcitrance over herbaceous biomass due to its strong and tough structure and high lignin content [34]. One of the most challenging processes in biomass is the separation of the plant cell components. Therefore, a preconditioning step is necessary to start the deconstruction of the interlocking cell system. The deconstruction process needs to be able to lower costs and improve efficiency of biofuel production [33]. Energy costs include the power of operation, the ability of a recovery, and recycle stream. Pretreatments also affect the downstream processing, commercial scalability, and pathway of biorefinery process therefore focus should be on the upstream processing and cost efficiency [34, 35].

Pretreatments are used for improving conversion yields of lignocellulosic biomass by changing the chemical structure and deconstructing the cellular structure. Exploring mechanical, thermal, or chemical inputs as pretreatment to deconstruct lignocellulosic material are required in terms of a biorefinery. Extractives from bark offer many valuable compounds. The carbohydrate composition of hot water extracts of pine and spruce bark contain mainly glucose, galacturonic acid, mannose, galactose, and arabinose. Other extractives included tannins and polyphenols [36]. The soluble carbohydrates are used to produce fuels and chemicals by fermentation or enzymatic hydrolysis [30, 37]. The following pretreatment examples focus on deconstructing the cellular structure to extract sugars for producing fermentable fuels.

Agbor et al. quotes, “In theory, the ideal pretreatment process produces a disrupted, hydrated substrate that is easily hydrolyzed but avoids the formation of sugar degradation products and fermentation inhibitors [33].” Pretreatment methods are needed for increasing the extractability of sugar by breaking down the lignin and the complex interlocking systems. As mentioned in debarking processes, mechanical pretreatments are used, this includes the use of mills to reduce the particle size of the wood as well as chopping, shredding, grinding, and size reduction [33, 38]. Mechanical processing changes the structural and morphological properties by fracturing the cell walls. The fracturing increased enzymatic digestibility by increasing the surface area. The drawback to mechanical treatment is the energy consumption needed [34, 35, 38].

Biological pretreatments use fungi that produce enzymes to break down lignin, hemicellulose, and polyphenols. Studies showed that lignin and hemicellulose both influenced enzymatic digestibility, but the degree of influence varied significantly between switchgrass and poplar suggesting that it is yet to be industrialized but is likely to be in combination with other pretreatments [33, 35]. Further biological understanding of lignin breakdown uses termites [39, 40]. Termites have the ability to overcome lignin recalcitrance in their digestive systems. Studying how their stomachs process the lignin will open many avenues for lignin processing.

Pretreatments of woody biomass include ionic liquid pretreatment, sulfite pretreatment, dilute acid pretreatment, acid-catalyzed steam explosion, and ethanol organosolv pretreatment. These treatments use chemical methods of alkali, acids, organic solvents, and ionic liquids. The main objective of pretreatments is to overcome the energy consumption for wood size reduction though milling in addition to deconstructing the structure of wood cells for sugar extraction [4, 34]. Additionally, extractives, resin, and mineral components are contained in wood, these can include fatty acids, fatty acid esters, resin acids, phenols, and mineral extractives that include silicon, calcium, potassium, magnesium, and phosphorus.

Torget et al. study concluded aspen and poplar hybrid bark are susceptible to dilute acid prehydrolysis as a pretreatment for enzymatic digestion of cellulose by the cellulase enzyme complex from *T. reesei*. The study also concluded that the response of bark to dilute acid pretreatment and enzymatic hydrolysis vary between species and genera that suggest different pretreatments may be needed for recalcitrant barks [41]. Thermo-chemical treatment in a water-alkaline medium (7% NaOH) is shown to destroy lignin and achieve low molecular weight phenol compounds such as 2-methoxyphenol, 2,6-dimethoxyphenol, 4-hydroxy-3methoxybenzaldehyde, 4-hydroxy-3,5-dimethoxybenzaldehyde, 1-(4-hydroxy-3-methoxyphenyl) ethanone, etc. [42].

Kumagai et al., used sulfuric acid as a pretreatment on woody biomass for enhancement of bio-oil production via pyrolysis. The study concluded that "moderate acid pretreatment produced shorter chain units of cellulose, hemicellulose, and lignin, thereby facilitating the conversion into oil by pyrolysis." The pretreatment process was using 1, 3, 6, and 9 M H_2SO_4 solutions (100mL) to 1g of wood sample. The mixture was agitated for 1 hour at ambient temperature, then wood samples were repeatedly washed in ion-exchanged water until the pH became neutral. The solution was then filtered and dried for 24 h at 105 °C [43].

Ethanol organosolv pretreatment uses a blend of ethanol and water with some mineral acid to extract lignin from wood chips. This process achieved over 90% cellulose-to-glucose conversion yield in 24 hours. The high purity lignin generated has potential to be used in antioxidants, adhesives, polyurethane foams, and carbon fibers. Additionally, furfural, hydroxymethylfurfural, formic acid, and levulinic acids were produced by the hemicellulose fraction of the ethanol organosolv process. The drawbacks from this process are the difficult recovery of hemicellulose and high energy processes to recover ethanol [34].

Sulfite pretreatment to overcome recalcitrance of lignocellulose was developed by the U.S. Forest Service, Forest Products Laboratory, and the University of Wisconsin-Madison. The method showed high performance for woody biomass saccharification for both hardwoods and softwoods. The process lowers the production of fermentation inhibitors (furfural and 5-hydroxymethylfurfural) and partial sulfonation by sulfite. It also increases lignin hydrophilicity to soften wood chips to reduce the energy consumption needed for size reduction. The lignosulfonate dissolved in the liquor has the potential to become a directly marketable coproduct within existing and future markets [34].

DeMartini et al. compared switchgrass and poplar for efficient extractive techniques. Ammonium oxlalate and sodium carbonate removed a wide variety of pectin and pectin-arabinogalactan epitopes and some xylan epitopes from poplar wood. 4 M KOH extraction improved extract quantities of xylan as well as fucosylated and non-fucosylated xyloglucans with addition rhamnogalacturonan and arabinogalactan epitopes. Chlorite extraction fragmented and removed lignin and released carbohydrates from the cell walls. Extractives with a 4 M KOH post chlorite extraction solubilized bound sets of wall polysaccharides after removal of lignin and associated glycans. Oxalate and carbonate treatments were also successful in extractions of xylan subsets. Endopolygalacturonase and pectin-methylesterase were applied to release of pectins and arabinogalactants. The two species gave clearly different results in yield due to the difference in compositional makeup, but the extractive techniques did show promise in the destruction of cellular structure for higher sugar yeilds [44]. Other solvents, such as ethanol-benzene, hexane, ethanol, and ether, are shown to be able to remove solvent-extractable constituents in wood and lignocellulosic biomass [18].

Biomass Storage Systems

Two primary challenges of biomass currently faced include the lack of understanding of how to stably store biomass for long durations and the difficulty deconstruct the chemical makeup biomass during pretreatment operations [45]. At a biorefinery, there will be queue time in which the biomass would have to be stored until processing can be executed for year-round operation. Engineering storage systems could provide a means in which biomass can be available year-round and reduce costs by minimizing off season feedstock variability. Current storage of biomass has shown to be susceptible to self-heating, degradation, and reduced quality as fuel and have an increased dry matter loss [16]. A biorefinery focuses on dry matter loss for the economic and sustainability concerns surrounding carbon retention. Dry matter loss is also an indicator of microbial activity and quality changes as a function of moisture [8].

There are two types of storage, wet and dry. Dry storage is lower in cost, but environmental conditions (such as humidity and temperature) fluctuate and cause instability of the biomass through microbial degradation or fire potential. Wet anerobic storage systems (i.e., ensiling) have been successful at preserving biomass in long term storage for livestock feed and forage. Ensiling is successful due to the anerobic conditions with low pH due to organic acids from the proliferation of lactic acid bacteria, reduce the microbial activity and thus prolong the biomass stability over long periods. Even though ensiling has higher cost, it aims to reduce downstream processing requirements for conversion to fuels and chemicals [8]. Anerud et al. used semi permeable fabric sheets on bark storage piles and showed an improvement in fuel quality and energy recovery in the covered piles compared to the uncovered piles [46].

Storage with either acid or alkali amendments directly added to the biomass to promote stability during storage. Sodium hydroxide has been researched in herbaceous biomass, such as corn stover, wheat, and barley straws and woody biomass [47, 48]. The sodium hydroxide breaks down the lignin and reduces dry matter loss during storage. Acid amendments decrease the pH and preserve nutrient content of the biomass.

Pyrolysis

Pyrolysis is a thermochemical conversion method in which biomass is combusted in an oxygen free environment and produces three fractions: liquid, gas, and solid [49, 50]. This technology has been around since Egyptian times and is being revitalized as a method to produce renewable fuels [51, 52]. One major advantage of pyrolysis is the ability to convert biomass directly into liquid fuel [53]. Fast pyrolysis maximizes the oil production by fast heating rates and temperatures between 400 and 650°C, whereas slow pyrolysis will maximize the char yield from slower heating rates [51].

Based on the type of biomass, pyrolysis can achieve high liquid yields of up to 75% [54-56]. Bio-oil is generally acidic, viscous, thermally unstable, and contains high amounts of water and oxygenated compounds). When heated, the oil will polymerize, changing the physical and chemical structure of the oil. The oil is generally a dark brown or red color (depending on the feedstock) and smells like a barbecue or campfire. The moisture content of the biomass correlates to the water contained in the oil after pyrolysis, generally 10-30%. Additionally, oil can exhibit multiphases with char particles, aqueous and organic liquids, and waxy or tar like solids [21, 51, 57].

Although bio-oil is highly prioritized in production and improvement, biochar is gaining attention to be utilized as a value-added product. Biochar is a carbonaceous porous structure, has a high surface area with abundant functional groups, and contain mineral and trace metals. These properties promote a high reactivity useful in removal of water pollutants, catalysis, soil amendments, and electrochemical energy storage [58-60]. Applications such as soil amendment to improvement of water-holding capacity, increase the stable pool of carbon, adsorption of organic and toxic compounds, adsorption, reaction with gases within the soil, nutrient retention and addition, and improvement in the growth of beneficial microorganisms [61]. Currently, the most common biochar applications are soil health improvement and solid fuels [58-60].

Research Goal

Forest residues can become a low-cost biomass feedstock for biofuels. The bark fraction has potential to become a value-added product in biofuels, but the complexity of the physical structure and chemical compositions restrict the conversion [9]. If increasing conversion of bark can be done by exploiting the queue time at a biorefinery gate with minimal costs and labor, the current waste stream can become a value-added product. Thus, increasing both economic value and energy production in the wood processing industry, from felling in the forest to debarking in wood processing industries. Very few studies (if any) have analyzed long term storage with low severity chemicals for thermochemical conversion of bark.

Storage of wood bark will be researched for utilization of bark by means increased oil production and of biochar created from microwave assisted fast pyrolysis (500°C). The experimental process will simulate storage time with low severity doses of sulfuric acid (0.1 and 1 % w/w) or sodium hydroxide (4% w/w). Analysis will review chemical compositional changes in the bark after storage and determine if alkali and alkaline earth metals (AAEM) can be reduced from the bark after treatment. Further analysis will go into the produced biochar to further the valorization of bark for potential in soil amendments and combustion applications.

Additionally, a developing chemical drying process for biomass will be briefly explored as another method that could increase pyrolysis oil yields. A drying agent, dimethyl ether, was used on forest residue (bark, needles, and white wood). Analysis will evaluate if there is any physiochemical changes in the biomass as well as to see if there is an advantage in pyrolysis yields, following the same analysis procedures as the bark.

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Chapter 2: Impact of Alkaline and Acid Pretreatment on Pine Bark via Pyrolysis Products

Abstract

Forest residues are one of the largest economical resources to produce sustainable fuels but have lower conversion potential due to their high ash content. High alkali and alkaline earth metals (AAEM) content present in residues, and in the bark fraction in particular, limit pyrolysis conversion. This study explores the use of low severity in-storage treatments to reduce AAEM content and develop co-products from this underutilized resource. Treatments of loblolly pine bark included acid (0.1% and 1% sulfuric acid, w/w dry basis) and alkali (4% sodium hydroxide, dry basis). Treated bark was then incubated anaerobically for 1 and 2 weeks, simulating an in-pile treatment at a refinery gate. Bark treated with 1% H_2SO_4 after 2 weeks had an 35.7% reduction in AAEM content, which led to an 11% increase in liquid yield. The results suggest that low acid storage is ideal to improve the pyrolysis conversion of bark.

Introduction

Forest residue is one of the largest biomass sources that is a low-cost, low carbon source for bioenergy. Forest residues are homogenous and have a wide variety of physical and chemical compositions such as branches, bark, needles, leaves, etc., further reducing the conversion efficiency. Currently, forest residues and bark are mainly considered a waste left in the forest after tree felling, put in a landfill, incinerated, or is used as a fuel source by the forest industry [1, 2]. Bark accounts for 9-15% of a tree by dry weight and is one of the most abundant solid residues from the forest industry that lacks utilization and valorization to higher value-added products [3, 4]. Global production of bark is estimated to be up to 400 million cubic meters per year [5]. The demand for wood is ever increasing and thus more production of bark. The increasing volume of bark brings interest to the forest and green energy sector to develop processing methods that add value to what is considered a waste.

There have been several processes suggested to add value to bark in the recent years, such as steam explosion, hot water extraction, chemical pretreatments, and even mechanical processes [6]. These methods are common ways of extracting valuable compounds that are found in bark, such as suberin, tannins, flavanols and flavonoids, antioxidants, and anti-inflammatories used in medicinal, pharmaceutical, cosmetic, and other industries [3, 7-11]. These processes have shown some progress in utilization of bark but still energy consumption, profitability, and conversion efficiency are still limited by its complex makeup [12-15].

Thermochemical processes, such as pyrolysis, gasification, hydrothermal liquefaction, etc., appear to be promising methods for the conversion of forest residues into biofuels. Pyrolysis is flexible to the types of materials and converts the material into three products: char, liquid, and gas. The major drawback of this process is the need to dry the material. The gas fraction contains hydrocarbons, hydrogen, and carbon monoxide that could be further used for fuel or chemical production. The liquid fraction can be a potential fuel supply, but the major setbacks are high-water content and the wide distribution of chemicals that require further refinement to achieve marketable products [16, 17]. Biochar (solid fraction) has growing potential in the agricultural industry as a soil amendment as well as other environmental remediation processes such as wastewater management, gas purification, and soil contaminants [18-20]. Liquid fractions produced from bark in thermochemical processes have shown to contain valuable compounds (hydrocarbons, phenols, aromatics, etc.). These compounds further provide a potential to valorize bark as a feedstock in biorefineries. [3, 5, 21].

Bark primarily consists of inorganics such as calcium (Ca), silicon (Si), phosphorus (P) magnesium (Mg) and potassium (K), or alkali and alkaline earth metals (AAEM) [22, 23]. AAEM have been associated with catalyst poisoning, corrosion, slagging, agglomeration, ash deposits and undesirable emissions in processing equipment [23, 24]. Treatments are often needed to remove AAEM to improve the quality and quantity of product yields, such as oil yield from pyrolysis. AAEM inhibit pyrolysis oil conversions by their catalysis of secondary cracking of vapors. The use of dilute-acid leaching and alkali treatments increases the solubility of AAEM [24, 25].

Storage also allows for the continuous supply of feedstock to biorefineries year-round. Wet anaerobic storage is to decrease dry matter loss (DML) quantity and quality of biomass. The use of dilute chemicals is used to help minimalize the change in biochemical composition during storage times and decrease the dry matter loss. Dilute acid or alkali treatments were shown to influence enzymatic hydrolysis for fuels and other chemicals. The dilute acid treatment removes hemicellulose so that the cellulose is assessable to enzymatic depolymerization. Alkaline methods solubilize lignin and leave hemicellulose less affected [26-29]. The use of sulfuric acid pretreatment on wood produced higher oil yield by pyrolysis due to the production of shorter chain units of cellulose, hemicellulose, and lignin during the pretreatment [30]. Bark could potentially show improvement with anaerobic storage with low chemical addition to reduce AAEM and increase pyrolysis oil yields.

This study investigates using the storage operation at a biorefinery to conduct low severity treatments of bark (low temperature, low chemical concentration) to improve the quality of this feedstock to obtain greater liquid yields in pyrolysis and improve quality of biochar, minimizing the production of gasses. The quality of conversion will be addressed by the composition changes from chemical storage pretreatment. The obtained liquid and char were characterized with respect to their yields and bulk chemistry (CHNOS content, moisture, and pH) to understand and determine the chemical nature and the potential to valorize pine bark.

Methods and Materials

Materials

Loblolly pine bark was handpicked out of loblolly pine residue obtained from Jasper, South Carolina sourced from FTX Consulting. Biomass was initially sized reduced using a Wiley Mill Model 4 to pass a 6mm screen (Fig. 2.1). The bark was manually divided into 4 tared zip-lock bags using riffle splitters (Humboldt sample splitter, 1 in, H-3990) for representative sampling. The riffle splitter divides the material into two samples of equal composition by directing material poured into the hopper into two different pans on opposite sides of the hopper using a series of chutes that alternately channel material to either of the opposing bins. Each portion of the divided material was then added back into the riffle splitter, ultimately yielding four representative samples.

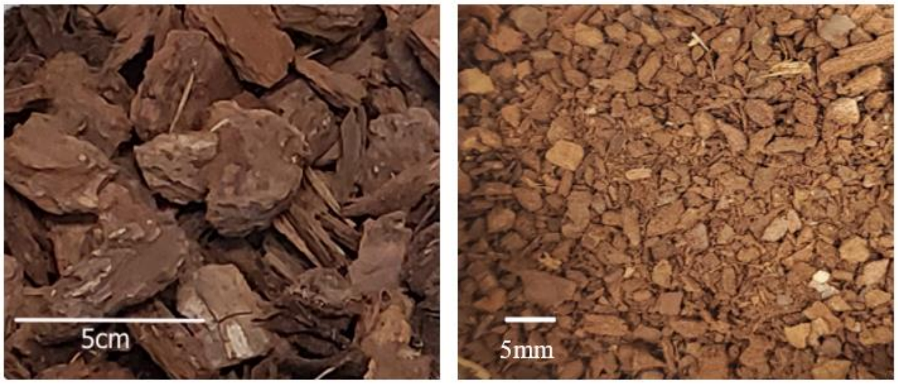

Figure 2.1 Sized reduced loblolly pine bark.

Loblolly pine bark anerobic pretreatment

There were three storage conditions: a control, an acid, and an alkali pretreatment (Table 2.1). Pretreatments were carried out on the size-reduced loblolly pine bark to compare alkali and acid with the control. The experiment was performed in triplicates for one and two weeks in anerobic storage at 40 wt% moisture wet basis (w.b.). Sulfuric acid (H2SO4) was used at two different concentrations, 0.1 wt% and 1 wt% by dry bark basis (d.b.). Alkali treatment used sodium hydroxide (NaOH) at 4 wt% (d.b.). The 40 wt.% (w.b.) moisture content was achieved by adding the according portion of water to the pretreatment conditions. The as-received bark (native) moisture content was determined to be 14 wt% (wb). Native bark was used as the key comparison to anerobic storage pretreatments.

Table 2.1 Storage treatment experimental setup.

Treatment	**Storage (wk)**	**Concentration (g/kg, d.b)**	**Moisture Content (%, w.b.)**
Native	NA	NA	NA
Untreated Control	1, 2	NA	40
H_2SO_4	1, 2	1	40
H_2SO_4	1,2	10	40
NaOH	1, 2	40	40

The next day the moisture-equilibrated bark was removed from the refrigerator and allowed to warm to room temperature before loading quart size mason jars (~1000 mL) used for anaerobic storage (Fig. 2.2). Biomass was loaded into the jars fitted with an airtight lid with a ball valve attached to the lid using a through-lid bulkhead fitting (SS-400-R1-4, Swagelok, Solon, OH) with a tube adapter and Masterflex C-Flex ULTRA tubing.

Between filling each jar, samples (n=3) were taken from the loading material bag for moisture analysis (Eq. 2.1). The headspace of the jars was alternately purged with nitrogen gas and evacuating with a vacuum pump for three cycles to ensure the anaerobic conditions. Tedlar gas collection bags (Tedlar® sampling bag, 6 x 6 inches, 0.6 liters, push-pull poly valve) were attached to the now anerobic jars and stored in the dark at ambient temperature (20°C).

Figure 2.2 Mason jar anerobic storage pretreatment setup.

Replicates (n=3) for each storage conditions were destructively sampled after one or two weeks. The biomass was mixed in the jar to have uniform distribution prior to sampling to collect moisture content (n=2) to establish the post-storage dry matter content. Dry matter loss in storage was then obtained based the weight loss before and after the pretreatment according to Eq. 2.

$$\%\, Moisture\ (wb) = \frac{g\ Biomass_{wet} - g\ Biomass_{dry}}{g\ Biomass_{wet}} \times 100 \qquad (2.1)$$

$$\%\, Dry\ Matter\ Loss\ = \frac{g\ Biomass_{pre\ storage} - g\ Biomass_{post\ storage}}{g\ Biomass_{pre\ storage}} \times 100 \qquad (2.2)$$

After storage, the biomass was washed with deionized water (8% solids loading) in 1000 mL flask placed in a shaking water bath set at 85°C for 2 hours. The washed samples were collected by vacuum filtration using a 110mm Buchner funnel fitted with glass fiber filter paper (Whatman, 110mm diameter, GF/C glass microfiber filter P/N 1822-110) or felt material (McMaster-Carr, 100-micron chemical resistant filter felt). The pH of the filtrate was collated by pH paper (HACH, 0-14 pH range) before disposal. The bark solids were dried at 40°C for 48 hours to size-reduced to pass a 0.75 mm sieve at 8000rpm (Retsch ZM200) for analytical analysis.

Microwave Pyrolysis

Dried bark after pretreatment was pressed into 1.0 ± 0.1g pellets in a custom die (16 mm square with 4 mm rounded corners) using a hydraulic press (Carver, Model 3853-OC) to 20000 lb-f (4000 psi) pressure for 30 seconds (Fig. 2.3). Each pyrolysis trial used three sample pellets for roughly 3g total sample mass.

Figure 2.3 Pellets made for pyrolysis.

Pyrolysis of bark samples and specifics about the pyrolysis unit and its operating conditions can be found as described by Klinger et al [31]. A brief overview is provided. Samples were placed in a clean quartz tube sealed at both ends with nitrogen entering the distal portion of the tube. To initiate pyrolysis the quartz tube was inserted into a furnace (500°C) that was then subjected to microwave energy generated from a microwave generator (3 kW, 58.7 dB, 2.426–2.476 GHz frequency, SM1250D, MKS Instruments) positioned above the furnace and focused on the sample using a waveguide (GA2006 2450 ± 30 MHz, Gerling Applied Engineering). The pyrolysis was carried out to 500°C with a heating rate of ~13°C/s.

