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Impact of post-pyrolysis wash on biochar powders and their respective granule formations

Anthony Fazzalari, *The Universiy of Western Ontario*

Supervisor: Briens, Cedric L., *The University of Western Ontario*
Co-Supervisor: Briens, Lauren A., *The University of Western Ontario*
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Abstract

Biochar can be an effective soil amendment, but concerns are soil contamination and dust emissions. This thesis developed various post-pyrolysis washing solutions to alleviate these concerns. Washing can reduce biochar hydrophobicity, improve its stability and adsorption properties and remove organic, inorganic, and PAH contaminants. The most effective wash was used to facilitate biochar granulation. Biochars from two different feedstocks were tested in a drum granulator with molasses binder. Washing biochar significantly increased the yield of optimally sized granules. Granules from washed biochar were dense, robust and free-flowing. The research showed how washing improved various biochar powders in terms of their chemical characteristics and, through granulation testing, their physical characteristics.

Keywords

biochar, soil amendment, hydrophobicity, post-pyrolysis, washing, wet drum granulation, molasses

Summary for Lay Audience

Biochar is known as the solid product produced by the pyrolysis of biomass. A pyrolysis reaction is a thermal decomposition of organic waste material heated in the absence of oxygen and produces three main products. Bio-oil, biochar and various gasses are produced during a pyrolysis reaction. Biochar is a stable carbon form of the original biomass material. Numerous studies have concluded that biochar improves soil fertility and removes carbon from the atmosphere.

However, there have been ongoing issues with spreading and applying biochars to soil. These concerns have raised awareness in needing to minimize dust emissions generated by spreading equipment. One proven method is to granulate biochar using various binder solutions to form small granules and spread them. While these granules minimize dust generation, they are still not deemed robust compared to conventional fertilizers used in agriculture.

A simple washing operation is proposed to decrease biochar hydrophobicity and allow it to retain water. In reducing biochar hydrophobicity, other characteristics can be improved, such as stability, adsorption capacity, and the removal of any harmful organic or inorganic contaminants that pose dangers to soil stability. This will ultimately result in biochar with fewer fine particles minimizing dust created during spreading.

Washing biochar is a cost-effective solution to turn it into an effective soil amendment that farmers can accept. Widespread use of biochar as a soil amendment will remove large amounts of carbon from the atmosphere.

Co-Authorship Statement

Chapter 3 is a research study that has been submitted for publication to a peer-reviewed journal. Chapter 4 is a research study that will be submitted to a peer-review journal. The authors' individual contributions are stated below for each journal article.

Chapter 3: Impact of post-pyrolysis wash on biochar properties

Authors: Anthony Fazzalari, Mamdouh Abou-Zaid, Cedric Briens, Lauren Briens

Status: To be submitted for publication

A. Fazzalari conducted all experimental work including pyrolysis of biomasses and biochar powder testing. Data analysis was conducted by A. Fazzalari with assistance from M. Abou-Zaid, C. Briens, and L. Briens. Manuscript was jointly written and revised by A. Fazzalari, C. Briens, and L. Briens.

Chapter 4: An investigation of drum granulation on post-pyrolysis washed biochar

Authors: Anthony Fazzalari, Cedric Briens, Lauren Briens

Status: To be submitted for publication

A. Fazzalari conducted all experimental work including granulation and granule testing. Data analysis was conducted by A. Fazzalari with assistance from C. Briens and L. Briens. Manuscript was jointly written and revised by A. Fazzalari, C. Briens, and L. Briens.

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Table of Contents

List of Tables

List of Figures

Chapter 1

1 Introduction

As major industries continue to grow, the need for energy in every sector of society is necessary. Because of global warming, greenhouse gas emissions must be reduced and reversed through carbon capture. Biomass is known as the fourth largest energy source behind natural gas, oil, and coal. Essential advantages of biomass are primarily renewability and versatility as an energy source [1]. Compared to other renewable resources, biomass resources are readily abundant across the world [2]. Biomass can be used to generate carbon-neutral energy. The pyrolysis process includes thermally degrading biomass at high pressure and in the absence of oxygen to produce bio-oil, various gases, and biochar [3]. While bio-oil and gases can be used as chemicals or combusted to provide carbon-neutral energy, biochar, if buried, can permanently remove carbon from the atmosphere. This introduction reviews the requirements for biochar application as a soil amendment, the important biochar properties for this application, and how granulation can help formulate biochar for its use as a soil amendment.