Char was weighed after each reaction. Bio-oil was collected by running a plunger through the tube into tared clear airtight glass vials, weighed, and stored in a refrigerator. The empty tube was weighed again for residual oil to complete the mass balance of char, oil, and gas production. Each experimental replicate (n=3) was pyrolyzed in duplicate for total of 6 measurements per experimental condition (treatment and storage time).

Characterization of the Loblolly Pine Bark and Pyrolysis Products

Ultimate Analysis of Bark After Storage was done to determine the elemental composition content in triplicate for bark and biochar collected after pyrolysis using an elemental analyzer (Vario EL cube, Elementar). The mass of carbon (C), hydrogen (H), nitrogen (N), and sulfur (S) atoms were directly determined by the elemental analyzer while oxygen (O) content was determined by the mass balance. The atomic oxygen/carbon (O/C) and hydrogen/carbon (H/C) ratios were calculated based on the ultimate analysis in Eq. 2.3,

$$\frac{\mathrm{O}}{\mathrm{C}}\,\mathrm{or}\,\frac{\mathrm{H}}{\mathrm{C}}=\frac{\mathrm{wt\%\ O_2\ or\ H_2}}{\mathrm{atomic\ weight\ of\ O_2\ or\ H_2}}\div\frac{\mathrm{wt\%\ C}}{\mathrm{atomic\ weight\ of\ C}}\,. \tag{2.3}$$

Proximate analysis was done for bark after storage and biochar to determine the moisture, volatile matter, fixed carbon, and ash of samples. Proximate analysis of triplicate samples of the initial bark and each stored biomass was obtained by thermogravimetric analysis (TGA701, Leco) following standardized ASTM D7582 method (https://www.astm.org/Standards/D7582.htm).

The composition and concentration of inorganic elements in the bark and char were determined by x-ray fluorescence spectroscopy (XRF). Dried initial and stored bark was pressed into 40 mm diameter pellets with a hydraulic press (Carver, Model 3853-OC) applying 20 tons of force for 10 seconds and then released over a 20 second interval. Each side of the pellet was analyzed by Epsilon 4 (Malvern Panalytical). Higher heating value (HHV) was calculated from elemental composition for bark, biochar, and bio-oil according to Eq. 2.4 [32],

$$HHV=0.338C+1.428\left(H-\frac{O}{8}\right)+0.095S \tag{2.4}$$

Where C, H, O, and S are carbon, hydrogen, oxygen, and sulfur weight composition (wt%) respectively. For verification of the equation, two samples (control and alkali week 1) had their HHV measured by a Isoperibol Calorimeter (LECO AC600). Results had <1% error between the estimated and measured HHV values. Results are shown in Appendix A.

The yield of char and oil (Y_{char}, Y_{oil}, respectively) of microwave pyrolysis products were calculated based on the weight fraction (Eq. 2.5). The Gas yield was calculated by the difference of the biomass feedstock and the mass of char and oil produced.

$$\mathrm{Y_{char/oil}}\ (\%) = \frac{\text{Mass of (char/oil) produced}}{\text{Mass of biomass fed}} \text{ x } 100 \tag{2.5}$$

Individual collections of the oil and char from the triplet experiments were combined to acquire enough sample for analysis and get average results. The oils from the replicates from each pretreatment (chemical, storage time) were combined into one sample for analysis. Collected oil was stored in glass vials at 4 °C. The pH of the oil was measured with pH paper (Hach 0-14 pH range). Before analysis, the glass vials were warmed up to 30°C then vigorously shaken to make homogenous samples for CHNOS analysis. Karf-Fisher titration (899 Coulometer, Metrohm) was used to determine the water content of the liquid phase of the oil. Hydranal$^{\mathrm{TM}}$ - Coulomat (Honeywell) was the medium used in the Karl-Fisher titration. The liquid fraction of the oil was diluted with methanol before titration with roughly a 1:20 dilution of oil to methanol. The oil and methanol were weighed by mass and the determined water content in ppm by Eq. 2.6,

$$R_{KF,oil} = \frac{R_{KF,dilution}(m_{methanol} + m_{oil}) - (R_{KF,methanol} \times m_{methanol})}{m_{dilution}}, \tag{2.6}$$

where the R_{KF} is the content of water in ppm calculated from the coulometer, m is mass in grams, and dilution is the oil and methanol mixture.

Statistical Analysis

Single-factor one-way analysis of variance (ANOVA) was performed in JMP 14.2.0 (SAS, Cary, NC) to identify significant differences. Paired student t test was performed to determine if the ANOVA was significant at $p < 0.05$.

Results and Discussion

This study aimed to assess the impact of low chemical storage in pine bark in terms of compositional and pyrolysis convertibility changes to gain a fundamental understanding of this potential treatment to increase barks utilization.

Dry Matter Loss After Anaerobic Storage

Matter Loss (DML) from storage could contribute to greenhouse gas emissions [33-35]. No measurable gases were produced in any condition during storage in this study. DLM of each replicate was determined and results are listed in Figure 2.4. DML was less than 5% under all pretreatment conditions. Within the length of the experiment alkali and acid treatments did not affect DML.

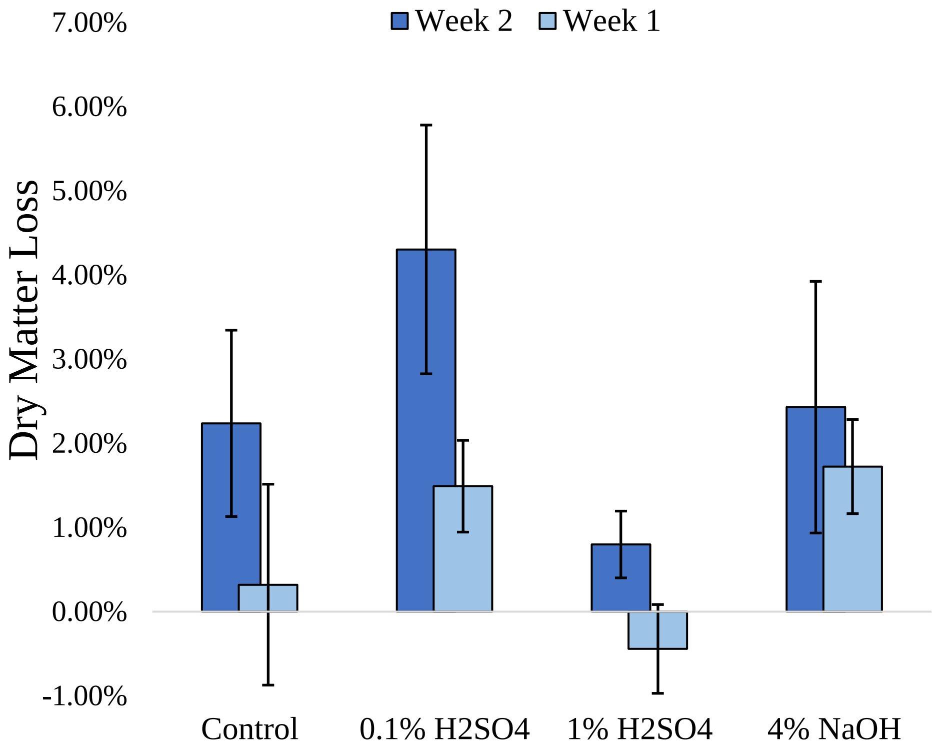

Figure 2.4 The effect of treatment and length of treatment on preservation of material (dry matter loss).

One objective of the current study is to remove alkaline and alkaline earth metals (AAEM) and this is most effectively done at low pH. The pH is correlated to the ash content. Lower pH leads to lower ash content in the bark [22]. The pH of the filtrates after the anaerobic pretreatments were measured. For 0.1% H_2SO_4 pretreatment filtrate the pH is 4, while for the 1% H_2SO_4 pretreatment filtrate the pH value is 2.25 (Table 2.2). Both acid treatments are lower than the filtrate for the control experiment. Less ash content is expected for the acid pretreated bark. The pH for 4% NaOH is 9 and 8 for weeks 1 and 2 respectively, which is expected to have highest ash content in the alkaline pretreated bark.

Table 2.2 pH for the filtrate of bark after anerobic pretreatment.

Treatment	Week 1	Week 2
Control	5.55	5.55
0.1% H_2SO_4	4	4.5
1% H_2SO_4	2.25	2.25
4% NaOH	9	8

Chemical Composition of Bark Before and After Treatments

The effect that each treatment and treatment length had on bark composition was determined and compared to the native "as-received" bark and untreated bark control.

Thermogravimetric analysis directly measures volatile matter, ash content, and fixed carbon content is calculated by subtracting the value for each of these from 100. The results are normalized to a dry weight basis (Table 2.3).

Volatile matter (VM) is the fraction of biomass that converts into vapors during the pyrolysis process. NaOH treatment reduced the VM to ~67 wt% for both weeks 1 and 2. The VM of the control and 0.1% H_2SO_4 treatments were statistically close to the native value of 70 wt%. The 1% H_2SO_4 treatment had a VM of 69.48 and 69.80 wt% for weeks 1 and 2, respectively. The NaOH treatment with the lowest VM suggests it will have lower oil production but have higher char yield.

Ash is the inorganic elements present in the biomass that adversely affect the combustion process. The native material had the lowest ash content of 1.24 wt%. Higher ash content in storage treatments can be contributed to DML during storage. H_2SO_4 treatments had an ash content of 1.47 wt% in week 1, in the second week the ash content was 1.31 wt%. Both acid treatments were not statistically different from the native ($p>0.05$). The control had an increased ash content of 1.78 wt% and 1.75 wt% for weeks 1 and 2, respectively. NaOH treatment had the highest reported ash content of 4.60 and 4.54 wt% for weeks one and two respectively. The higher pH of the NaOH treatment was accurate to a higher ash content. The H_2SO_4 treatments were not lower in ash content compared to the control as anticipated by the lower pH compared to the control.

Fixed carbon is the fraction of biomass that usually doesn't decompose during pyrolysis conversion and generally contributes to biochar production. There was no significant difference of the fixed carbon except in the 1% H2SO4 treatment. The fixed carbon content in the 1% H2SO4 treatment was 29.05 and 28.89 wt% for weeks 1 and 2, respectively. All remaining treatments were roughly 28 wt%. The combination of high ash, low volatile matter, and higher fixed carbon indicate that the NaOH treatment could have a higher biochar production and low bio-oil yield compared to the other treatments. The combination of high ash, low volatile matter, and higher fixed carbon indicate that the alkali-treatment could have a higher biochar production and low bio-oil yield compared to the other treatments.

Table 2.3 Proximate analysis of bark after storage.

Treatment	**Storage (wk)**	**Volatile Matter (% d.b.)**	**Ash (% d.b.)**	**Fixed Carbon (% d.b.)**
Native	0	70.58 ± 0.35	1.24 ± 0.02	28.19 ± 0.37
Control	1	70.37 ± 0.44	1.78 ± 0.24	27.85 ± 0.38
	2	70.47 ± 0.43	1.75 ± 0.21	27.77 ± 0.53
0.1% H_2SO_4	1	70.74 ± 0.33	1.47 ± 0.15	27.79 ± 0.30
	2	70.93 ± 0.38	1.46 ± 0.12	27.61 ± 0.38
1% H_2SO_4	1	69.48 ± 0.15	1.47 ± 0.11	29.05 ± 0.08
	2	69.80 ± 0.38	1.31 ± 0.19	28.89 ± 0.39
NaOH	1	66.79 ± 0.48	4.60 ± 0.20	28.61 ± 0.48
	2	66.92 ± 0.44	4.54 ± 0.31	28.54 ± 0.37

The ultimate analysis provided carbon, hydrogen, and oxygen contents, which are key components in evaluating biomass' fuel value. Nitrogen and sulfur are evaluated for environmental emissions due to the production of NO_x and SO_x [36]. The reduction of oxygen and increase in carbon are indicators for increasing calorific value and improving pyrolysis conversion. As shown in Table 2.4, carbon, hydrogen, and oxygen were similar in both the native and the 1% H_2SO_4 treatment of 52 wt% 5.7 wt%, and 40 wt% respectively. The control and the 0.1% H_2SO_4 treatment had an increase in carbon content (58 wt%) and decrease in oxygen (34 wt%) compared to the control suggesting an increase in calorific value compared to the native bark, no change in H was detected. The NaOH had an increase in carbon (56 wt%) and a decrease in oxygen (33 wt%) and hydrogen content (5.4 wt%), signifying higher calorific value compared to the native, but not as much as the control and 0.1% H_2SO_4. The nitrogen in all treatments increased from the native material, 0.25 wt%, to 0.4 wt%, though these values are still within reported ranges of loblolly pine bark [22, 37]. As expected, the sulfuric acid treatments did increase sulfur content from 0.02 wt% in native, control, and NaOH treatment, to 0.03 wt% and 0.09 wt% for 0.1% and 1% H_2SO_4 respectively. Overall, NaOH and 0.1% H_2SO_4 treatments seem to be the best for increasing calorific fuel value due to increasing carbon and decreasing oxygen contents.

Atomic hydrogen-carbon (H/C) and oxygen-carbon (O/C) ratios are used to evaluate the characteristics of biofuels. Generally, the lower the ratios the higher the energy content of the biomass due to reduced water vapor, smoke, and energy loss during the combustion process [38]. H/C ratio is a material property that is correlated with the degree of thermochemical alteration that produces fused aromatic ring structures in the material [39]. Ratios are also used to determine the degree of aromaticity and maturation, as is often described in Van Krevelen diagrams [40]. Van Krevelen plots can be used to evaluate the abundance of compounds from different classes, the correlations between the different compound classes (e.g., methylation–demethylation, hydrogenation–dehydrogenation reactions, etc.), and to compare the abundance of compounds containing different numbers of the same heteroatom (e.g., between compounds containing one or two oxygen atoms) [41]. The highest H/C and O/C ratios are seen in the native material, 0.67 and 0.58, respectively. The storage control and 0.1% H_2SO_4 treatment dropped the H/C to 0.59 and O/C to 0.44. The 1% H_2SO_4 treatment had a slight decrease from the native material, 0.57 for O/C and 0.65 for H/C. Finally, the NaOH treatment seemed to lowest O/C and H/C to the lowest values of 0.44 and 0.57, respectively. Therefore, the control, NaOH, and 0.1% H_2SO_4 should have a higher energy content than the native and 1% H_2SO_4 treatment.

Table 2.4 Ultimate analysis of bark after storage (dry basis (d.b.) wt%).

Treatment	**Storage (wk)**	**H (%)**	**C (%)**	**N (%)**	**O^a (%)**	**S (%)**	**O/C**	**H/C**
Native	0	5.86 ± 0.23	52.30 ± 0.22	0.25 ± 0.06	40.33 ± 0.45	0.02 ± 0.00	0.58	0.67
Control	1	5.66 ± 0.13	58.06 ± 1.91	0.40 ± 0.06	34.07 ± 1.86	0.02 ± 0.02	0.44	0.59
	2	5.72 ± 0.14	57.95 ± 2.04	0.39 ± 0.07	34.17 ± 1.95	0.02 ± 0.02	0.44	0.59
0.1% H_2SO_4	1	5.72 ± 0.13	58.25 ± 2.15	0.42 ± 0.07	34.10 ± 2.07	0.03 ± 0.03	0.44	0.59
	2	5.77 ± 0.15	58.03 ± 2.34	0.42 ± 0.05	34.28 ± 2.25	0.03 ± 0.02	0.44	0.60
1% H_2SO_4	1	5.66 ± 0.12	52.51 ± 1.85	0.41 ± 0.04	39.85 ± 1.76	0.09 ± 0.01	0.57	0.65
	2	5.65 ± 0.17	52.60 ± 1.56	0.39 ± 0.03	39.95 ± 1.42	0.09 ± 0.01	0.57	0.64
4% NaOH	1	5.37 ± 0.25	56.52 ± 2.10	0.39 ± 0.07	33.10 ± 1.91	0.02 ± 0.02	0.44	0.57
	2	5.38 ± 0.20	56.54 ± 2.28	0.38 ± 0.06	33.14 ± 2.13	0.02 ± 0.02	0.44	0.57

[a] Calculated from difference

Higher Heating Value (HHV), or the calorific value, describes the energy density of a material and was derived based on the ultimate analysis. The higher energy density of a feedstock can indicate higher energy density in the products in thermal conversion. The calculated HHVs (Table 2.5) for both native material and 1% H_2SO_4 were 18 MJ/kg, which is consistent with the results from ultimate analysis where 1% H_2SO_4 and the native material had the same O and C content. The NaOH treatment had increased to 20.8 MJ/kg but did not have the highest HHV expected from the O/C and H/C ratios being the lowest. The control and 0.1% H_2SO_4 treatment had the highest HHV of 21.7 MJ/kg. Overall HHV analysis indicated the barks increased potential for energy conversion after storage treatment. The higher calorific values can also support the current use of bark as a burning/heat fuel.

Table 2.5 Calculated HHV of bark after storage.

Treatment	**Storage (wk)**	**Calculated HHV (MJ/kg)**
Native	0	18.85
Control	1	21.63
	2	21.66
0.1% H_2SO_4	1	21.77
	2	21.73
1% H_2SO_4	1	18.73
	2	18.72
4% NaOH	1	20.86
	2	20.88

Inorganic content including magnesium (Mg), silicon (Si), potassium (K), and calcium (Ca) in the bark was analyzed by x-ray fluorescence (XRF) (Fig 2.5). Mg, K, and Ca are minor inorganic content compared with Si. The control experiment only using anaerobic treatment reduced the SiO2 and K_2O but no effect on MgO and CaO. The acid treatments including 0.1% H_2SO_4 and 1% H_2SO_4 further reduced the MgO, K_2O, and CaO content but no significant improvement on the SiO_2 compared with the control experiment. Furthermore, the 1% H_2SO_4 led to the lowest level of MgO and CaO. The NaOH pretreatment led to similar levels of SiO_2 to the control experiment and comparable level of K_2O, MgO, and CaO to native bark. In summary, the NaOH treatment shows no advantage over the control experiments while the 1% H_2SO_4 shows the best result for the removal of K_2O, MgO, and CaO.

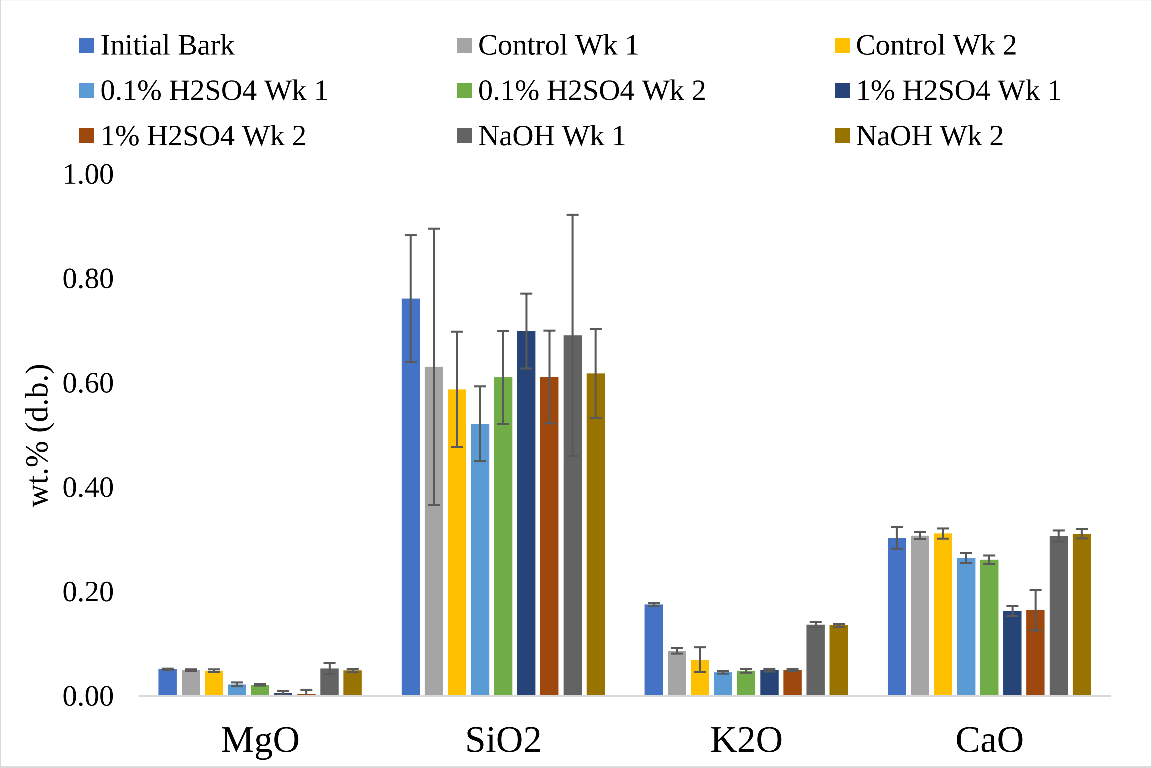

Figure 2.5 Effect of treatment on Mg, Si, K, and Ca wt% content in bark.

Pyrolysis Yields

Pyrolysis yields three products: biochar, bio-oil, and gas. Collected bio-oil products are displayed in Fig. 2.6. Product yields are displayed in Fig. 2.7. Native bark had an average char yield of 36%, an oil yield of 41% and gas yield of 23%. The control had the lowest char production of all the storage treatments with 33% and 30% for weeks 1 and 2, respectively. The oil production did not vary between the control and native bark. The NaOH treatment significantly decreased oil yields down to an average of 30% and 24% for weeks 1 and 2, respectively. 0.1% H_2SO_4 had a char yield of 36% and 33% and oil 43% and 42% for weeks 1 and 2, respectively. The highest liquid yield, 45%, was seen in the 1% H_2SO_4 treatment. The highest char yield, 39%, was seen in the NaOH week 2 treatment, week 1 had 37% char yield. These results were anticipated from the properties presented in the bark after treatment as discussed.

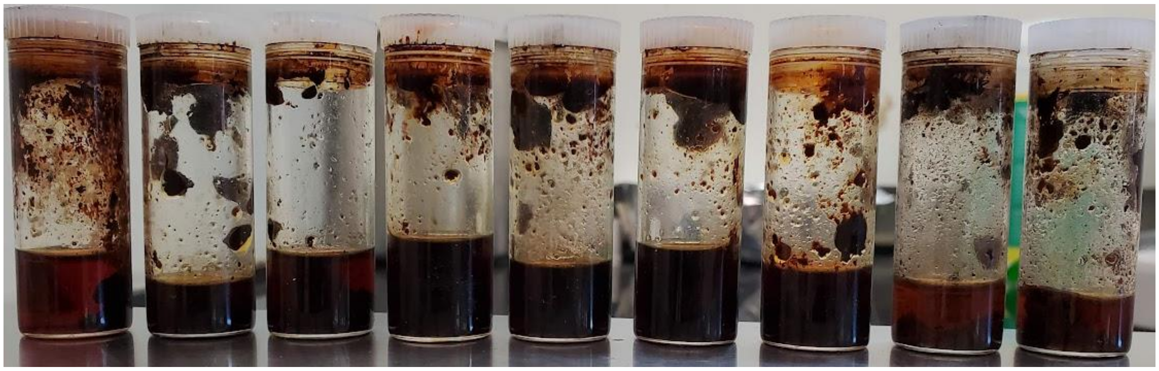

Figure 2.6. Collected bio-oils. From left to right: native, control week 1, control week 2, 0.1% H_2SO_4 week 1, 0.1% H_2SO_4 week 2, 1% H_2SO_4 week 1, 1% H_2SO_4 week 2, 4% NaOH week 1, and 4% NaOH week 2.

Native bark and the control both had a large distribution of products between experimental runs. The alkali treatments oil production and week 1 of 1% acid treatment had the least variance between the six pyrolysis runs. The second week of storage decreased the average product yield in both char and oil, consequently gas production increased as storage time increased. The effect of treatments did show potential improvement in product yields over native bark. The 1% H_2SO_4 treatment did increase oil production up to 11%, although not analytically significant ($p>0.05$). The 0.1% H_2SO_4 treatment had up to a 5.5% increase in oil production. This increase in oil yield could be contributed to the higher reduction of AAEM from acid treatments. This upholds the validity that AAEM content does influence the pyrolysis yields. The NaOH treatment, as expected, significantly decreased the oil production of the bark. Native bark and the control both had a large distribution of products between experimental runs. The NaOH treatments oil production and week 1 of 1% H_2SO_4 treatment had the least variance between the six pyrolysis runs. Low variance increases the consistency of product yields. The second week of storage decreased the average product yield in both char and oil, consequently gas production increased as storage time increased.

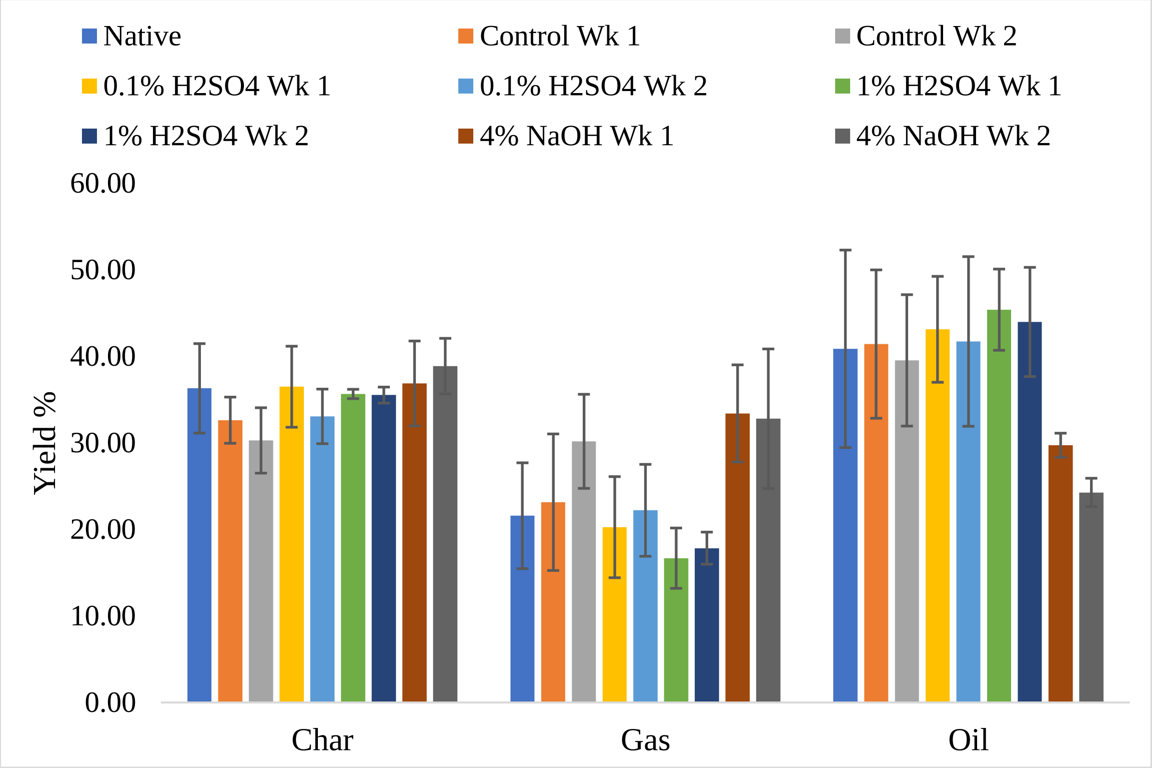

Figure 2.7 Yield (%) of char, gas, and oil products after bark pyrolysis at 500°C.

Biochar Analysis

The same analysis process to determine CHNOS content of bark was repeated on the pyrolysis produced biochar. Table 2.6 reports CHNOS and the O/C and H/C ratios with the calculated HHV. There was no significant change in the hydrogen, carbon, oxygen, and nitrogen was not altered significantly from the control at 2 wt%, 77 wt%, 13-17 wt%, and 0.6 wt%, respectively. But, the 1% H_2SO_4 treatment had an icrease C to 85 wt% and O decreased to 8 wt%. 1% H_2SO_4 treatment, as expeceted, increased sulfur content to 0.07 wt%. Unlike the bark CHNOS, the 1% H_2SO_4 biochar showed the most improvement with increased C and decreased O.

Biochars O/C ratio represents the polar functional groups and stabilty of biochar in the soil whereas the H/C ratio indicaties biochars carbon structure as the conversion of hydrocarbons into aromatic rings. Proposed standards of biochar stability for soil (European Biochar Certificicate and International Biochar Initiative (IBI)) state that the H/C ratio should not be greater than 0.7. The O/C value can be attributed to the stability of the biochar remaining in the soil. A ratio of $O/C < 0.2$

shows that the char can stay stable in the soil for more than 1000 years [42-44].All treatment O/C ratios were under the 0.2 value showing that bark as a biochar can persist in the soil for over 1000 years. The highest O/C being 0.18 in the second week 0.1% acid treatment. The native, control and week 1 of 0.1% acid treatment had O/C of 0.16. The alkali treatment had O/C of 0.14 and 0.11 for weeks 1 and 2 respectively. The lowest O/C ratios are in the 1% acid treatment with 0.1 and 0.07 for weeks 1 and 2 respectively. H/C ratio decreased from 0.2 in the native down to the lowest of 0.15 in control week 2, 1% acid week 2, and alkali week 1. Control week 1 was 0.19. 0.1% acid week 1 and alkali week 2 were both 0.16. 0.1% aicd week 2 was 0.17 and finally 1% acid week 1 was 0.18. The resulting biochars from bark meed the IBI standard as a material that can be used for carbon sequestration in soil.

Table 2.6 Ultimate analysis of biochar under different storage pretreatments.

Treatment	**Storage (wk)**	**H (%)**	**C (%)**	**N (%)**	**O[a] (%)**	**S (%)**	**O/C**	**H/C**	**Calculated HHV (MJ/kg)**
Native	0	2.58 ± 0.02	77.04 ± 0.04	0.54 ± 0.04	16.72 ± 0.05	0.02 ± 0.01	0.16	0.20	26.73
Control	1	2.42 ± 0.79	76.38 ± 2.84	0.63 ± 0.05	15.92 ± 2.98	0.03 ± 0.01	0.16	0.19	26.43
	2	1.96 ± 0.15	77.43 ± 2.67	0.68 ± 0.03	15.52 ± 2.79	0.03 ± 0.01	0.15	0.15	26.20
0.1% H_2SO_4	1	2.03 ± 0.25	77.15 ± 2.01	0.68 ± 0.06	16.16 ± 2.03	0.03 ± 0.00	0.16	0.16	26.09
	2	2.23 ± 0.58	77.07 ± 3.68	0.69 ± 0.08	17.99 ± 3.36	0.04 ± 0.01	0.18	0.17	26.03
1% H_2SO_4	1	2.43 ± 0.62	82.02 ± 4.84	0.66 ± 0.10	11.14 ± 4.34	0.07 ± 0.01	0.10	0.18	29.21
	2	2.19 ± 0.55	85.44 ± 2.50	0.70 ± 0.10	7.77 ± 2.14	0.07 ± 0.00	0.07	0.15	30.63
4% NaOH	1	1.83 ± 0.58	72.49 ± 8.25	0.54 ± 0.04	13.50 ± 8.55	0.03 ± 0.01	0.14	0.15	24.71
	2	2.07 ± 0.94	75.78 ± 4.00	0.55 ± 0.12	11.38 ± 3.32	0.02 ± 0.01	0.11	0.16	26.54

[a] Calculated from difference

Biochar has a higher calorific value than the feedstock bark. The alkali treatment had the lowest estimated HHV of 25 MJ/kg after 1 week of storage. The alkali second week of storage and the control had HHv of 27 MJ/kg. The control and 0.1% acid treatment had HHV of 26 MJ/kg. The 1% acid treatment had the highest HHV's of 29 and 31 MJ/kg for weeks 1 and 2 respectively. Results showed that the thermochemical conversion of bark to biochar will produce a higher calorific solid fuel.

Pyrolyzed pine bark can produce biochars that are of marketable quality for soil amendment and carbon sequestration applications due to large surface areas and porosity. Additionally, the increase in HHV can serve as an improved energy source for heating purposes. To evaluate the treatments on biochars' suitability for specific applications will require additional analysis such as physical and structural characterizations and properties.

Gathered from all the analysis of bark after treatments, it was suspected sulfuric acid would lead to higher oil production from pyrolysis due to lower pH in filtrate, lower oxygen and higher carbon content reported in ultimate analysis, the higher calorific values, and higher reduction of AAEM. The 1% acid treatment had similar HHV (~19 MJ/kg) and ultimate values to the native material, whereas the 0.1% acid had the highest HHV (21.7 MJ/kg), this suggested that possibly the lower concentration of acid would produce more oil in pyrolysis. A large contribution to oil production could be the reduction of AAEM (seen in refrences), which 1% aicd would have the advantage. The control didn't change significantly from the native material and no AAEM was significantly reduced, but there was an increase of HHV (21.6 MJ/kg) due to the lower O and higher C content. The control then might have an increase in oil, albeit insignicicant. Sodium hydroxide showed that it would most likely produce the highest char yield due to the higher pH, highest ash content in proximate analysis, and no sinificant changes in inorganic content from the native material, thus reducing oil production as well.

Gas Analysis

The CO, CO_2, HC, CH_4, and H_2 composition of the pyrolysis syngas was measured. The maximum weight percent values from each sample are given in Table 2.7. The pyrolytic gasses are richer in CO, CO_2, and hydrocarbons (HC) than hydrogen and methane. The yield of hydrogen was generally low, down to 0.33% in week one of 0.1% H_2SO_4, where the native bark had 5.25%. The maximum hydrogen was 12.99% in 1% H_2SO_4 week two, as well as CH_4 of 8.02%. Hydrocarbons were the highest in the 1% H_2SO_4 week two treatment with 21.49%. Syngas is combustible and can be used as a fuel, as well as become a source for other chemicals. Higher CO fraction can produce for pure CO production that can be applied to various industrial processes as well as CO_2 utilization. Higher fractions of H_2 and CO from pine bark is used to synthesize other chemicals, such as dimethyl ether, polyalcohol, and Fischer-Tropsch fuels (Wang 2020). The control seemed to negatively affect the syngas production, reducing all components from the native material followed by 0.1% H_2SO_4 and NaOH treatments. Although, NaOH did increase CO_2 from 20.37% in the native to the highest values of 28.99 and 27.09% for weeks 1 and 2 respectively. Overall, 1% H_2SO_4 seems to also provide a more robust syngas.

Table 2.7 Average gas composition.

Treatment	**Storage (wk)**	**CO (%)**	**CO_2 (%)**	**HC (%)**	**CH_4 (%)**	**H_2 (%)**
Native	0	15.08 ± 5.83	20.37 ± 5.22	17.99 ± 6.02	5.38 ± 2.84	5.25 ± 2.32
Control	1	9.69 ± 4.84	11.05 ± 4.33	9.19 ± 5.82	3.48 ± 3.50	1.56 ± 2.67
	2	9.10 ± 1.91	10.06 ± 3.51	7.99 ± 4.68	2.29 ± 1.30	1.30 ± 1.15
0.1% H_2SO_4	1	12.31 ± 5.39	18.14 ± 9.02	16.15 ± 4.36	4.51 ± 2.15	0.33 ± 0.33
	2	16.18 ± 8.97	15.90 ± 8.62	13.59 ± 7.21	5.06 ± 2.74	6.37 ± 5.54
1% H_2SO_4	1	18.27 ± 3.58	18.48 ± 2.99	18.39 ± 2.28	6.34 ± 1.12	5.38 ± 1.47
	2	27.90 ± 0.53	22.01 ± 2.55	21.49 ± 2.50	8.02 ± 0.86	12.99 ± 1.86
4% NaOH	1	17.55 ± 9.09	28.99 ± 10.33	15.45 ± 8.88	4.77 ± 4.01	7.58 ± 9.07
	2	13.20 ± 4.21	27.09 ± 13.58	14.13 ± 10.53	4.62 ± 3.43	3.74 ± 2.71

Conclusion

A potential to valorize pine bark was evaluated by low severity chemicals with anerobic storage for increase pyrolysis conversion. Alkali and alkaline earth metals (AAEM) are known to hinder pyrolysis conversion. Sulfuric acid and sodium hydroxide were used to reduce AAEM and increase the liquid fraction in pyrolysis. Sulfuric acid treatments showed a reduction of AAEM in bark. The highest increase in liquid yield of 11% is seen in the 1% acid treatment but was not statistically significant. Alkali treatment increased the ash content, reduced volatile matter, and did not reduce AAEM content of bark leading to a significant decreased liquid yield over the native bark. Therefore, treatments did not have a significant change in pyrolysis yields, but characteristics of the resulting products could be researched further. The solid fraction (biochar) produced from pyrolysis could be a marketable product in soil amendment, carbon sequestration, and even solid fuel applications. The liquid fraction (bio-oil) can be used for chemical and biofuel production. The studies treatment for valorization of bark may not be in the products quantity, but in the products quality.

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Chapter 3: Influence of Alkaline and Acid Pretreatment of Pine Bark Derived Biochars

Abstract

Biochar uses are increasing, being researched as products for soil amendments, carbon sequesters, and solid fuels. Biochar procured from sulfuric acid (H_2SO_4 - 0.1% w/w and 1% w/w, dry basis) or sodium hydroxide (NaOH - 4% w/w dry basis) anerobic stored (1 and 2 weeks) pine bark from pyrolysis at 500°C was characterized to investigate the change of key performance indicators by treatments. Key performance indicators include proximate composition, thermal recalcitrance, combustion and energy characteristics, pH, and electrical conductivity. The recalcitrance index increased from 0.67 in native bark up to 0.90 from storage treatments. pH values were slightly alkaline (7.73-10.37) except 1% H_2SO_4 had a pH of 6.66. The higher heating values of 1% H_2SO_4 treatment increased from native bark (26.73 to 30 MJ/kg) and the microstructure shown a significant increase in its surface area (31 to 140 m^2/g). Whereas the sodium hydroxide treatment had a reduction in heating value (24.71 MJ/kg) and surface area (28.51 m^2/g) indicating that it is not satisfactory for heating or soil amendment applications. The 1% H_2SO_4 treatment showed the most significant improvement in becoming both a solid fuel source and soil amendment.

Introduction

Lignocellulosic biomass has become widely investigated as a sustainable production of biofuels (liquid transportation fuels). Although bio-oil is highly prioritized in production and improvement, biochar is gaining attention to be utilized as a value-added product. Applications such as soil amendment to improvement of water-holding capacity, increase the stable pool of carbon, adsorption of organic and toxic compounds, adsorption and reaction with gases within the soil, nutrient retention and addition, improvement in the growth of beneficial microorganisms [1]. Currently, the most common biochar applications are soil health improvement and solid fuels [2-4].

Biochar, aside from soil amendment, can be applied to environmental remediations, energy storage, composites, and catalyst production. The nature of the feedstock dictates the biochar characteristics such as the size, fraction, and abundance of pores, pH, content of volatile compounds, water-holding capacity, ash content, bulk density, specific surface area, cation exchange capacity, stability, and nutrient retention [5-8].

The use of biochar for solid fuels has a positive outlook due to their low ash content compared to coal. Combustion characteristics are key indicators for the use of biochar as a solid fuel. These characteristics are ignition, peak, and burnout temperatures. The ignition temperature is the minimum temperature at which a fuel ignites spontaneously in an environment without an ignition source. This is important for safety in storing and transporting. The higher the burnout temperature the less of combustible components in the biomass. Peak temperature is at the temperature at which maximum combustible component of the biochar is released. The burnout temperature is the temperature when the fuel is mostly consumed. These two temperatures are parameters needed for the operation of biomass combustion, fuel selection, consumption and combustor design [9, 10].

Environmental remediation applications include wastewater management, gas purification, and removal of soil contaminant. Biochar can remove both inorganic and organic pollutants through adsorptive and degradative processes as well as the use for air purification by removing molecules such as carbon dioxide or hydrogen disulfide [3, 6]. Biochar is also useful in heavy metal adsorption for a low-cost process to remove metal ions in aqueous environments with a low-concentration range [6]. Activating biochar can also help improve adsorption properties by chemical or physical application [2, 6]. The adsorptive efficiency of biochar is directly proportional to the physicochemical properties such as functional groups, surface area, cation exchange capacity, etc.[2, 7]

The use of energy storage applications includes supercapacitor production, battery production, and fuel cell production. Chemical activation introduces functional groups on the surface of the activated carbon that effect the electrochemical properties. Activated biochar can show good capacitive performance and is researched as anodic materials in battery production [3]. Other uses include biochar-based composites such as: inorganic reinforced plastics, catalysis, redox-mediated reactions, electrochemical measurement devices, and biological procedures such as anti-bacterial use [3].

Figure 3.1 depicts the type of biochar applications by what thermochemical treatments have been used [6] and Figure 3.2 breaks down the chemical and physical characterization of biochar [7].

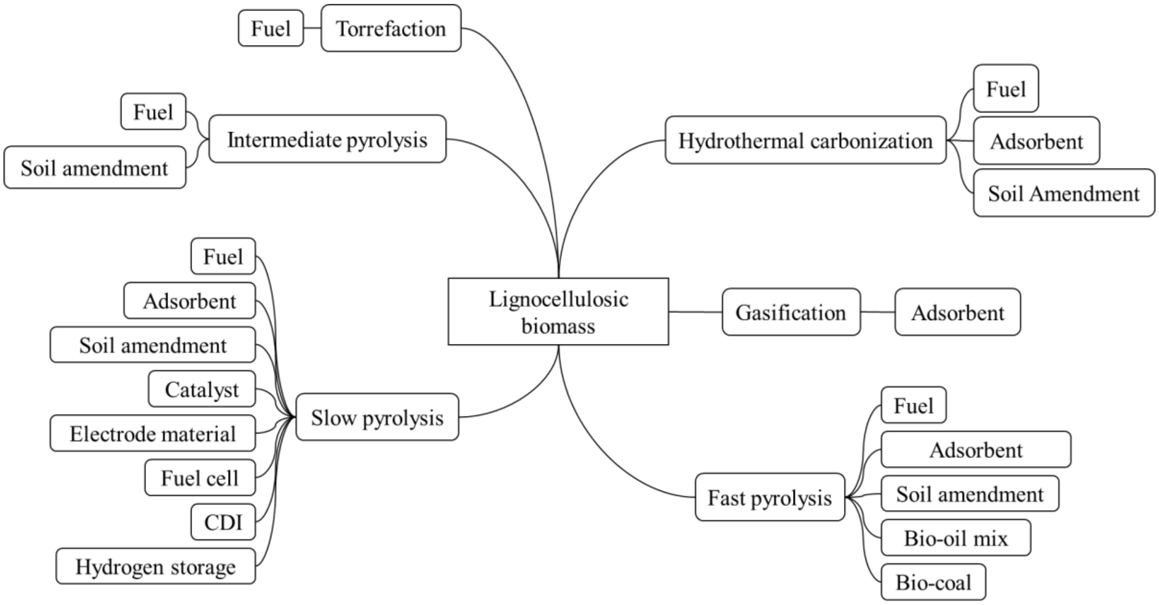

Figure 3.1 Overview of thermochemical treatments of biomass and of their applications of the resulting chars. CDI: Capacitive deionization.

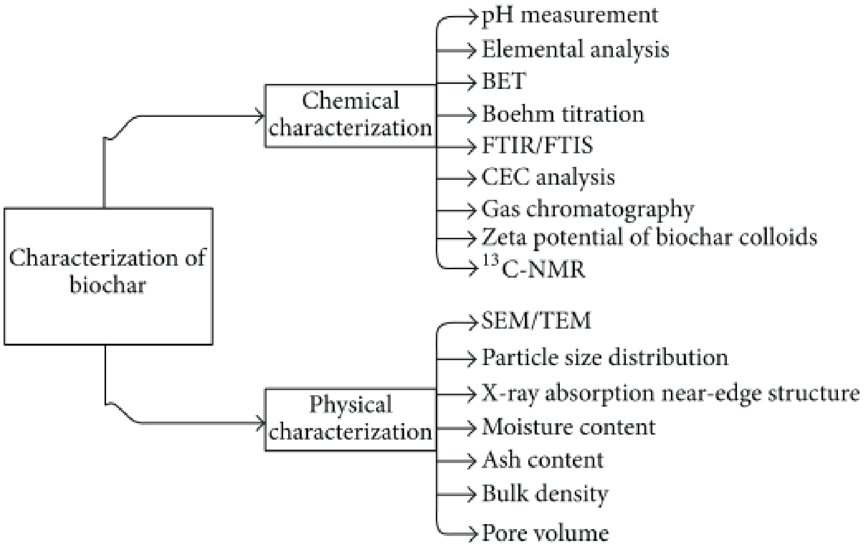

Figure 3.2 Proposed methods to determine characteristics of biochar.

International Biochar Initiative (IBI) provide a standard definition of biochar and biochar characteristics related to the use of biochar as a soil amendment. Adaptations and uses are intended for any nation or region. These standards are not required, but act as a guideline/baseline for safety considerations of biochar in soil. The IBI is ever evolving to understand the positive functions of biochar in soil.

Methods and Materials

Materials

Loblolly pine bark from Jasper, South Carolina sourced from FTX Consulting. The bark was subjected to storage (1 or 2 weeks) and either acid (0.1% H_2SO_4 w/w d.b, 1% H_2SO_4 w/w d.b.) or alkali treatment (4% NaOH w/w db). The bark was pyrolyzed at 500°C with a microwave pyrolysis apparatus. (These are the chars produced in Chapter 2).

Analysis method and parameters studied for biochar follow the Standard Product Definition and Product Testing Guidelines for Biochar (IBI) used in soil [11].