1.1 Biochar as a Soil Amendment

Biochar is a carbon-rich material produced from biomass with characteristics that make it an effective soil amendment product [4]. Research has shown that, when utilized in soil, biochar can improve the water holding capacity, microbial activity, and carbon capture measures and reduce leaching caused by other chemical sprays and fertilizers used that attributes to runoff pollution [5]. Carbon capture and other nutrient retention mechanisms help promote plant growth in soils that are damaged or in need of an increased microbial environment. The increasing microbial activity allows soils to break down biomass residues and, thus, promote plant growth. During the pyrolysis process, surface functional groups are created that inhibit the biochar effectiveness and prevent plants from absorbing valuable nutrients by attaching themselves to heavy metals within the current soil environment [6]. Therefore, chemical, and physical modifications must be made to biochar for its qualities to become more effective and improve its granular characteristics such as strength, density, shape, and size.

For biochar to be an acceptable soil amendment, there must be chemical and physical modifications to its structure. Absorption, Electrical conductivity (EC), stability, hydrophobicity, polyaromatic hydrocarbon removal, and many more are characteristics that could be diminished or enhanced depending on their contribution to soil improvement. Various types of feedstocks, as well as conditions, can produce biochar with wildly varying properties. For instance, biochar made from wood products increases plant growth, whereas ones produced from agricultural environments have a lesser effect [7]. Besides feedstock type, pyrolysis temperature dramatically affects the characteristics of any biochar. For example, biochar stability and persistence in the soil increase with production temperature, which means that higher temperature biochar is more stable. Lower temperature biochar is less stable as it decomposes more rapidly [8]. Different environments also play an essential role in determining which biochar is more suitable as a soil amendment. For example, a study of two different biochars showed that one biochar was more effective in environments that needed fungal growth, while the other was more utilized for gram-negative bacterial growth [9].

1.2 Physical and Chemical Characteristics of Biochar

Biochar has various characteristics that affect its ability to become a successful soil amendment. However, some of these characteristics hinder its function in specific environments and types of soils. The physicochemical properties of biochar can cause soil nutrients and carbon availability to change and protect microorganisms against predators, modifying the microbial diversity and taxonomy of the soil [10]. However, there are pre-treatment methods to diminish and even eliminate possible contaminants created through the pyrolysis process that produces biochar. As mentioned before above, the creation of functional groups on the biochar surface, formed through pyrolysis, indicates that some biochar may be more acidic than others. Also, the effect of temperature has a significant impact on the pH levels found in biochar that can significantly affect a specific soil environment [11]. Polyaromatic hydrocarbons are also created during the pyrolysis process, contributing to infecting crops and causing illness to humans [12]. These chemical characteristics are a concern that must be faced when looking at the pre-treatment of biochar for it to be a successful soil amendment.

A possible solution to the issues stated above is improving the cultivation by increasing the particle size and enlarging the powder to reduce dust and health issues. Through numerous pre-treatment methods, there is a possibility that the characteristics physically and chemically can be altered for improvement without reducing the benefits biochar adds to the soil. Size enlargement is also beneficial for the biochar starting material itself and its respective contribution to soil amendment. By increasing the size of biochar particles, the mass would increase as well, thus minimizing the potential for biochar to become airborne and remain within or on the surface of the soil after spreading.

1.3 Granulation

Wet granulation is the process of producing agglomerates, called granules, through the addition of a liquid binder added to a powder bed. The binder solution is sprayed onto the bed, then agitated. For drum granulation, the agitation is provided by the rotating drum which causes the powder bed to tumble. The advantage of drum granulation over other wet granulation methods is easy scalability.[13].

In the case of hydrophilic powders in wet drum granulation, the binder solution is sprayed on the tumbling powder bed, form granule nuclei, and grow through the process of coalescence and consolidation into larger granules [14]. However, for hydrophobic powders in wet drum granulation, the binder solution droplets do not penetrate quickly into the bed. Instead, droplets sit on the powder surface and pull biochar particles up and around forming liquid marbles [15]. Hydrophilic and hydrophobic properties lead to different granulation mechanisms.

There are three main drum granulation parameters that affect granule properties during the granulation process. First rotational speed of the drum followed by binder concentration and lastly the amount of binder added to the drum. These main drum granulation parameters play a major impact on the granule coalescence and consolidation in hydrophilic powders which ultimately affects the quality of the granules produced in a granulation run. When two granules, within the drum granulation process form one larger granule it is known as granule coalescence [16]. Whereas, granule consolidation is when continued granule collisions and deformation causes the granule to be more compact which will increase its strength.