The replicate char samples of each condition (treatment and storage time) were combined for a single composite sample for pH, EC, and combustion analysis. Elemental analysis of each individual replicates was measured before combination.

Compositional Analysis

Proximate and ultimate analysis of the biochar followed the same methodology as the bark in Chapter 1. Proximate analysis to determine the volatile matter, ash, and fixed carbon content by thermogravimetric analysis (TGA701, Leco) following standardized ASTM D7582 method (https://www.astm.org/Standards/D7582.htm). Ultimate analysis to find the carbon, hydrogen, nitrogen, and sulfur content using elemental analyzer (Vario EL cube, Elementar). Oxygen was determined by mass balance.

Higher heating value (HHV) was calculated from elemental composition according to Eq. 3.1 [12],

$$HHV = 0.338C + 1.428\left(H - \frac{O}{8}\right) + 0.095S\,, \tag{3.1}$$

where C, H, O, and S are carbon, hydrogen, oxygen, and sulfur wt% respectively. This is the same estimation used on the bark biomass in Chapter 2, Eq. 2.4. For verification of the equation, two char samples (control and alkali week 2) had their HHV measured by a Isoperibol Calorimeter (LECO AC600). Results had <1% error between the estimated and measured HHV values. The measured results are shown in Appendix A.

Atomic O/C, H/C, and N/C ratios were calculated using Eq. 3.2, where C, H, N, and O are the wt% of carbon, hydrogen, nitrogen, and oxygen determined by ultimate analysis, respectively.

$$\frac{\mathrm{O}}{\mathrm{C}} \text{ or } \frac{\mathrm{H}}{\mathrm{C}} \text{ or } \frac{C}{N} = \frac{\text{wt\% } \mathrm{O_2} \text{ or } \mathrm{H_2}, or\ C}{\text{atomic weight of } \mathrm{O_2} \text{ or } \mathrm{H_2} \text{ or C}} \div \frac{\text{wt\% C or N}}{\text{atomic weight of C or N}}. \tag{3.2}$$

Carbon yield (Eq. 3.3) is added to biochar characterization,

$$\text{Carbon Yield (\%)} = \frac{\mathrm{C_{biochar}}}{C_{\mathrm{biomass}}} \times \text{Biochar Yeild}, \tag{3.3}$$

where C is the atomic carbon determined from ultimate analysis.

Fuel Property Calculations

Using proximate analysis results to calculate energy characteristics of the biochar: fuel ratio, energy densification, and energy yield.

The fuel ratio can indicate improved combustion efficiency and reduced toxic pollutant emissions during its combustion. The fuel ratio can be compared to bituminous coals range of 1.5 to 2 for combustion efficiency [10, 13]. The fuel ratio is presented in Eq. 3.4. Energy densification determined from the ratio given in Eq. 3.5 [10, 14]. Energy yield (Eq. 3.6), where Y_{biochar} is the yield of biochar from pyrolysis, $\mathrm{HHV_{biomass}}$ is the initial higher heating value before pyrolysis, and $\mathrm{HHV_{biochar}}$ is the higher heating value after pyrolysis [15, 16].

$$\text{Fuel Ratio} = \frac{\text{fixed carbon (FC)}}{\text{Volatile matter (VM)}} \tag{3.4}$$

$$\text{Energy Densification} = \frac{\mathrm{HHV_{biochar}}}{\mathrm{HHV_{biomass}}} \tag{3.5}$$

$$\text{Energy Yield (\%)} = \mathrm{Y_{biochar}} \frac{\mathrm{HHV_{biochar}}}{\mathrm{HHV_{biomass}}} \times 100 \tag{3.6}$$

pH and Electrical Conductivity (EC) Measurements

The pH and electrical conductivity (EC) were determined using the methodology of Singh et al. where the pH and EC was measured in a 1:20 (w/v) biochar to DI water ratio after 24 h on a shaking table at 25°C [17, 18]. The used ratio was 0.3g of biochar to 6g of DI water and was mixed in 10mL centrifuge tubes. The samples were set to rest for 30 minutes before measuring pH with Mettler Toledo pH meter (Model: Seven Compact pH/ion meter S220). The pH meter was calibrated using pH of 4, 7, and 10 buffers. EC of the biochar suspension was measured after taking the pH with a calibrated EC meter (OHAUS™ Aquasearcher™, AB33EC).

Brunauer-Emmett-Teller (BET analysis)

The biochar powders were analyzed for BET surface area and pore size distribution using Micromeritic ASAP 2020 Plus Adsorption Analyzer.

Combustion Characteristics of Biochar

Biochar was analyzed for ignition, peak, and burnout temperatures, and thermal recalcitrance using thermogravimetric analysis (TGA701, Leco) set to 10°C/min heating rate to 950°C in air [2, 10, 14, 19]. An intersection method was used in this study. The T_i is the intersection point in the thermogravimetric curves (TG) graph of the line tangent to the point where the differential thermogravimetric curves (DTG) peak occurs and the line tangent to the point of initial devitalization after the sample is dried. T_b is the intersection point in the TG graph of the line tangent to the point where the DTG peak occurs and the line tangent to the point where the weight loss stabilizes [15, 20].

Thermal (oxidation) recalcitrance ($R_{50,\text{ biochar}}$) of biochar analyzed by TGA curves of biochars for moisture and ash contents. The ratio (Eq. 3.7) has been proposed to be where $T_{50,\text{ biochar}}$ and $T_{50,\text{ graphite}}$ are the temperatures at which 50% mass loss of biochar and graphite, respectively. $T_{50,\text{ graphite}}$ used in this study is 886°C [10, 21].

$$R_{50} = \frac{T_{50\text{ biochar}}}{T_{50\text{ graphite}}} \tag{3.7}$$

Statistical Analysis

Single-factor one-way analysis of variance (ANOVA) was performed in JMP 14.2.0 (SAS, Cary, NC) to identify significant differences in results. Paired student t test was performed to determine if the ANOVA was significant at $p < 0.05$.

Results and Discussion

This study was to characterize biochar produced from pyrolysis of bark that was stored with low severity acid or alkali addition. Characterization can indicate if the biochar can be a value-added product for soil amendment or fuel.

There was also a noticeable whitish deposition on the surface of the biochar (in native, control, and alkali treatment) after pyrolysis. An oxygen leak was a concern because the gas analyzer would detect an oxygen level above 2ppm during a run. A percent oxygen sensor (Alpha Omega Instruments Series 2000) was used to investigate all connection points of the apparatus. No oxygen was detected in the microwave chamber, but an oxygen leak was detected from the filter to the gas analyzer. This solved why there was oxygen shown in the system by the gas analyzer. Additionally, SEM images were taken of the black and white deposits of the char. Imaging was to help determine if the white ash was due to oxygen present in the reaction. SEM imaging showed that the white deposit was crystalline silica with additional inorganics of potassium, calcium, magnesium, and some aluminum (shown in Appendix B). This whitish deposition was then considered to be inorganic salts that were left on the biochar's surface after the carbonization process [10].

Compositional and Physiochemical Properties of Biochar

Proximate analysis reports the volatile matter, ash, and fixed carbon of the biochar (Table 3.1). The control increased the volatile matter (34.19 and 31.81) and ash (4.63 and 4.38) and decreased the fixed carbon (61.19 and 63.81) compared to the native material with 27.60, 3.10, and 69.31 wt% respectively. The 0.1% H_2SO_4 treatment increased volatile matter (32.23 and 32.34) and decreased fixed carbon (63.81 and 63.82) with little variation between the storage times, while the ash content increased in week 1 (3.95) and decreased in week 2 (2.02). The 1% H_2SO_4 marginally decreased the volatile matter (26.14 and 25.57) and slightly increased fixed carbon (70.18 and 70.61) and ash (3.68 and 3.82). The higher acid concentration in the parent biomass also did not significantly change from the native bark, and the biochar reflects that characteristic. NaOH treatment had similar volatile matter as the native bark (27.76 and 27.40) but had a significant increase in ash (11.61 and 10.20) and a decrease in fixed carbon (60.64 and 62.40). Higher carbon would be beneficial as a soil amendment, suggesting that the 1% H_2SO_4 will show promise over the other treatments. Whereas the control and NaOH treatment are not promising as a soil amendment due to the higher ash and lower fixed carbon contents.

Table 3.1 Proximate analysis of stored pretreated bark derived biochar.

Sample	Storage (wk)	Volatile Matter (% d.b.)	Ash (% d.b.)	Fixed Carbon (% d.b.)
Native	0	27.60 ± 0.39	3.10 ± 0.12	69.31 ± 0.27
Control	1	34.19 ± 0.09	4.63 ± 0.34	61.19 ± 0.24
	2	31.81 ± 2.01	4.38 ± 0.79	63.81 ± 1.23
0.1% H_2SO_4	1	32.23 ± 0.58	3.95 ± 0.24	63.82 ± 0.82
	2	32.34 ± 1.26	2.02 ± 2.49	65.64 ± 1.23
1% H_2SO_4	1	26.14 ± 0.37	3.68 ± 0.60	70.18 ± 0.97
	2	25.57 ± 0.48	3.82 ± 0.47	70.61 ± 0.01
4% NaOH	1	27.76 ± 0.10	11.61 ± 0.24	60.64 ± 0.14
	2	27.40 ± 0.38	10.20 ± 0.23	62.40 ± 0.15

Ultimate analysis of the biochar and the higher heating values (HHV) of the bark are reported in Table 3.2. The control and 0.1% H_2SO_4 were not significantly different from the native biochar in the H, C, N, O, and S content of 2.58, 77.04, 0.54, 16.72, and 0.02 wt% d.b. respectively. In the 1% H_2SO_4 treatment, C was increased to 82.02 and 85.44 wt%, N increased to 0.66 and 0.70 wt%, and O decreased to 11.14 and 7.77 wt% for weeks 1 and 2 respectively compared to the native biochar. This is a different characteristic compared to the parent biomass where the native and 1% H_2SO_4 had similar elemental composition. C and O decreased in the NaOH to 72.49 and 75.78 wt% and 13.50 and 11.38 wt%, for weeks 1 and 2, respectively. The HHV of the biochars were not significantly different from 26 MJ/kg, although the 1% H_2SO_4 treatment did increase to 29 and 31 MJ/kg for weeks 1 and 2, respectively. The HHV of the biochars in comparison to the parent bark feedstock (Table 2.5) showed an improved fuel quality. The biochars can serve as a better energy source for heating purposes in comparison to their parent biomass.

Table 3.2 Ultimate analysis (wt%) of bark biochar and estimated HHV.

Sample	Storage (wk)	H (%)	C (%)	N (%)	O[a] (%)	S (%)	Estimated HHV (MJ/kg)
Native	0	2.58 ± 0.02	77.04 ± 0.04	0.54 ± 0.04	16.72 ± 0.05	0.02 ± 0.01	26.73
Control	1	2.42 ± 0.79	76.38 ± 2.84	0.63 ± 0.05	15.92 ± 2.98	0.03 ± 0.01	26.43
	2	1.96 ± 0.15	77.43 ± 2.67	0.68 ± 0.03	15.52 ± 2.79	0.03 ± 0.01	26.20
0.1% H_2SO_4	1	2.03 ± 0.25	77.15 ± 2.01	0.68 ± 0.06	16.16 ± 2.03	0.03 ± 0.00	26.09
	2	2.23 ± 0.58	77.07 ± 3.68	0.69 ± 0.08	17.99 ± 3.36	0.04 ± 0.01	26.03
1% H_2SO_4	1	2.43 ± 0.62	82.02 ± 4.84	0.66 ± 0.10	11.14 ± 4.34	0.07 ± 0.01	29.21
	2	2.19 ± 0.55	85.44 ± 2.50	0.70 ± 0.10	7.77 ± 2.14	0.07 ± 0.00	30.63
4% NaOH	1	1.83 ± 0.58	72.49 ± 8.25	0.54 ± 0.04	13.50 ± 8.55	0.03 ± 0.01	24.71
	2	2.07 ± 0.94	75.78 ± 4.00	0.55 ± 0.12	11.38 ± 3.32	0.02 ± 0.01	26.54

[a] Calculated from difference

Atomic hydrogen/carbon (H/C), oxygen/carbon (O/C), and carbon nitrogen (C/N) ratios explain the stability of biochar in the soil, the length of time the biochar can persist in the ground, and the biochar's polar functional groups [11, 14, 22]. The O/C ratio represents the polar functional groups and stability of biochar in soil. IBI dictates a biochar H/C maximum of 0.7 for carbon sequestration in soil [23]. H/C ratio indicates biochar carbon structure as the conversion of hydrocarbons into aromatic rings. Low H/C can indicate high aromaticity with increased resistance [11]. All treatments had a H/C ratio below the 0.7 maximum, indicating they are acceptable for soil amendment. Results of the O/C, H/C, and C/N are shown in Table 3.3. The lowest H/C ratio was 0.15 seen in the control week 2, 1% H_2SO_4 week 1, and NaOH week 1. The native had the highest H/C ratio with of 0.2. The O/C ratios had more significant differences between treatments ranging from 0.07 in 1% H_2SO_4 week 2 to 0.18

in the 0.1% H_2SO_4 week 2. The native, control, and 0.1% H_2SO_4 week 1 all had a O/C ratio of 0.16. The NaOH had 0.14 and 0.11 and 1% H_2SO_4 week 1 was 0.10. The C/N ratio affects the rate of decomposition of organic matter and release of soil nitrogen [24]. High C/N ratio leads to N immobilization in the soil [25]. The biochar derived from the native bark had a C/N of 165.09, the treatments lowered the ratio, even if not significantly. The lowest C/N was 130.48, seen in the 0.1% H_2SO_4 treatment. The similar HHV values for all the treatments but the 1% H_2SO_4 treatments suggests that the O/C ratio reduction has a greater influence than the H/C ratio.

Table 3.3 Atomic H/C, O/C, and C/N ratios and carbon yield of biochar calculated from ultimate analysis.

Treatment	Storage (wk)	O/C	H/C	C/N	Carbon Yield
Native	0	0.16	0.20	165.09	53.48
Control	1	0.16	0.19	141.06	42.92
	2	0.15	0.15	132.98	40.47
0.1% H_2SO_4	1	0.16	0.16	132.59	48.33
	2	0.18	0.17	130.48	43.91
1% H_2SO_4	1	0.10	0.18	145.32	55.69
	2	0.07	0.15	142.50	59.79
4% NaOH	1	0.14	0.15	157.73	47.28
	2	0.11	0.16	161.77	52.10

The fuel ratio of the biochar represents the proportion of its fixed carbon to the volatile content. The 1% H_2SO_4 treatment had the highest fuel ratios of 2.68 and 2.76 for weeks 1 and 2 respectively. The remaining treatments (control, 0.1% H_2SO_4, and NaOH) were lower than the native fuel ratio (2.48). The lowest fuel ratios are seen in the control, 1.79 in the first week and 2.01 for the second week. Weeks 1 and 2 of the 0.1% H_2SO_4 treatment had a fuel ratio of 1.98 and 2.03 for week 1 and 2 respectively. Fuel ratios of 2.18 and 2.28 were the NaOH treated week 1 and 2 fuel ratios respectively. Higher fuel ratios enable stable and lasting combustion process, suggesting the 1% H_2SO_4 treatment is ideal for a soil amendment.

The energy densification decreased in all the chars except in the 1% H_2SO_4 treatment. The native material had an energy densification of 1.42, the 1% H_2SO_4 treatment increased to 1.56 and 1.64 for weeks 1 and 2, respectively. The lowest energy densification was shown in the first week of NaOH treatment of 1.18. The 0.1% H_2SO_4 treatment had the second lowest energy densification of 1.2, for both weeks. The control had energy densifications of 1.22 and 1.21 for weeks 1 and 2, respectively. Higher energy densification is ideal for use as a solid fuel, and the 1% H_2SO_4 treatment shines out as becoming applicable to both a solid fuel and soil amendment.

Table 3.4 Fuel ratio, energy densification, and energy yield of biochar (d.b.).

Treatment	**Storage (wk)**	**Fuel Ratio**	**Energy Densification**	**Energy Yield (%)**
Native	0	2.48	1.42	51.47
Control	1	1.79	1.22	39.86
	2	2.01	1.21	36.65
0.1% H_2SO_4	1	1.98	1.20	43.75
	2	2.03	1.20	39.60
1% H_2SO_4	1	2.68	1.56	55.60
	2	2.76	1.64	60.24
4% NaOH	1	2.18	1.18	43.67
	2	2.28	1.27	49.42

Determination and attraction of nutrients and mineral ions directly affect the soil surface charge due to the pH of the soil solution. During carbonization acidic functional groups are removed and salts from AAEM are enriched, thus biochar is more alkaline [11]. The pH and electrical conductivity are presented in Table 3.5. The pH ranged from the lowest of 6.66 from the 0.1% H_2SO_4 to 10.37 in the sodium hydroxide treatment. The 1% H_2SO_4 had a pH of 7.93. The native material had a pH of 7.73. The control had a neutral pH of 7. Low ash content lowers pH [11]. The alkaline pH would be beneficial as a soil amendment for acidic soils, promoting suitable soil for plant cultivation. Alkali salts provided biochar with considerable alkalinity.

Electrical conductivity (EC) shows the quantity of salt enclosed in the biochar. As the salt concentration of the solution increases, its capacity to conduct electrical current increases. The EC of the NaOH treatment was 4.57 and 3.45 µS/cm for weeks 1 and 2 respectively. The EC in the native material was 249.5 µS/cm, the control week 1 had an increased EC of 263 and a decrease in week 2 to 218.3 µS/cm. The highest EC was seen in the 0.1% H_2SO_4 treatment, 312.9 µS/cm whereas week 2 had a decrease in EC to 179.77 µS/cm. The 1% H_2SO_4 had lower EC of 146.57 and 177.13 µS/cm for weeks 1 and 2, respectively. Soil with EC values of 25–57 µS/ cm, 45–114 µS/cm and ≥115 µS/cm, are classified as moderately saline, strongly saline, and very strongly saline, respectively [10]. Based on this classification, the biochars in this study can be classified as moderately saline to very strongly saline, excluding the sodium hydroxide treatment. This indicates that the application of these biochars for soil enrichment will increase soil salinity. The significantly low EC of the sodium hydroxide treatment infers there is little salt in the biochar. This is interesting considering the treatment showed similar inorganic content to native bark. The NaOH treatment may have a fixed structure with no free cations whereas there is still free hydroxide anions to lower the pH.

Table 3.5 pH and EC of biochar.

Treatment	Storage (wk)	pH	EC (µS/cm)
Native	0	7.73 ± 0.05	249.50 ± 6.42
Control	1	7.01 ± 0.01	263.03 ± 0.74
	2	7.36 ± 0.02	218.30 ± 1.18
0.1% H_2SO_4	1	6.66 ± 0.03	312.90 ± 6.56
	2	6.96 ± 0.05	179.77 ± 1.05
1% H_2SO_4	1	7.93 ± 0.05	146.57 ± 0.96
	2	7.57 ± 0.02	177.13 ± 1.15
4% NaOH	1	10.37 ± 0.01	4.57 ± 0.08
	2	10.12 ± 0.01	3.45 ± 0.02

Brunauer-Emmet-Teller (BET) nitrogen gas physisorption method traditionally studies the morphological characteristics and physical properties of biochar. Surface area and the pore volume, size, and area. Density Functional Theory (DFT) method determined the pore area and BJH (Barrett, Joyner, Halenda) method determined the pore volume and adsorption pore size. The increase in the porosity of biochar is due to the decomposition of lignin, the quick release of H_2 and CH_4 and the reaction of aromatic condensation. Surface area increases during pyrolysis due to the decomposition of cellulose and hemicelluloses, and the formation of channel structures. The surface area is associated with contaminant removal (e.g., heavy metals) and water holding capacity [26].

The results (Table 3.6) show that increasing pretreatment storage time helps increase the surface area of biochar. Compared with 0.1% t H_2SO_4 treatment he higher concentration, 1% H_2SO_4 treatment significantly increased the surface area, 166.65 m^2/g for week 2 whereas the week 1 had 140.9 m^2/g, the same as week 2 of the 0.1% H_2SO_4 treatment. The NaOH treatment decreased the surface area and pore area significantly compared with the control experiment. NaOH may block some of the pores, or dead-ended pores, as the longer treatment storage time led to smaller surface area. The pore size did not change between treatments. Surface area increase might be due to the acid promotion of decomposition of cellulose and hemicelluloses, and the formation of channel structures. The 1% H_2SO_4 treatment is most advantageous to provide high surface area biochar as an adsorbent.

Table 3.6 BET of pine bark biochar.

Treatment	**Storage (wk)**	**Surface Area (m^2/g)**	**Pore Volume (cm^3/g)**	**Adsorption Pore Size (Å radius)**	**Pore Area (m^2/g)**
Native	0	31.04	0.021	15.63	16.59
Control	1	83.72	0.041	15.40	35.36
	2	121.4	0.066	15.64	58.26
0.1% H_2SO_4	1	81.50	0.054	15.65	45.71
	2	140.96	0.060	15.41	53.95
1% H_2SO_4	1	140.85	0.065	15.62	57.15
	2	166.65	0.076	15.58	66.42
4% NaOH	1	28.51	0.019	15.74	19.03
	2	22.91	0.014	15.73	13.68

Combustion Characteristics of Biochar

Reported values of T_i and T_b are reported in Table 3.7. T_i increased the highest from the native (262°C) to 309°C in 1% H_2SO_4 treatment. The alkali treatment had a decreased T_i of 200 and 154°C. The control and 0.1% H_2SO_4 were lower than the native with 249°C and 241°C, the 1st week of 0.1% H_2SO_4 had the lowest Ti of 213°C. T_b is significantly higher than reported values [9, 10, 14, 15]. Unlike the typical combustion data from literature, there was no temperature at which there was no longer any change of mass. All the biochar samples were still experiencing change up to the maximum temperature (950°C). Hence the reported burnout temperatures are at the maximum temperature of the TGA analysis (Fig. 3.3). Individual TGA plots are displayed in Appendix C.

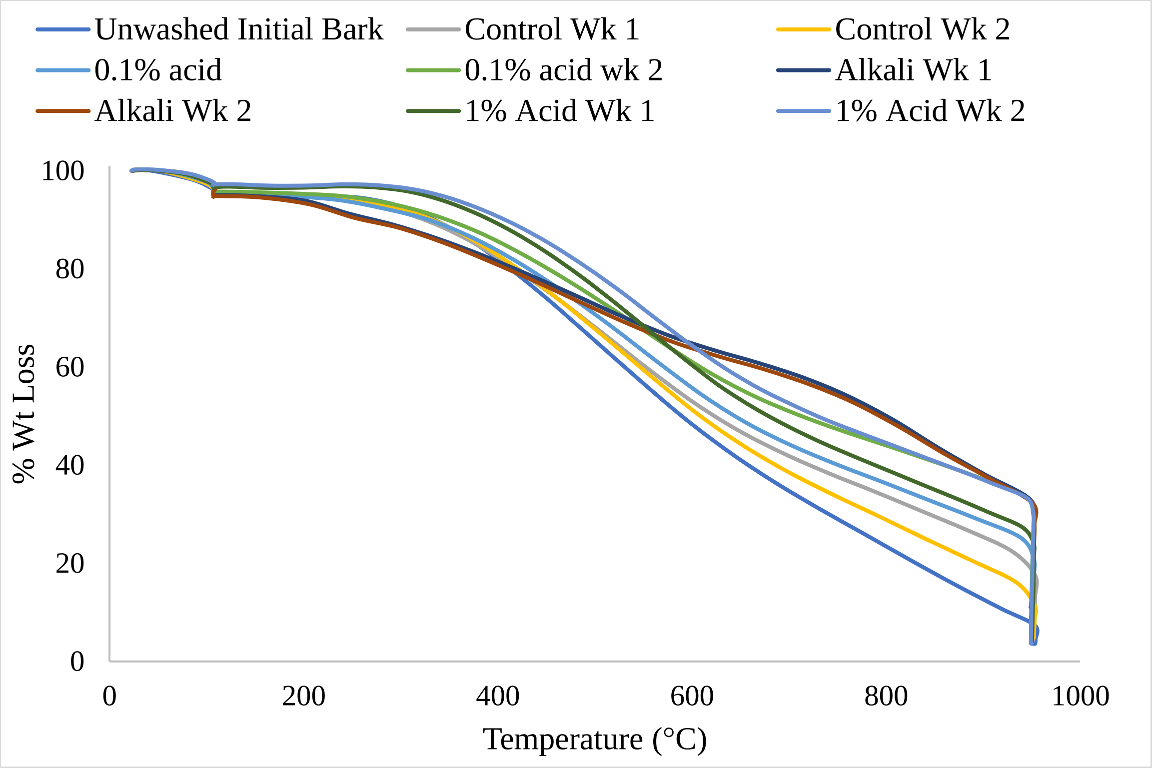

Figure 3.3. Combustion analysis of biochar in air from room temperature to 950°C.

R_{50} is an energy-based quantitative approach to estimate the energy required to thermally degrade biochar. If R_{50} is > 0.7, the biochar has a classification of Class A, meaning a minimal susceptibility to biodegradation. If $0.50 < R_{50} < 0.7$ then it is Class B, some susceptibility to biodegradation, and lastly if $R_{50} < 0.5$ then it is Class C with high susceptibility to biodegradation [10, 19, 22, 27-29]. The results (Table 3.4) categorized the control, 0.1% H_2SO_4, 1% H_2SO_4, and NaOH treatments in Class A with R_{50} values of 0.71, 0.75, 0.74 and 0.90 for week 1 respectively. Week 2 had increased R_{50}, in the H_2SO_4 treatments, 0.1% H_2SO_4 increased to 0.83 and in the 1% H_2SO_4, the R_{50} value increased to 0.9.

The native bark was in Class B, with a R_{50} of 0.67. Week 2 of the control had a R_{50} of 0.69, placing it just on the cusp of a Class A biochar.

Table 3.7 Solid fuel characteristics of biochar.

Treatment	**Storage (wk)**	**T_{max} (°C)**	**R_{50}**	**T_i (°C)**	**T_b (°C)**
Native	0	568.55 ± 36.59	0.64	262.17 ± 2.09	953.53 ± 0.40
Control	1	578.43 ± 61.82	0.65	249.35 ± 34.00	952.49 ± 0.91
	2	586.81 ± 36.22	0.66	231.95 ± 1.70	952.30 ±0.82
0.1% H_2SO_4	1	598.99 ± 42.75	0.68	213.27 ± 31.83	950.77 ± 1.10
	2	667.46 ± 118.57	0.75	241.83 ± 64.12	949.67 ± 0.29
1% H_2SO_4	1	615.24 ± 45.88	0.69	308.79 ± 3.83	951.21 ± 0.93
	2	688.08 ± 133.72	0.78	294.02 ± 21.49	949.74 ± 0.90
4% NaOH	1	838.85 ± 51.01	0.95	200.49 ± 2.30	950.04 ±0.59
	2	826.62 ± 39.19	0.93	154.12 ± 2.15	950.01 ± 0.22

Discussion

The lowering of the AAEM content in the bark before pyrolysis has shown to lower the pH from alkaline to neutral. The higher AAEM content of the alkaline treatment did show higher pH but reduced the EC significantly. The NaOH treatment could have a fixed structure in which there are no proton exchanges. The high pH indicates hydroxides are present in solution. The hot water wash could have changed the physical structure of the biomass. XRF analysis did show that NaOH did not seem to alter the AAEM content in the biomass, it would be advantageous to analyze the crystallization of AAEM by X-ray diffraction.

There was no significant change in the proximate analysis of the parent bark or the subsequent biochar. Fuel ratio and energy densification indicate that the 1% H_2SO_4 treatment would be the most effective in combustion and has the highest T_i. The biochar that had the lowest fuel properties was the control followed by the NaOH treatment, suggesting this treatment would not improve combustion efficiency. Furthermore, the NaOH treatment significantly lowered the T_i indicating that it is not stable but does have strong resistance to biodegradation.

Native bark showed that it is functional as a soil amendment. Treatments did improve some of the properties, such as the increase in surface area and change of EC values. Once again, the 1% H_2SO_4 treatment had the most robust of changes. The improvement of physiochemical properties by the higher acid treatment indicates it can be beneficial to applications such as soil amendments, adsorbents, and as catalysts.

Conclusion

Chemical storage treatment on bark has shown to affect the key performance indicators of the biochar. Results of this study showed alkali treatment decreases the fuel properties and the surface area indicating that it would not be the best option in solid fuel or soil amendment applications. The NaOH treatment also increased the ash content that can lead to slagging, corrosion, and emission problems if used as a solid fuel. The 1% H_2SO_4 treatment had the highest improvements in both the fuel properties and surface area, indicating it would be beneficial in both fuel and soil amendment applications.

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Chapter 4: Effect of Chemical Drying by Dimethyl Ether (DME) on Pyrolysis Yields

Abstract

Drying biomass is one of the biggest energy consumers in industry. Chemical drying has been explored to reduce energy consumption while being environmentally friendly. This study investigates the effect of dimethyl ether (DME) chemical drying on pyrolysis yields of bark biomass. Dimethyl ether did not significantly change the composition of the initial bark material, thus not significantly changing the pyrolysis yields. DME slightly increased the char and oil yields, from 31.58 to 34.45 and 40.42 to 45.12, respectively. Subsequent products, char and oil, were analyzed. Char had no significant change from the initial material. The oil produced from DME treatment increased the carbon content from 69.26 to 97.14 wt% and decreasing oxygen content from 29.22 to 1.29 wt%. DME treatment may not show significant improvement in pyrolysis yields, but it does preserve the chemical composition of the biomass.

Introduction

The following introduction and experimentation on the dimethyl ether (DME) drying treatment and process method on biomass are described and executed by Dr. Hyeonseok Lee from the Idaho National Laboratory. The information is given for background, as the intent of this study was to investigate if the DME drying would affect pyrolysis yields. The biomass was provided, and study was conducted alongside the bark from Chapters 2 and 3.

The drying process in manufacturing is one of the biggest energy consumer [1]. Alternatives for drying are being considered to minimize the energy consumption by using solvent based drying. A recent methodology uses a dehydration technique using liquefied dimethyl ether (DME) as a green drying solvent operation. This technique is economically efficient and environmentally friendly by virtue of the unique physical and chemical properties of DME [2, 3].

The DME soluble compound in the DME-based drying step can remove and isolate the water, decontaminate, and have extractive applications in biomass. Experimental data and published literature demonstrate that the water extraction efficiency shows above 80% of initial moisture is removed depending on the biomass [4]. The process uses a compressible gas as a cleaning solvent, operating at elevated pressure to keep DME in a liquid state solvent, which improves mass-transfer kinetics [5]. Reduced surface tension and viscosity of the solvent facilitate the transfer into the sample [6].

Methods and Procedures

Material

Forest residue was sized reduced using forest concepts rotary sheer crumbler (Forest Concepts M24M Modular Tower Crumbler) and fractioned using an air classifier (Spudnik 992 Airsep Eliminator) into three fractions: whitewood, needles, and bark. The bark fraction includes some traces of whitewood and needles. (Fig. 4.1). This air separated bark fraction will be referred to as bark mixture this article.

Figure 4.1. Air classified bark fraction.

Dimethyl Ether Drying Methodology

The DME process schematic is depicted in Fig. 4.2. A condensable solvent system has been developed based on a hydrocarbon extraction platform for use with DME as the working solvent. To prevent seal and gasket failures, the system was modified in accordance with ASTM specification D7901 provides limited guidance on the safety and handling of DME. The DME withing this system operates in a closed loop, with liquified DME solvent returned to the operating tank after extraction and decontamination. The solvent transfers through the chilled injection coil to the extraction vessel, where the solvent diffuses into the sample material. Liquified DME, water, and extracted contaminants is then transferred to the collection vessel and expansion vessel, where heat is supplied to drive the vaporization of solvent, permitting separation and recovery of DME from contaminants. Vaporized solvent is returned to the solvent tank through a recovery pump and discharge coil. This decontamination process operates under 85 psi, and temperature range between minimum of -4°C (at injection coil) and maximum of 35°C (at expansion vessel).

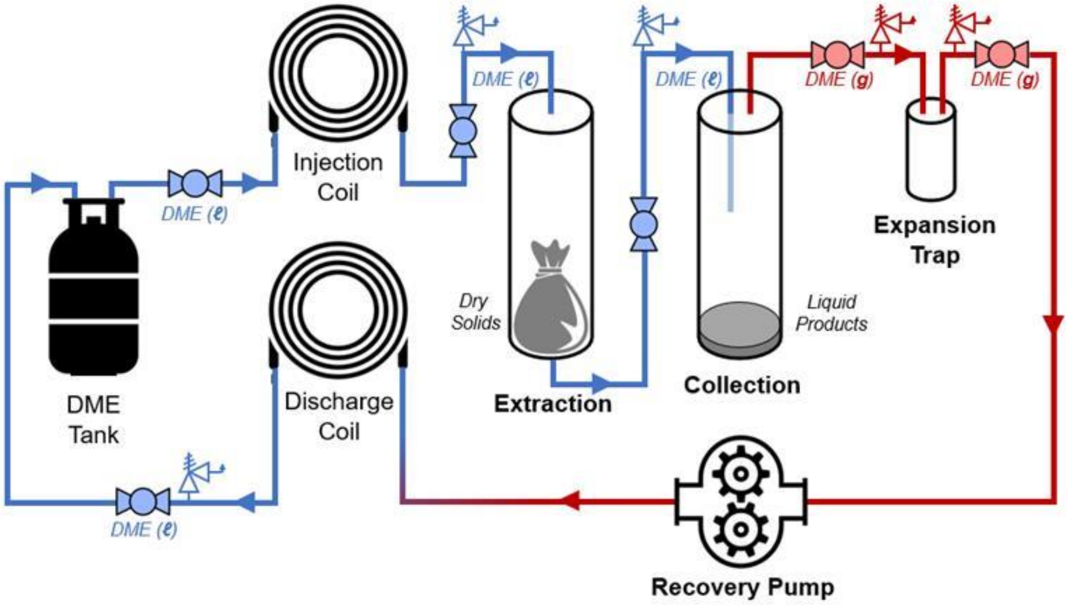

Figure 4.2 Schematic representation of DME drying process.

Analysis of biomass, biochar, and bio-oil

All analytical methods as described in Chapters 2 and 3 are repeated on the bark mixture biomass.

The elemental biomass composition content was determined in triplicate using an elemental analyzer (Vario EL cube, Elementar), to find the weight percent of carbon (C), hydrogen (H), nitrogen (N), and sulfur (S) atoms. Oxygen (O) content was determined by the mass balance.

Proximate analysis determines the moisture, volatile matter, fixed carbon, and ash of samples. Proximate analysis of triplicate samples of the initial bark and each stored biomass was obtained by thermogravimetric analysis (TGA701, Leco) following standardized ASTM D7582 method (https://www.astm.org/Standards/D7582.htm). Biochar from pyrolysis was also analyzed in this method.

The composition and concentration of inorganic elements was determined by x-ray fluorescence spectroscopy (XRF). Dried initial and stored bark was pressed into 40 mm diameter pellets with a hydraulic press (Carver, Model 3853-OC) applying 20 tons of force for 10 seconds and then released over a 20 second interval. Each side of the pellet was analyzed by Epsilon 4 (Malvern Panalytical).

Higher heating value (HHV) was calculated from elemental composition according to Eq. 4.1 [7],

$$HHV = 0.338C + 1.428\left(H - \frac{O}{8}\right) + 0.095S \tag{4.1}$$

Where C, H, O, and S are carbon, hydrogen, oxygen, and sulfur wt% respectively. Bark, biochar, and bio-oil were all subject to this equation.

Biomass was pressed into 1.0±0.1g pellets in a custom die (16mm square with 4mm rounded corners) using a hydraulic press (Carver, Model 3853-OC) to 20000 lb-f (4000 psi) pressure for 30 seconds. Each pyrolysis trial used three sample pellets for roughly 3g total sample mass. Pyrolysis of biomass samples and specifics about the pyrolysis unit and its operating conditions can be found as described by Klinger et al [8]. A brief overview is provided. Samples were placed in a clean quartz tube sealed at both ends with nitrogen entering the distal portion of the tube. To initiate pyrolysis the quartz tube was inserted into a furnace (500°C) that was then subjected to microwave energy generated from a microwave generator (3 kW, 58.7 dB, 2.426–2.476 GHz frequency, SM1250D, MKS Instruments) positioned above the furnace and focused on the sample using a waveguide (GA2006 2450 ± 30 MHz, Gerling Applied Engineering). The pyrolysis was carried out to 500°C with a heating rate of ~13°C/s.

Char was weighed after each reaction. Bio-oil was collected by running a plunger through the tube into tared clear airtight glass vials, weighed, and stored in a refrigerator. The empty tube was weighed again for residual oil to complete the mass balance of char, oil, and gas production. Each experimental replicate (n=3) was pyrolyzed in duplicate for total of 6 measurements per experimental condition (treatment and storage time).

Statistical Analysis

Single-factor one-way analysis of variance (ANOVA) was performed in JMP 14.2.0 (SAS, Cary, NC) to identify significant differences. Paired student t test was performed to determine if the ANOVA was significant at $p < 0.05$.

Results

The bark mixture was given (as is) by Idaho National Laboratory. This study was done as a side investigation if the DME drying had any effect on compositional changes and pyrolysis yields.

Compositional Analysis of Biochar

Proximate analysis results showed little difference between the DME treatment and the initial bark mixture (Table 4.1). Volatile content was 71.97%, ash was 2.46%, and 25.58% of the initial biomass, whereas 71.21%, 2.93%, and 25.86%, respectively, for the DME treatment. Ultimate analysis (Table 4.2) (CHNOS) also had little changes between the native and treated bark mixture. The H, C, N, O, and S content for both initial and DME treated was 5.5 wt%, 52 wt%, 0.5 wt%, 38 wt%, and 0.04 wt%, respectively. This suggests that the DME treatment is able to preserve the biomass qualities after drying.

Table 4.1 Proximate and ultimate analysis of the bark mixture and DME treated.

Treatment	**Volatile (% d.b.)**	**Ash (% d.b.)**	**Fixed Carbon (% d.b.)**
Initial Bark Mixture	71.97 ± 0.04	2.46 ± 0.03	25.58 ± 0.07
DME Treated	71.21 ± 0.85	2.93 ± 0.06	25.86 ± 0.80

Table 4.2. Ultimate analysis of bark mixture and associated atomic ratios (O/C, H/C, and C/N).

Treatment	**H (%)**	**C (%)**	**N (%)**	**O[a] (%)**	**S (%)**	**O/C**	**H/C**	**C/N**
Initial Bark Mixture	5.49 ± 0.02	52.51 ± 0.14	0.51 ± 0.02	38.99 ± 0.13	0.04 ± 0.00	0.56	0.63	120.84
DME Treated	5.38 ± 0.06	52.81 ± 0.08	0.58 ± 0.02	38.25 ± 0.05	0.06 ± 0.01	0.54	0.61	106.47

[a] Calculated from difference

The calorific value (HHV) of the native material to the DME treatment had no significant change (Fig. 4.3). Both the native biomass and the DME biomass had a HHV of 18 MJ/kg. The table also shows the biochars HHV (28 MJ/kg). The biochar has the higher calorific value over the biomass. This follows the same trend with the native bark and the 0.1% acid treatment in Chapter 1, where the ultimate analysis had little change.

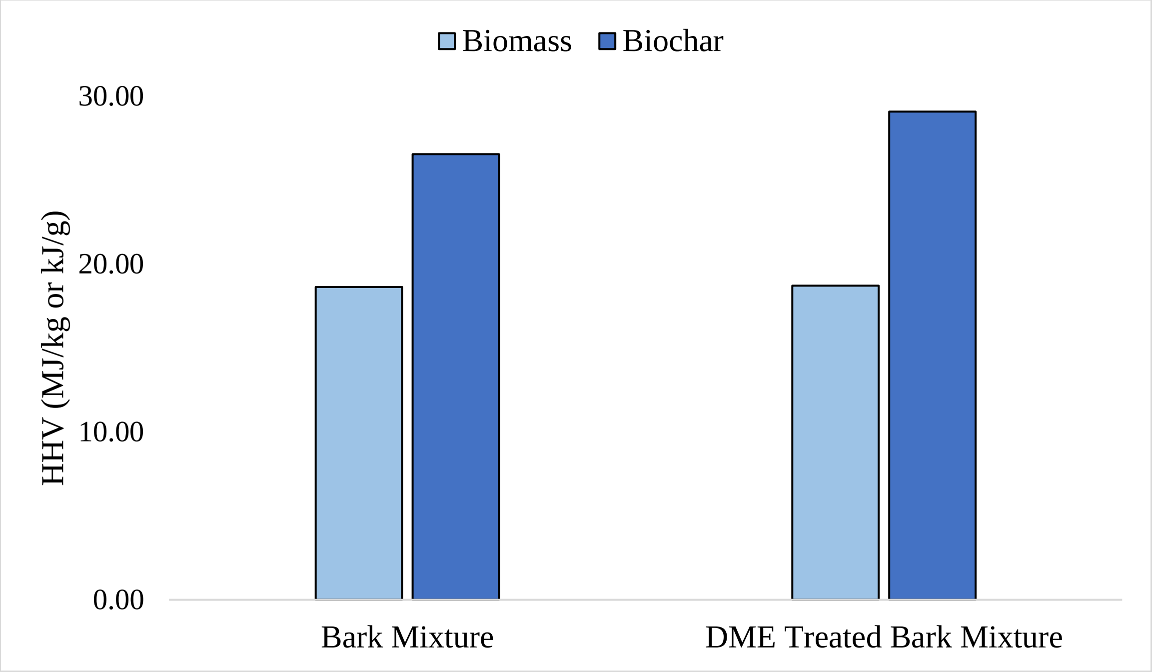

Figure 4.3 Estimated HHV of bark mixture biomass and produced biochar.

XRF analysis (Fig. 4.4) showed little change in Mg and K, but Ca and Si decreased in the DME treatment to 0.37 wt% from 0.45 wt%, and Si decreased to 0.75 wt% from 1.65 wt%. This could potentially increase oil yield, but not significantly.

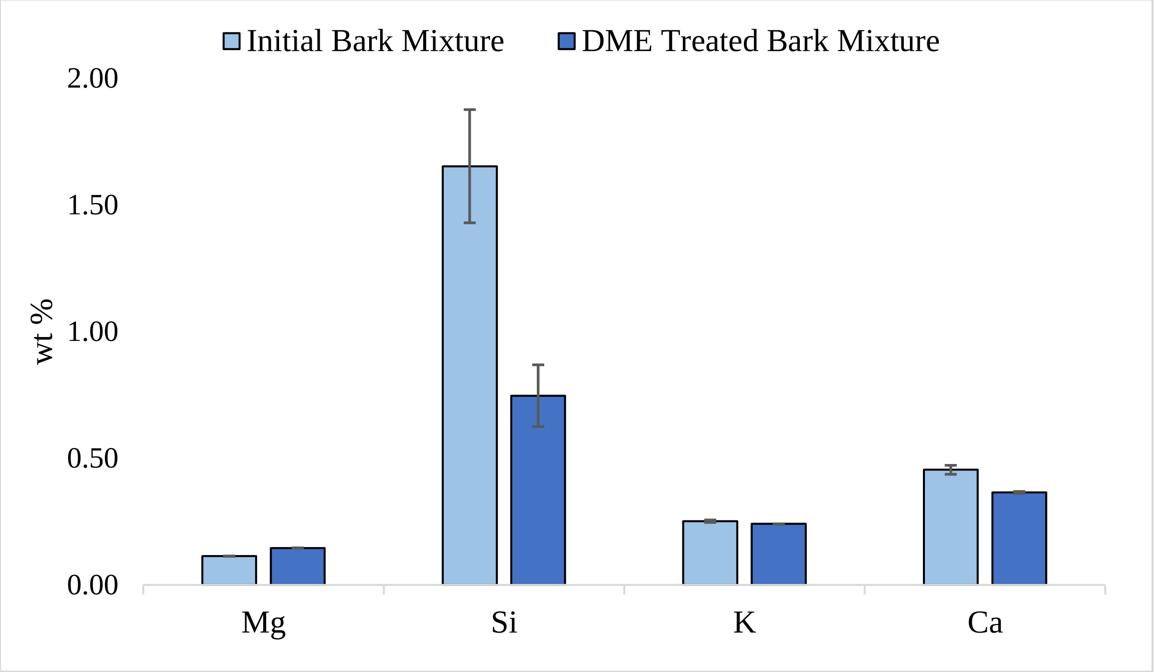

Figure 4.4. Initial and DME treated mixed bark XRF results.

Pyrolysis

Pyrolysis was carried out at 500°C. Char and oil yields (Fig. 4.5) from the bark mixture were 31.58 and 40.42% respectively. DME treatment had increased the char yield to 34.45% and the oil yield to 45.12%. This increase is not statistically significant (determined by ANOVA analysis, 0.05). This is expected since the chemical composition of the bark mixture did not change with the DME treatment.

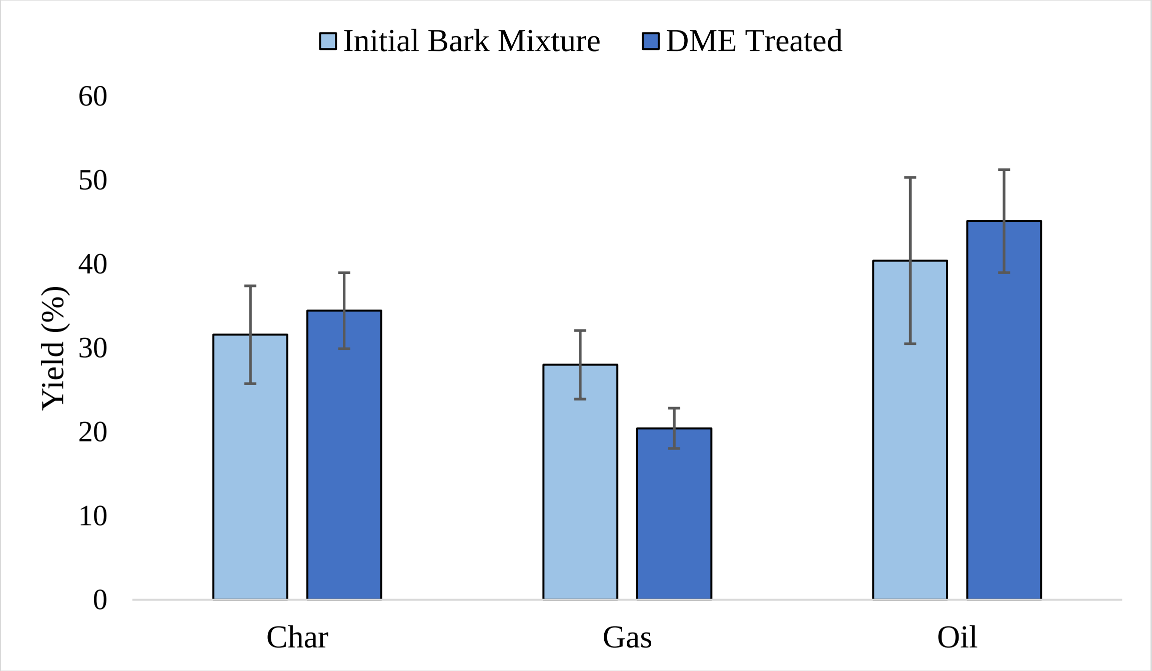

Figure 4.5. Bark mixture yields via pyrolysis at 500°C.

Biochar

Biochar ultimate analysis followed the similar patterns where if the characteristics of the biomass are similar in treatments, then the biochar will have same characteristics (Table 4.4). Volatile content was about 30% in both the native and DME. There was a slight decrease in the fixed carbon of the DME treatment, 64.43 to 62.48 wt%. The CHNOS results had no significant change.

Table 4.3 Proximate and ultimate of initial bark mixture and DME treated bark mixture derived biochars.

Treatment	**Volatile (% d.b.)**	**Ash (% d.b.)**	**Fixed Carbon (% d.b.)**	**H (%)**	**C (%)**	**N (%)**	**O (%)**	**S (%)**
Initial Bark Mixture	29.56 ± 1.61	6.01 ± 0.27	64.43 ± 1.88	2.49 ± 0.70	79.57 ± 4.03	0.77 ± 0.06	11.13 ± 3.44	0.03 ± 0.00
DME Treated	30.85 ± 0.96	6.68 ± 0.32	62.48 ± 0.64	2.73 ± 0.65	78.28 ± 2.54	0.77 ± 0.04	11.51 ± 1.97	0.03 ± 0.00

Since both proximate and ultimate results were not significantly different, the fuel ratio, energy densification, and energy yield will not have significant differences as well. In Table 4.5, the DME treatment show that the fuel ratio did have a slight decrease from 2.18 to 2.03 and the energy yield increased from 48.24% to 54.13% thus an increase in carbon yield from 47.85 to 51.05. The energy densification was the about equal to 1.5. The O/C and H/C ratios were about equal as well (0.10 and 0.2, respectively). The initial bark mixture was slightly higher in its C/N ratio (120.37) compared to the DME treatment (117.99). The H/C values were below 0.7, signifying the char can be used for carbon sequestration and a soil amendment.

Table 4.4 Physiochemical characteristics of initial bark mixture and DME treated bark mixture derived biochars.

Sample	Fuel Ratio	Energy Densification	Energy Yield (%)	Carbon Yield	O/C	H/C	C/N
Initial Bark Mixture	2.18	1.53	48.24	47.85	0.10	0.19	120.37
DME Treated	2.03	1.51	52.13	51.05	0.11	0.21	117.99

Thermogravimetric curve and the first derivative (Fig. 4.6) was used to calculate the recalcitrance ratio (R_{50}) and the ignition (T_i), peak (T_{max}), and burnout (T_b) temperatures shown in Table 4.6. As shown in the physiochemical properties, no significant differences were observed from the DME treatment. The R_{50} for both was 0.65, therefore it is a Class B biochar and is moderately susceptible to degradation. The maximum temperature was roughly 580°C for both. The ignition temperature was lower in the DME treatment at 155°C where the initial bark mixture was at 219°C. These ignition temperatures are lower than what is reported in literature [11-13].

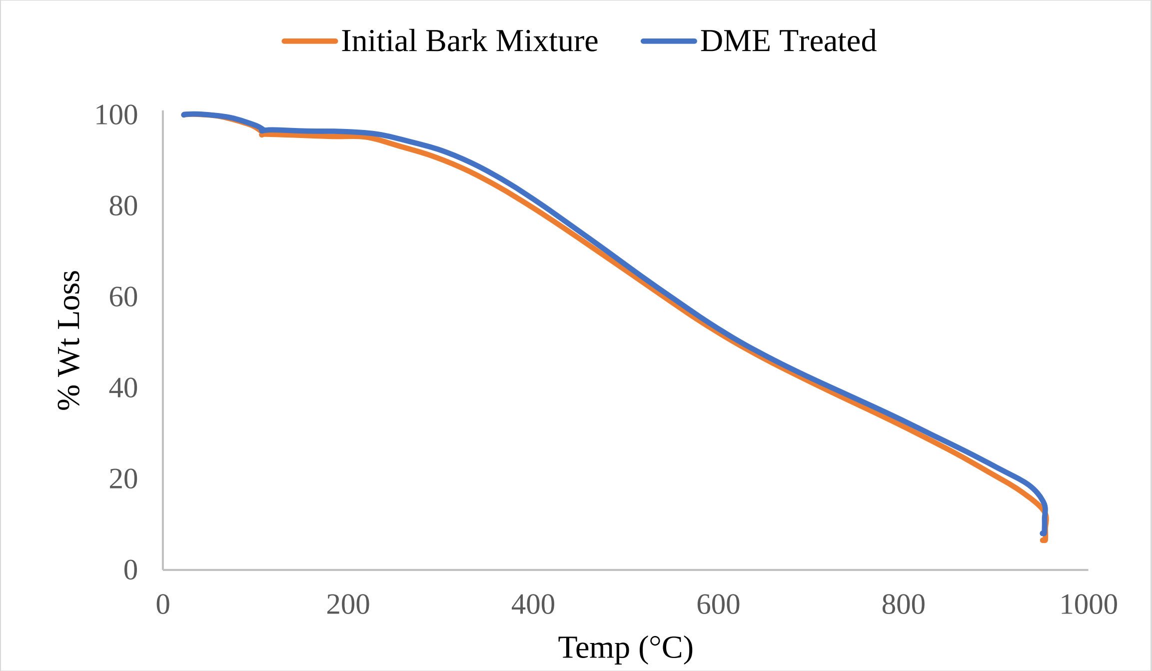

Figure 4.6. Thermogravimetric curves for initial bark mixture and DME treated bark mixture derived biochars.

Table 4.5. Combustion characteristics of initial bark mixture and DME derived biochars.

Sample	**T_{max} (°C)**	**R50**	**T_i (°C)**	**T_b (°C)**
Initial Bark Mixture	580.23 ± 43.97	0.65	219.56 ± 49.48	953.53 ± 0.08
DME Treated	571.92 ± 65.05	0.65	155.12 ± 22.81	952.47 ± 0.13

Conclusion

The bark fraction of forest residue was dried using a newly developed method using dimethyl ether (DME). This study investigated if the drying process changed the physiochemical properties of the bark fraction as well as if conversion via pyrolysis was improved. The results showed that the DME treatment had preserved the physiochemical properties of the bark, therefore not having any significant changes in pyrolysis conversion. This drying method could be explored further to determine if DME can both dry biomass cost-effectively and act as a biomass preservative.

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Chapter 5: Conclusion

Summary

The overarching goal of this research was to explore innovative approaches to transform storage to a value-add operation by taking advantage of the residence time to overcome the physiochemical properties in pine bark. Experiments in Chapter 2 were to determine if the use of low severity chemical anerobic storage can reduce alkali and alkaline earth metals (AAEM) and increase liquid yields via pyrolysis. Chapter 3 was solely focused on the biochar produced in Chapter 2 to determine if the subsequent biochar in Chapter 2 could be applicable to becoming a soil amendment or solid fuel. Chapter 4 was an additional experiment for investigating if a newly developed chemical drying process on biomass could have any physicochemical changes to increase pyrolysis yields and characterize the biochar.

Storage experiments showed the 1% H_2SO_4 treatment does decrease alkaline and alkali earth metals, showed an increase in oil yield (although not enough to deem statistically significant), and had significantly improved char qualities (i.e., the surface area, HHV, combustion characteristics). These traits indicate that an acid treatment may be the most effective way to utilize storage time of bark at a biorefinery to improve conversion yields and become a value added product. The alkali treatment seemed to negatively affect the bark in pyrolysis conversion as well as diminish wanted qualities in biochar. Sodium hydroxide does not support the goal of improving oil yields by removing AAEM, nor does it provide quality biochar for solid fuel or soil amendment applications. The investigation if the chemical dried bark by liquified dimethyl ether (DME) had improved pyrolysis yields showed no significant changes in any physiochemical properties from the feedstock bark.

Future

Supplementary analysis would be beneficial to further understand all avenues that acid treatments have on bark, and subsequent biochar and bio-oil. The acid treatment had the most improved qualities of reducing AAEM, showed increase in oil production, and had ideal qualities in the subsequent biochar to be applicable in soil amendments and solid fuels. Examining the extractives of the filtrate (i.e., sugars and tannins) after the hot water wash would be valuable, as sulfuric acid has been used previously for improving enzymatic hydrolysis of biomass. Sugars can be fermented for additional fuels, such as ethanol. A lower temperature wash (25-40°C) should also be evaluated because the hot water wash could have changed the structure of the biomass, possibly seen in the sodium hydroxide treatment. Since acid treatments did show improvement, additional storage experiments with an increased acid concentration could show further improvement but using alternative acids, such as acetic acid or nitric acid. Ideally, sulfur should be removed from biomass rather than added. Determining a maximum acid concentration at which oil production yield is significantly improved, or when it will become more destructive then constructive, could be investigated as well. The maximum concentration could then also be evaluated economically for cost of chemicals to the profitability of products.

Further analysis on the oil should also be investigated using a GC-MS, ICP, or other methods to evaluate compounds, such as catechol, guaiacol and phenols. But, due to an incident, the oils would have to be reproduced from new experiments. The cation exchange capacity of the biochar should also be conducted, as it is a standard measurement in soil analysis.

Appendix A – Storage

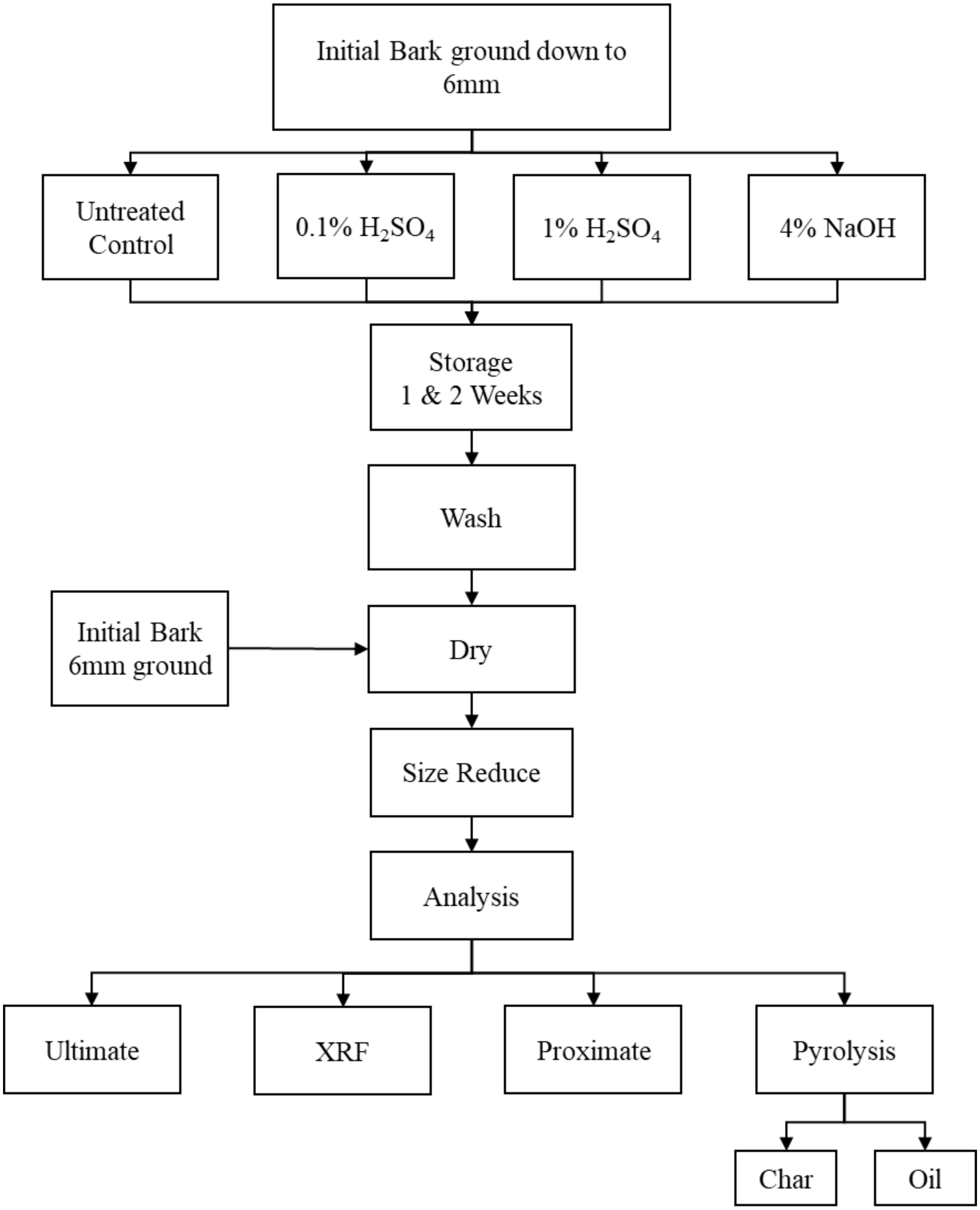


Figure A.1. Storage experiment process flow chart.

Figure A.2. Filtrate of week 1 bark storage treatments. From left to right: control, 0.1% H_2SO_4, and 4% NaOH.

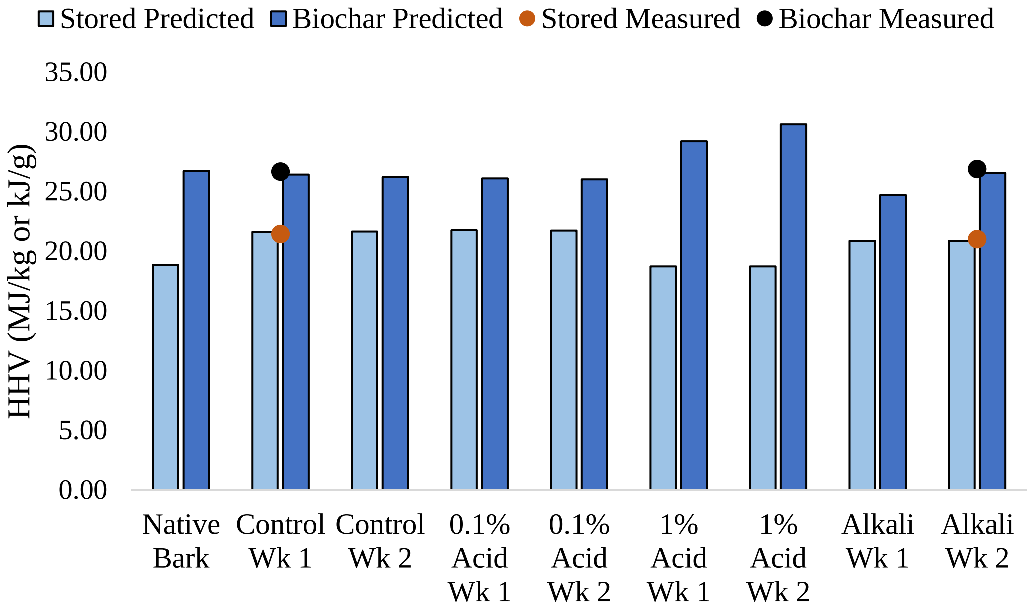


Figure A.3. Measured and estimated HHV of biomass and biochar.

No analysis was conducted on the bio-oil due to equipment failure. The oils were heated in an oven in which the samples were placed to >85°C. The caps popped off the untreated control week 1, 0.1% acid week 1, and 1% acid week 1 samples. The remaining samples still had their lids attached, but no longer had a tight seal, and there was a solid plug that formed on top of the liquid. A vortex mixer was able to break the seal to collect a new moisture content. The control week 1 had no liquid remaining.

Figure A.4 From left to right: native, control wk 1, control wk 2, 0.1% acid wk 1, 0.1% acid wk 2, 1% acid wk 1, 1% acid wk 2, alkali wk 1, and alkali wk 2. The top image is the oils just after combining and the bottom image is the oils after they were in the oven.

Appendix B – SEM Images of White Deposits on Biochar

SEM images of biochar after pyrolysis with white ash and black char analysis. Thanks to Timothy Yoder for doing the imaging.

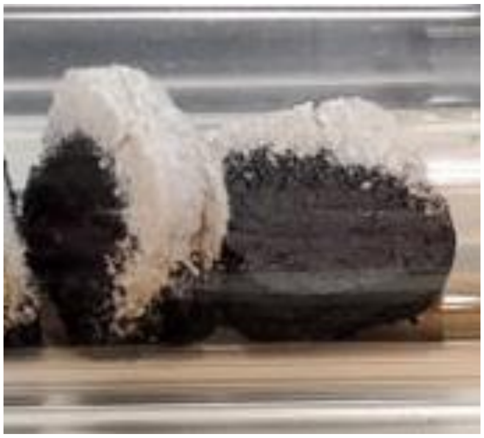


Figure B.5. Biochar with white residue after pyrolysis at 500°C

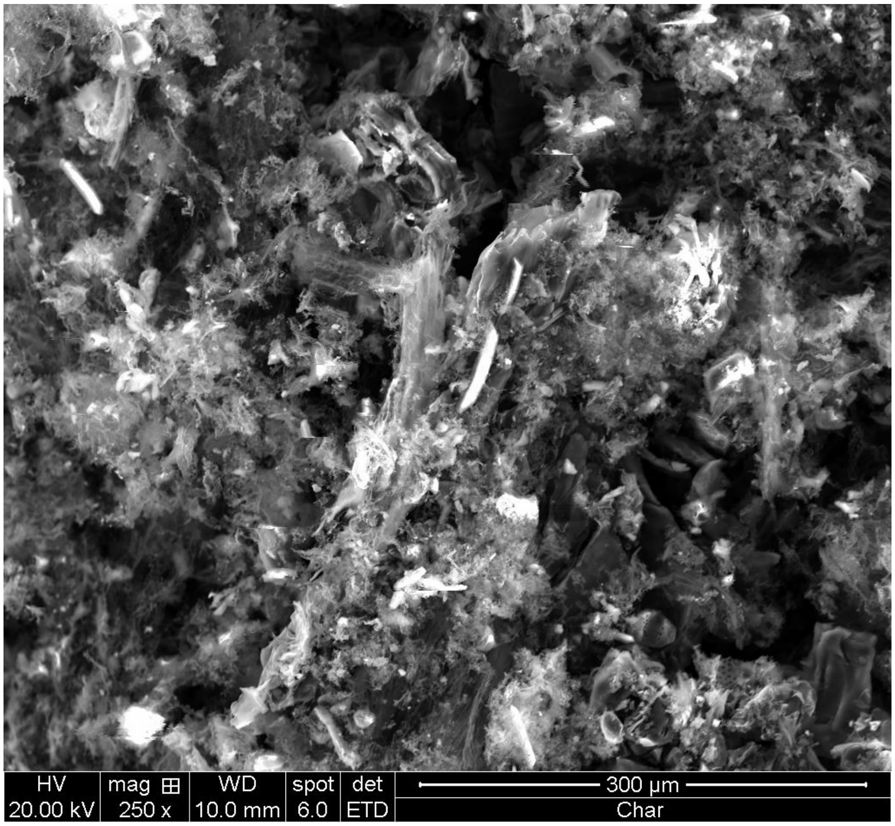


Figure B.6. The white areas have both distinct crystals that seem to be mostly Ca or Si, and then a “fuzzier” appearance with multiple elements identified.

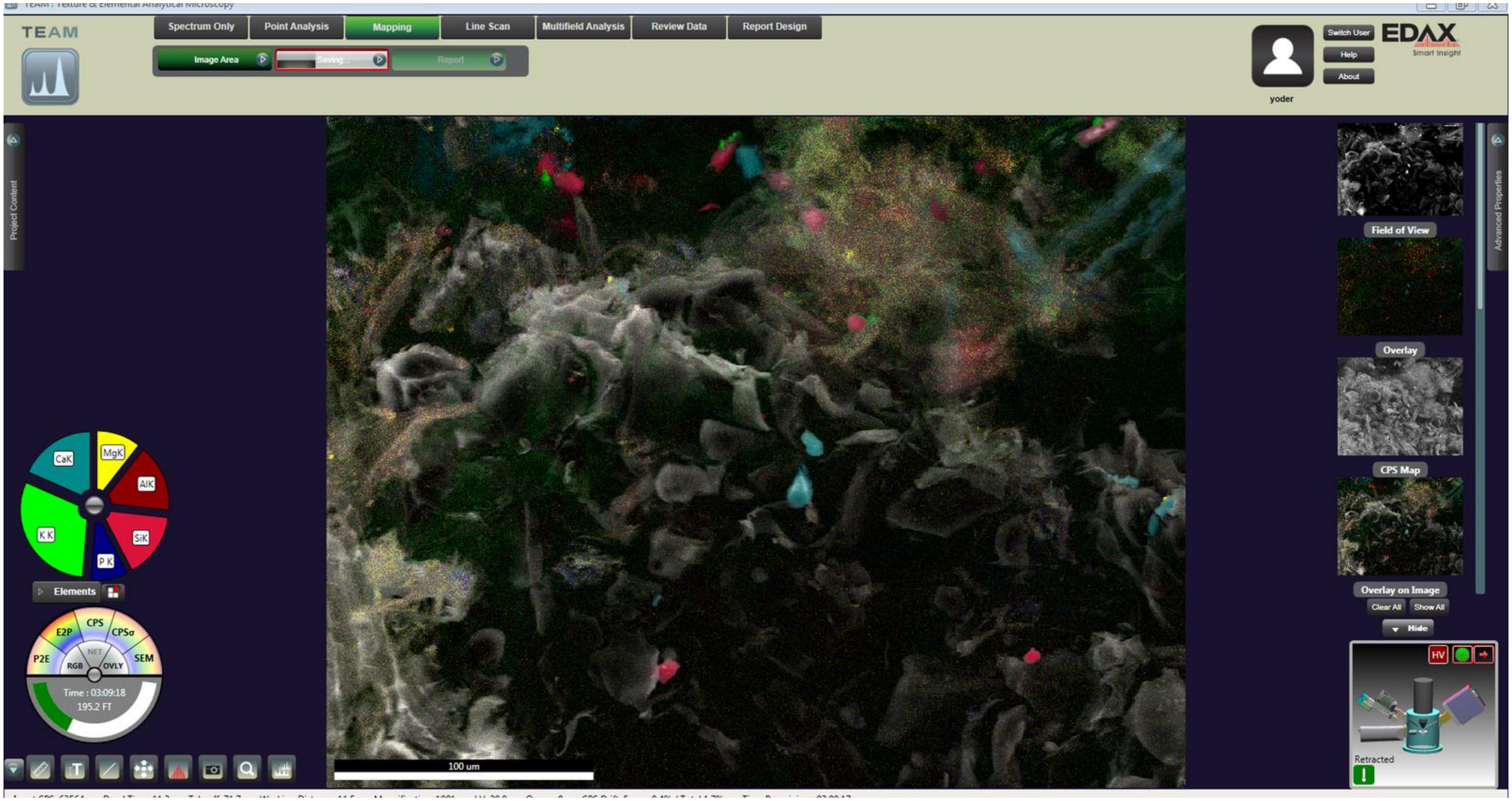


Figure B.7. SEM image of biochar with white residue present.

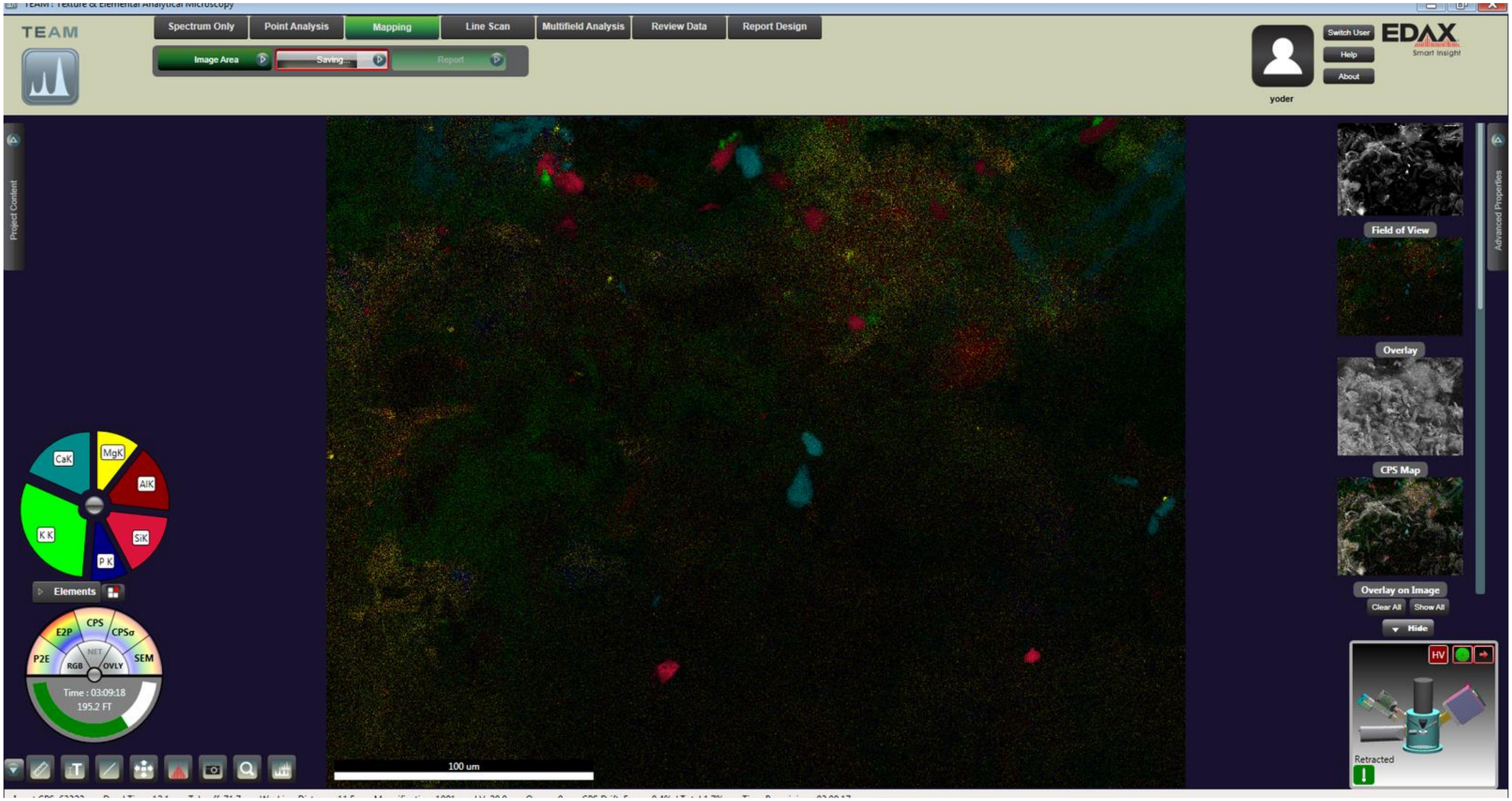


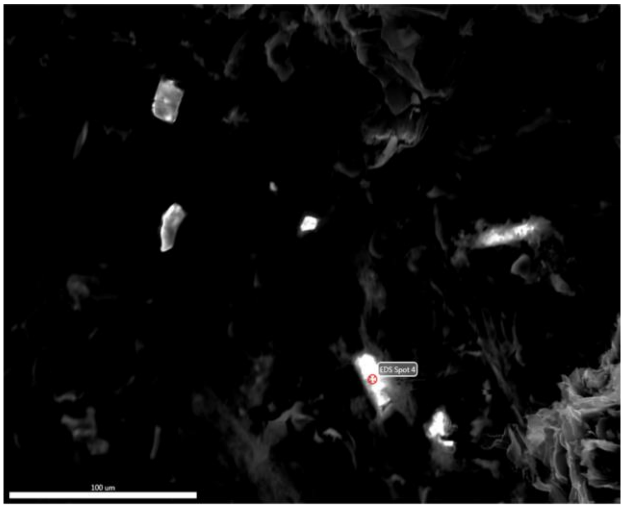
Figure B.8. SEM image of biochar with element colorization.

EDAX TEAM

Char

Author:	yoder
Creation:	11/18/2021 8:39:36 AM
Sample Name:	Char-1

Area 4

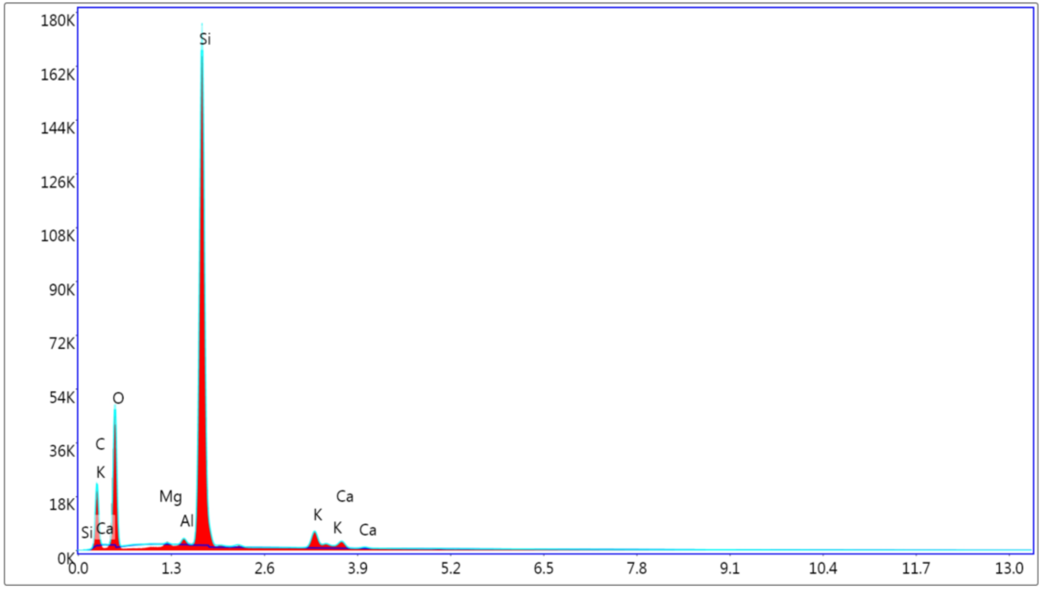


eZAF Smart Quant Results

Element	Weight %	Atomic %	Net Int.
C K	25.24	38.77	3137.15
O K	26.26	30.28	9780.35
MgK	0.14	0.11	141.24
AlK	0.5	0.34	549.46
SiK	42.9	28.18	49583.25
K K	3.31	1.56	2060.39
CaK	1.65	0.76	888.19

EDS Spot 4

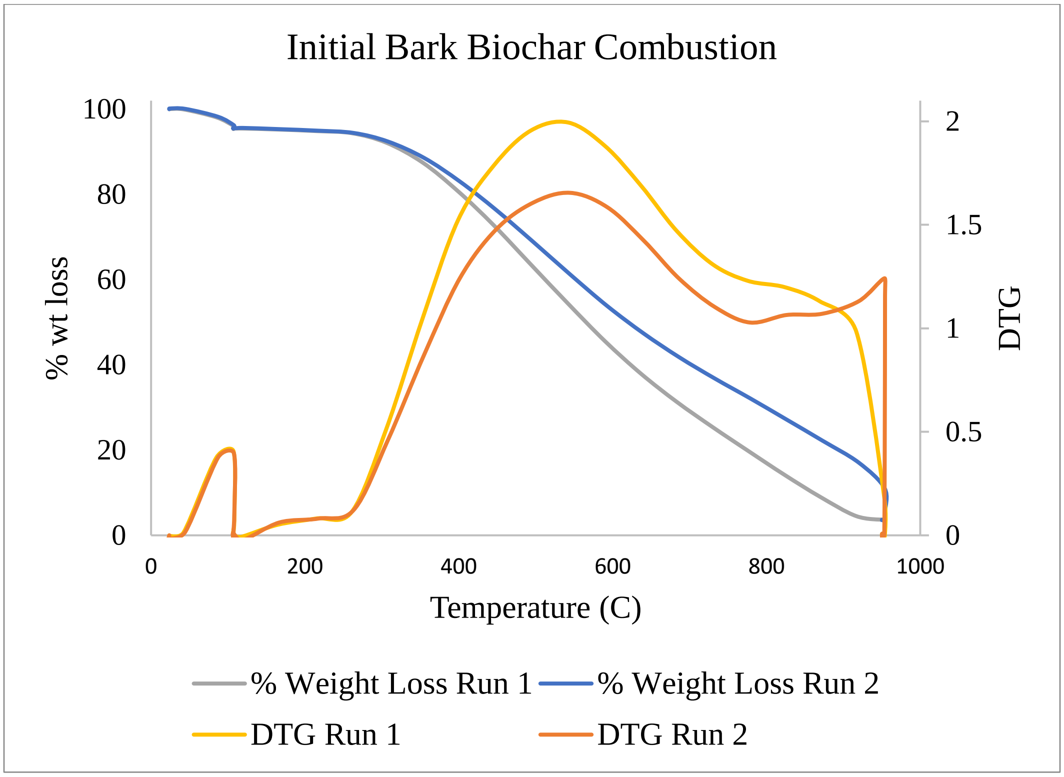
kV:	Mag:	Takeoff:	Live Time(s):	Amp	Resolution:(eV)
20	1001	70.7	30	0.96	129.3

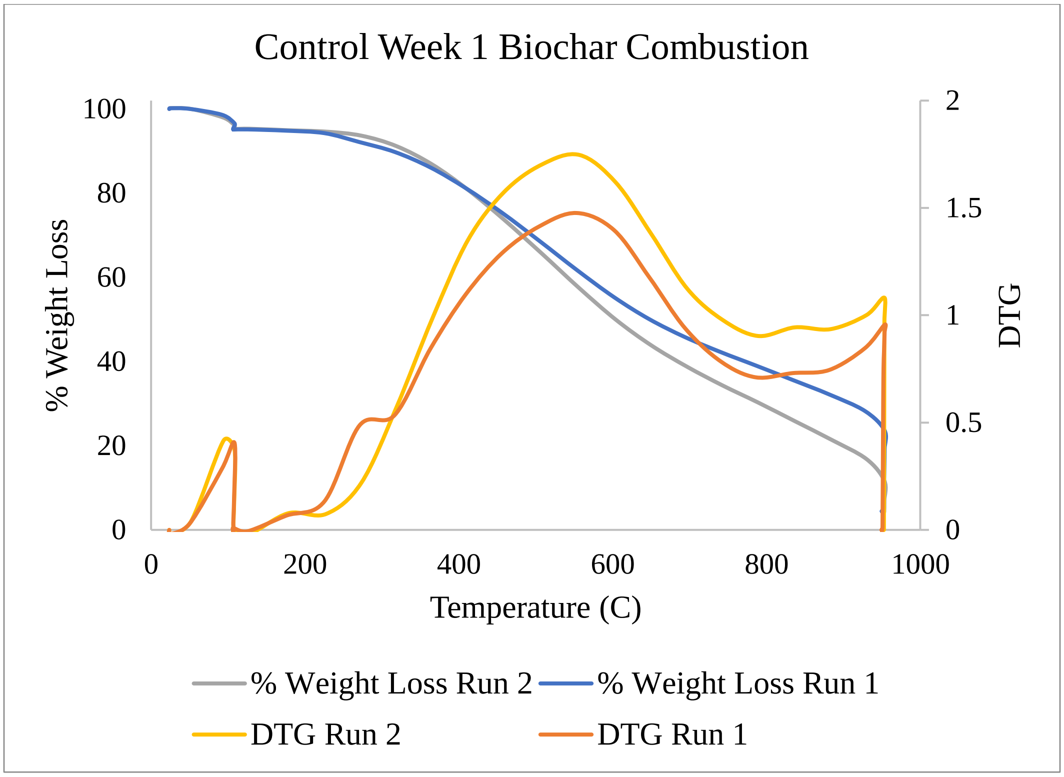


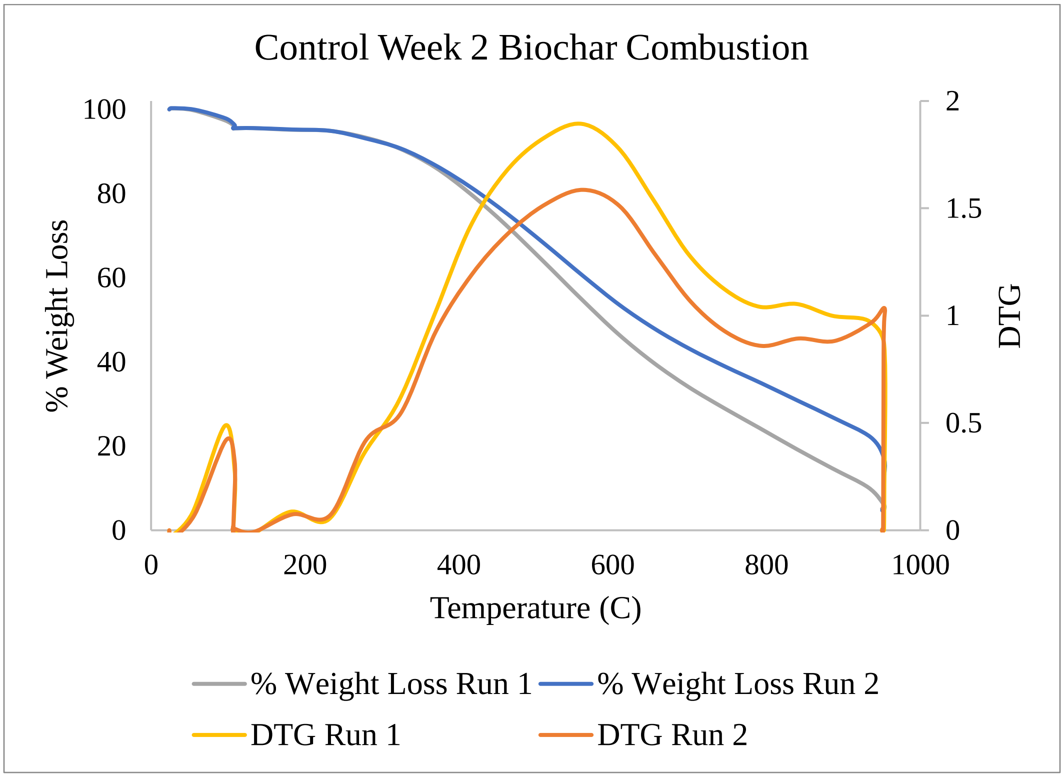
Lsec: 30.0 0 Cnts 0.000 keV Det: Octane Elect Plus

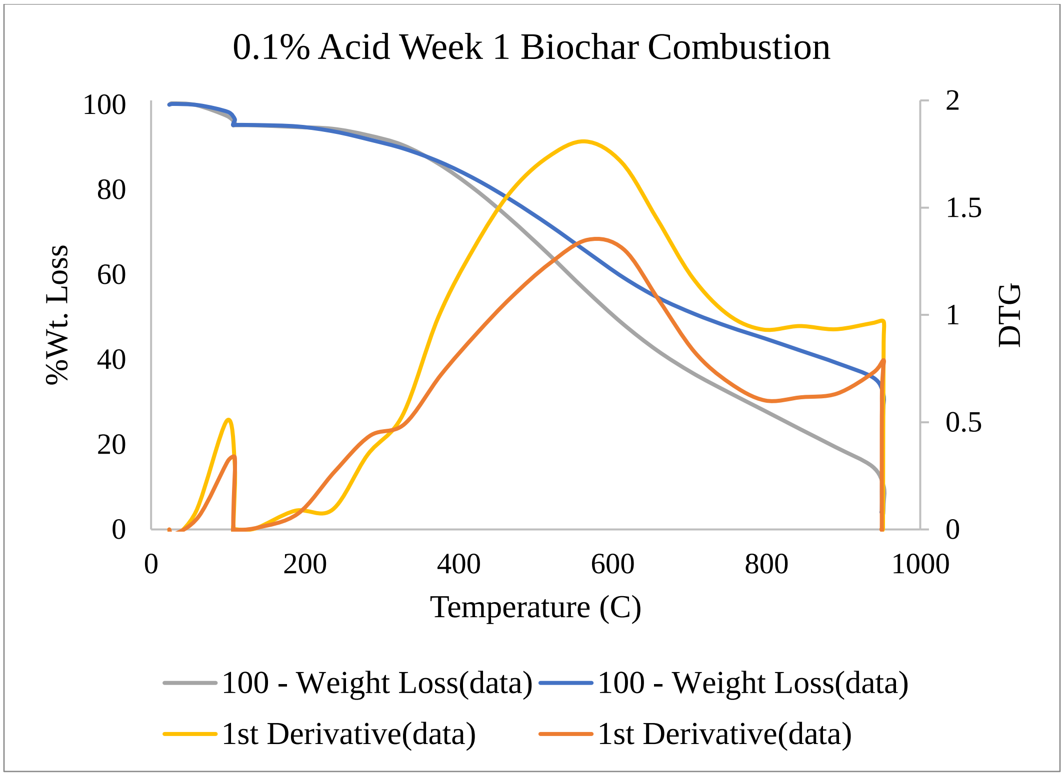
Appendix C – Combustion Characteristics of Biochar

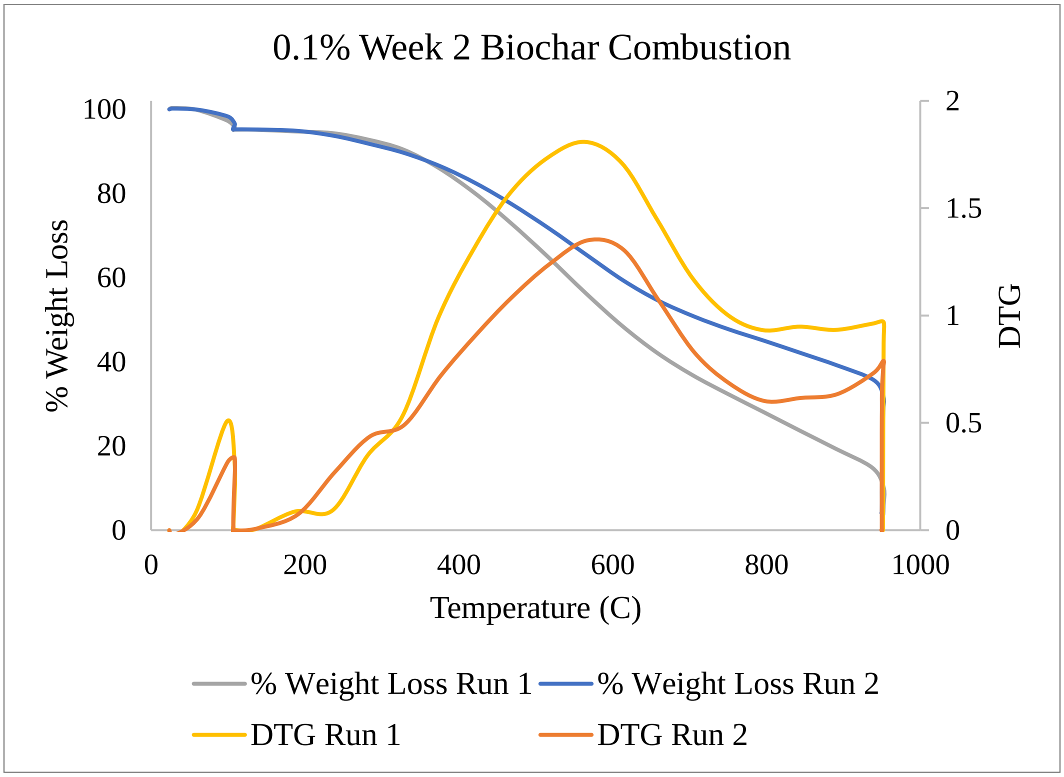
TGA graphs of biochar combustion. 1st run is the blue and orange lines, the 2nd run is the grey and yellow lines. The blue and grey lines indicate the % wt loss, and the orange and yellow lines indicate the first derivative.

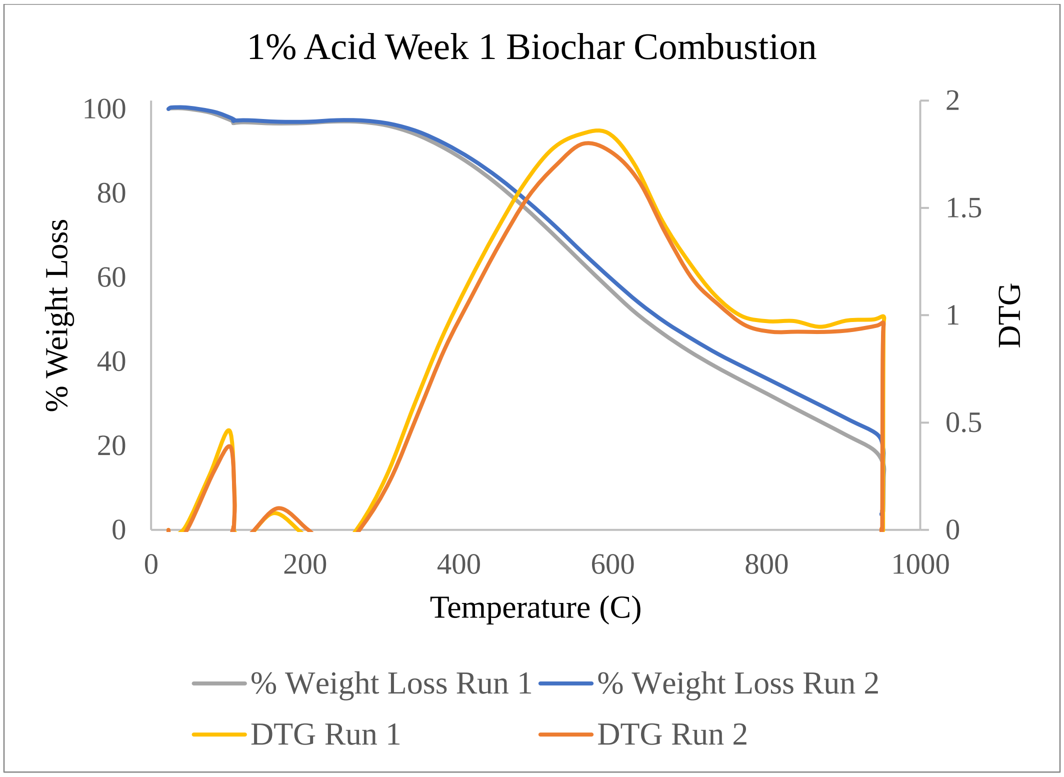


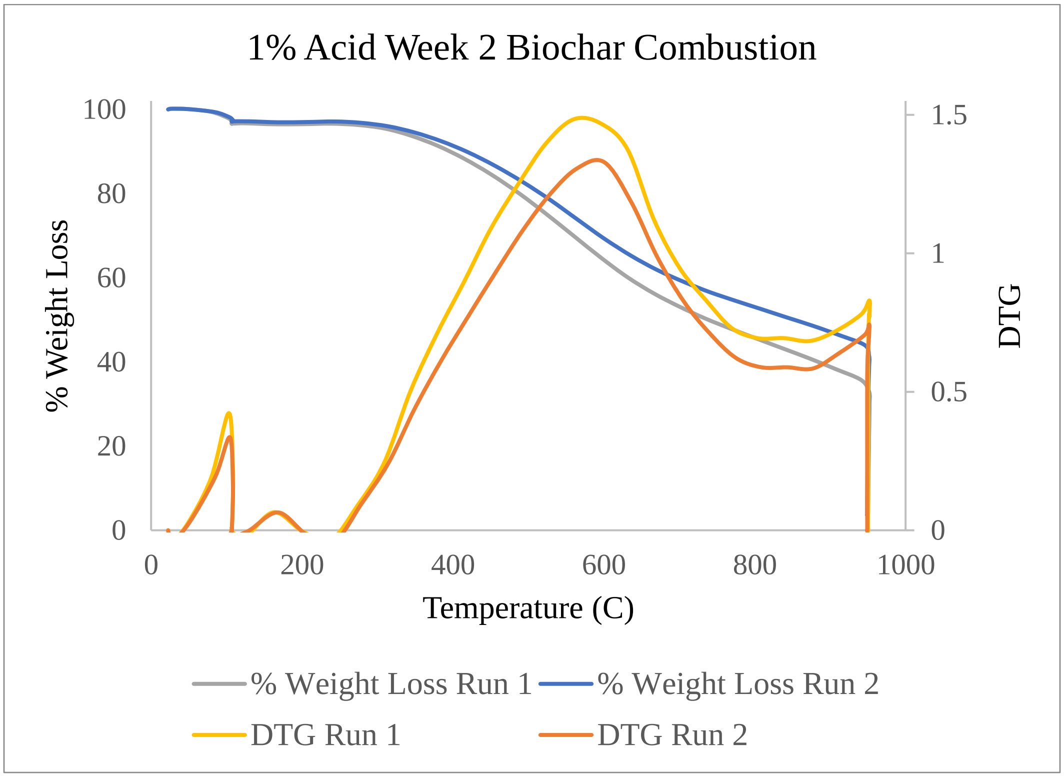

Control Week 1 Biochar Combustion
% Weight Loss
0
20
40
60
80
100
DTG
0
0.5
1
1.5
2
0
200
400
600
800
1000
Temperature (C)
% Weight Loss Run 2
% Weight Loss Run 1
DTG Run 2
DTG Run 1

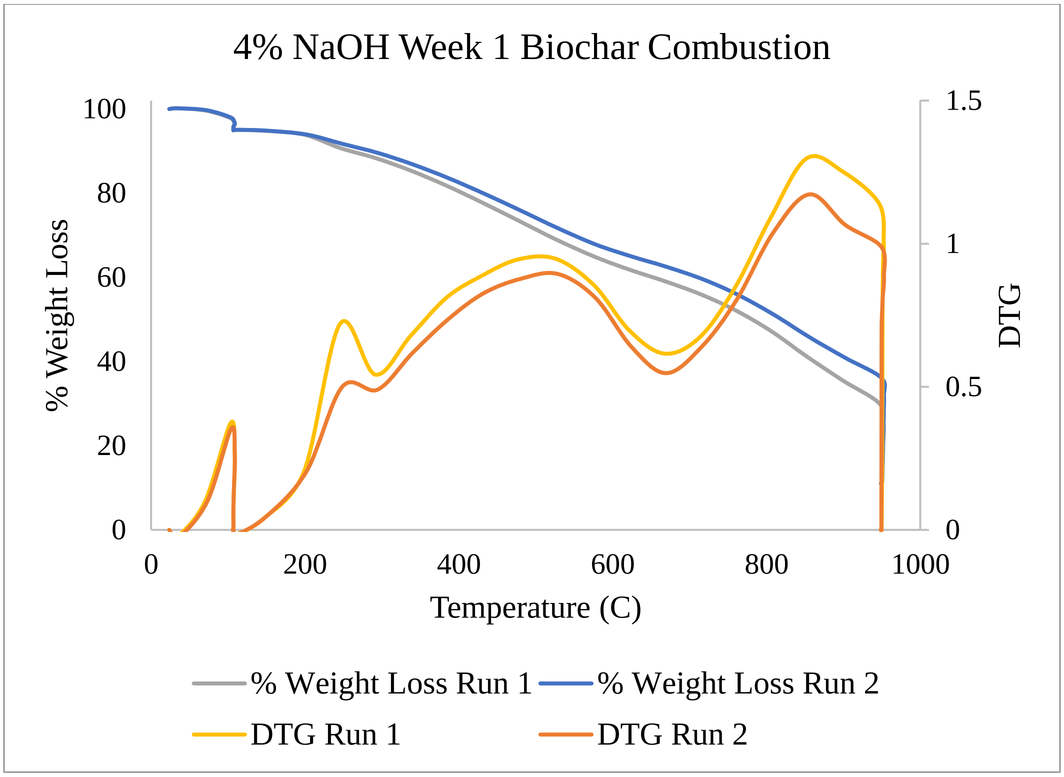

Control Week 2 Biochar Combustion
% Weight Loss
0
20
40
60
80
100
DTG
0
0.5
1
1.5
2
0
200
400
600
800
1000
Temperature (C)
% Weight Loss Run 1
% Weight Loss Run 2
DTG Run 1
DTG Run 2

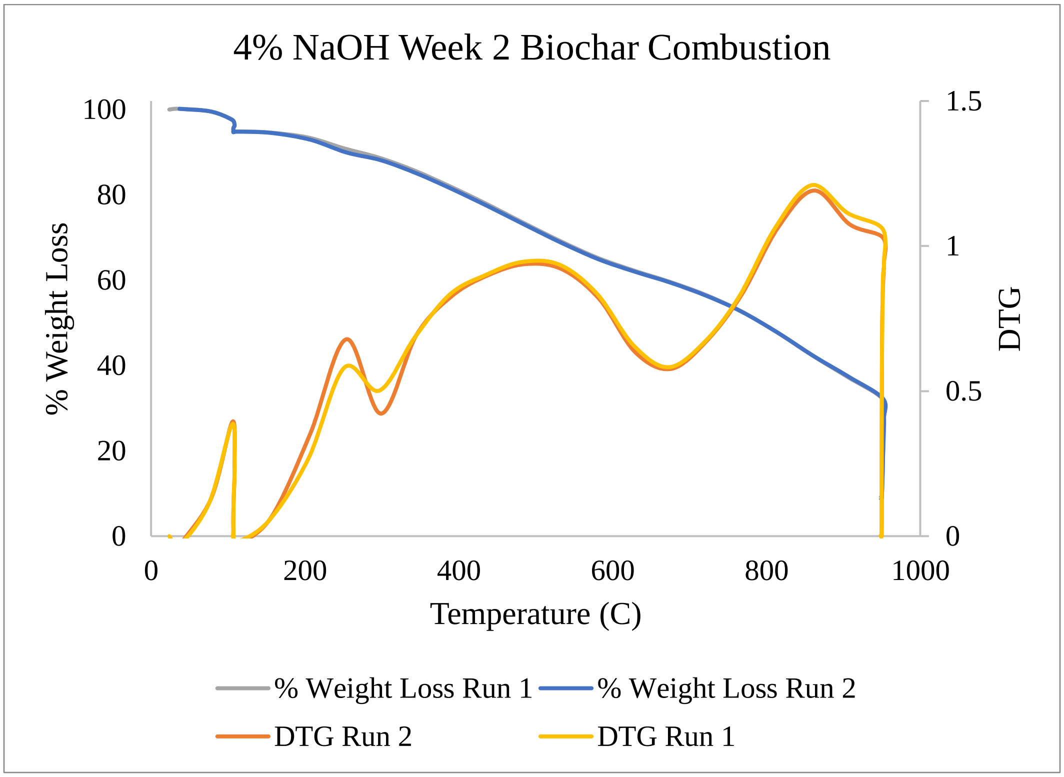

0.1% Acid Week 1 Biochar Combustion
%Wt. Loss
100
80
60
40
20
0
0
200
400
600
800
1000
Temperature (C)
2
1.5
1
0.5
0
DTG
100 - Weight Loss(data)
100 - Weight Loss(data)
1st Derivative(data)
1st Derivative(data)


0.1% Week 2 Biochar Combustion
% Weight Loss
100
80
60
40
20
0
0
200
400
600
800
1000
Temperature (C)
2
1.5
1
0.5
0
DTG
% Weight Loss Run 1
% Weight Loss Run 2
DTG Run 1
DTG Run 2


1% Acid Week 1 Biochar Combustion
% Weight Loss
100
80
60
40
20
0
DTG
2
1.5
1
0.5
0
0
200
400
600
800
1000
Temperature (C)
% Weight Loss Run 1
% Weight Loss Run 2
DTG Run 1
DTG Run 2


1% Acid Week 2 Biochar Combustion
% Weight Loss
100
80
60
40
20
0
DTG
1.5
1
0.5
0
0
200
400
600
800
1000
Temperature (C)
% Weight Loss Run 1
% Weight Loss Run 2
DTG Run 1
DTG Run 2


4% NaOH Week 1 Biochar Combustion
% Weight Loss
100
80
60
40
20
0
DTG
1.5
1
0.5
0
0
200
400
600
800
1000
Temperature (C)
% Weight Loss Run 1
% Weight Loss Run 2
DTG Run 1
DTG Run 2


4% NaOH Week 2 Biochar Combustion
% Weight Loss
100
80
60
40
20
0
DTG
1.5
1
0.5
0
0
200
400
600
800
1000
Temperature (C)
% Weight Loss Run 1
% Weight Loss Run 2
DTG Run 2
DTG Run 1

Appendix D –Bark Mixture with Storage Comparisons

An additional experiment using the bark mixture included 1.5-week storage at 40% moisture (w.b). Storage preparation followed as described in Ch. 2. The stored bark mixture also didn't significantly change the physiochemical properties of the biomass or biochar.

Table D.1. Bark mixture biomass proximate analysis.

Treatment	**Volatile**	**Ash**	**Fixed Carbon**
Initial Bark Mixture	71.97 ± 0.04	2.46 ± 0.03	25.58 ± 0.07
Stored Bark Mixture	73.07 ± 0.44	2.02 ± 0.04	24.92 ± 0.40
DME Treated	71.21 ± 0.85	2.93 ± 0.06	25.86 ± 0.80

Table D.2. Bark mixture biomass ultimate analysis and atomic ratios (O/C, H/C, C/N)

Treatment	**H**	**C**	N	**O**	**S**	**O/C**	**H/C**	**C/N**
Initial Bark Mixture	5.49 ± 0.02	52.51 ± 0.14	0.51 ± 0.02	38.99 ± 0.13	0.04 ± 0.00	0.56	0.63	120.84
Stored Bark Mixture	5.60 ± 0.10	52.49 ± 0.50	0.52 ± 0.02	39.33 ± 0.40	0.04 ± 0.01	0.56	0.64	116.88
DME Treated	5.38 ± 0.06	52.81 ± 0.08	0.58 ± 0.02	38.25 ± 0.05	0.06 ± 0.01	0.54	0.61	106.47

Table D.3. Bark mixture biochar ultimate analysis and atomic ratios (O/C, H/C, C/N)

Treatment	**H**	**C**	**N**	**O**	**S**	**O/C**	**H/C**	**C/N**
Initial Bark Mixture	2.49 ± 0.70	79.57 ± 4.03	0.77 ± 0.06	11.13 ± 3.44	0.03 ± 0.00	0.10	0.19	120.37
Stored Bark Mixture	2.37 ± 0.39	81.20 ± 1.54	0.75 ± 0.04	9.74 ± 1.27	0.02 ± 0.00	0.09	0.18	126.97
DME Treated	2.73 ± 0.65	78.28 ± 2.54	0.77 ± 0.04	11.51 ± 1.97	0.03 ± 0.00	0.11	0.21	117.99

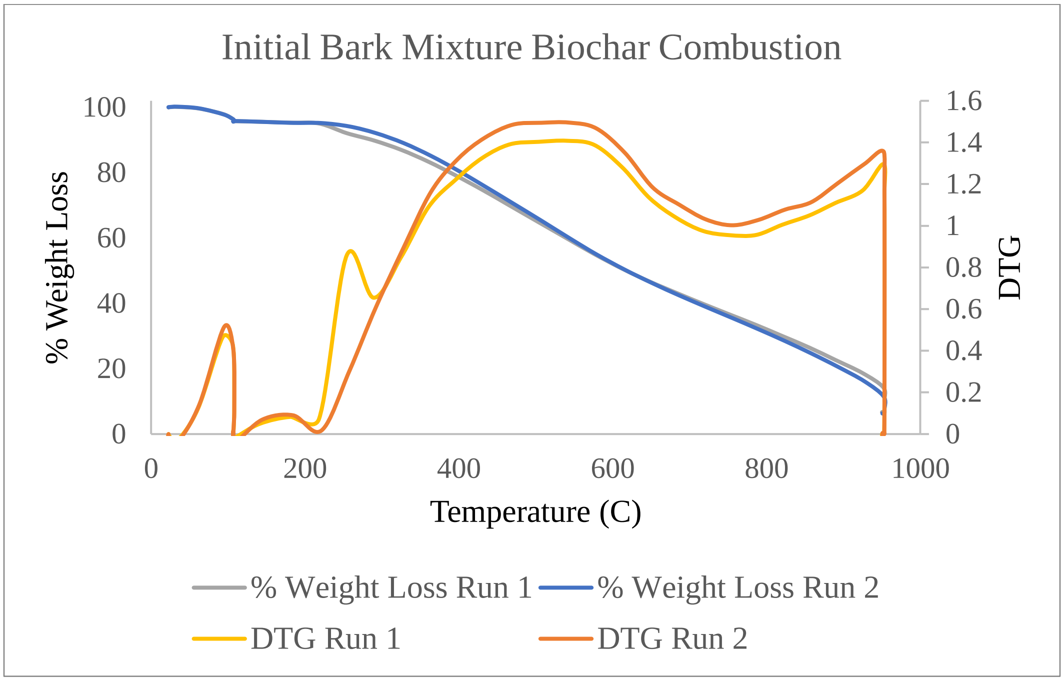
Table D.4. Biochar of bark mixture proximate analysis

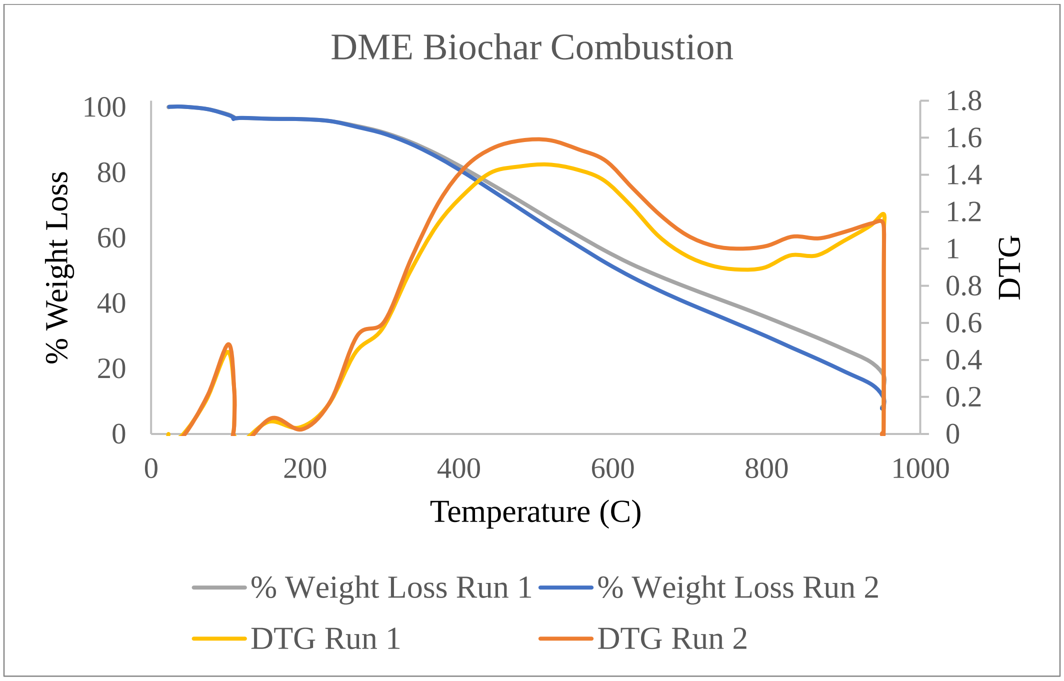
Treatment	**Volatile**	**Ash**	**Fixed C**
Initial Bark Mixture	29.56 ± 1.61	6.01 ± 0.27	64.43 ± 1.88
Stored Bark Mixture	27.59 ± 0.69	5.92 ± 0.31	66.50 ± 1.00
DME Treated	30.85 ± 0.96	6.68 ± 0.32	62.48 ± 0.64

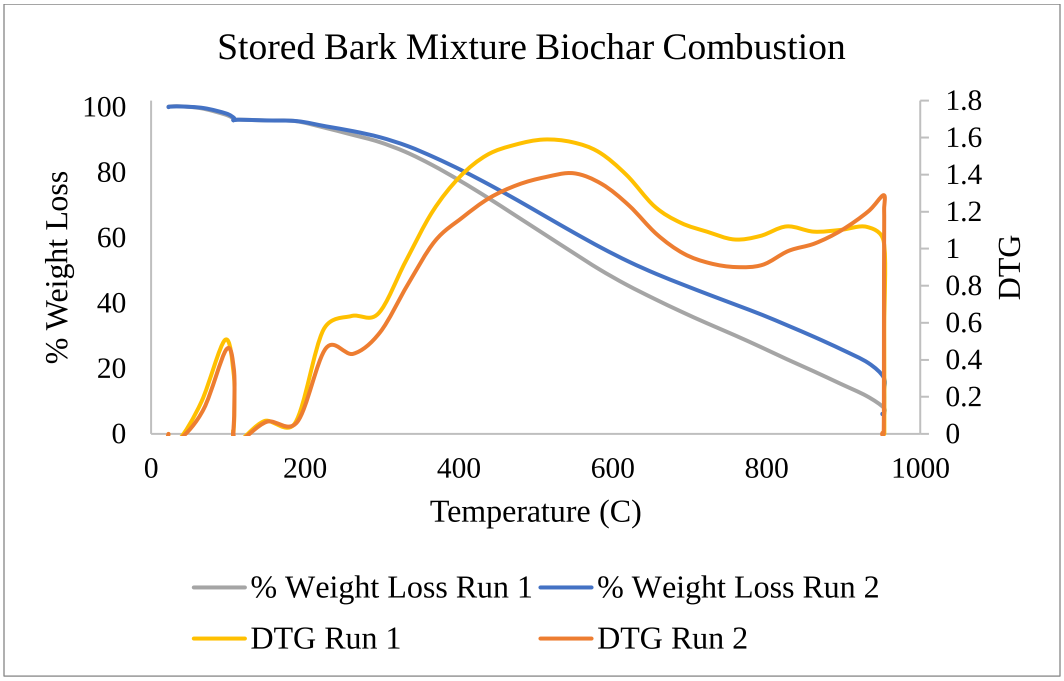
Table D.5. Biochar physiochemical characteristics of bark mixture initial, stored, and DME treated.

Treatment	**Carbon Yield**	**Fuel Ratio**	**Energy Densification**	**Energy Yield**
Initial Bark Mixture	47.85	2.18	1.53	48.24
Stored Bark Mixture	52.18	2.41	1.55	52.42
DME Treated	51.05	2.03	1.51	52.13

Combustion Characteristics






Stored Bark Mixture Biochar Combustion
% Weight Loss
100
80
60
40
20
0
DTG
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
200
400
600
800
1000
Temperature (C)
% Weight Loss Run 1
% Weight Loss Run 2
DTG Run 1
DTG Run 2