For hydrophilic powders, growth by coalescence is affected by the drum rotational speed. Powder agitation within the drum granulator is mainly attributed to the rotational speed, which results in an increase in kinetic energy of collisions [17]. This will create a larger number of collisions within the drum, which will result in successful coalescence of granules and increase the average granule size. A higher rotational speed also reduces porosity and increases strength.

Binder concentration and binder amount impact granules formed from hydrophilic powders. Binder concentration has demonstrated effects of coalescence and consolidation of granules. An increase in binder concentration can ultimately inhibits the movement of binder through its powder capillary pores [14]. This results in reducing particle wetting, granule deformation, and coalescence of granules. Likewise, the amount of binder solution plays a major role in granule coalescence and consolidation as well. Interparticle friction can be greatly affected due to the binder solution wetting particle-particle contacts [18]. Thus, increasing the binder solution amount increases the granule deformations and coalescence of granules. Similarly, to binder concentration amount, the increase in coalescence results in larger granules with increased strength.

The granulation mechanism for hydrophobic powders is very different than that from hydrophilic granules. Increasing the drum rotational speed, can increase the agitation of the powder bed which is essential for ensuring distribution of the liquid binder droplets and the layering of particles around the liquid marble structures required for granule growth. Increasing the drum rotational velocities beyond a critical value results in a change of flow regime from cataracting to centrifugal. The drum rotational velocity can be determined using the Froude number. This equation is defined as the ratio of centrifugal force to gravity and when equal one, equilibrium of forces is achieved, and critical flow occurs [19]. If the Froude number is larger than 1, centrifugal flow regime occurs [19]. At this point, liquid binder and granule formation will become limited.

Binder concentration and binder amount have also been seen to effect hydrophobic powders. An increase in binder concentration has been proven to increase the drop penetration time for a liquid droplet to penetrate a hydrophobic biochar powder bed [20, 21]. This indicates that powder particles will take longer to layer itself around the binder droplet due to this increase in concentration. Also, by increasing the amount of liquid binder added increases the amount of marbles formed within the granulation process. However, if too much liquid is added, it can cause these marbles to form together and create large clusters that are not an adequate size for spreading equipment.

1.4 Thesis Objective

The first objective of this thesis is to develop a cost-effective washing procedure to improve biochar properties and, in particular, make it easier to granulate. Its second objective is to wet drum granulate unwashed and washed biochar powders with constant wet drum granulation parameters to differentiate the affect the best wash scenario had on the biochar powders and their respective granules produced.

1.5 Thesis Overview

A literature review is presented in chapter 2 summarizing biochar characteristics, how it contains attributes to be used as a soil amendment, and its granulation parameters. This literature review focuses mainly on the different properties of biochar and possible pre-treatment methods used to enhance its features as a soil amendment. It also reviews other potential applications of biochar. Lastly, granulation was also reviewed in this chapter to understand the different types of granulation, the factors specifically affecting drum granulation, and finally, the selection of a binder to form granules with the acceptable 1-4 mm size range.

After completing chapter 2, additional research was required into the pre-treatment of 3 different biochar powders. This pre-treatment improved their soil amendment characteristics and properties needed for wet drum granulation. Chapter 3 examines various types of washing methods to maximize the reduction in hydrophobicity. Optimizing the reduction in hydrophobicity also improved other characteristics needed for soil improvements such as stability, reduction in organic and inorganic contaminants, adsorption, and removal of PAH compounds found within the biochar powder.

Progressing from the findings in chapter 3, chapter 4 examined the best wash case scenario in the previous chapter and compared the physical differences between washed and unwashed biochar granules and their respective granulation mechanisms. Investigating properties of two different biochars such as yield, granular strength, granular density, and granule shape showed that the washing operation contributed to positive results in both washed biochar cases.

Chapter 5 provides an overall conclusion from this study and delivers a general idea into future work related to optimizing the washing operation and further investigation into the wet drum granulation of pre-treated biochar.

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Chapter 2

2 Literature review of biochar properties, applications, and granulation the use as a soil amendment

2.1 Introduction

Because of global warming, greenhouse gas emissions must be reduced and reversed through carbon capture. Biomasses such as various digestates or wood products are an alternative renewable, carbon-neutral fuel and chemical source [1]. Biochar from biomass pyrolysis also provides an opportunity for carbon capture.

2.2 Biochar

Biochar is the solid product that remains after biomass pyrolysis. Biomass such as agricultural waste is heated to a pyrolysis temperature, above 350 °C, selected according to the feedstock and the required application. A typical biomass feedstock mainly contains components of cellulose, hemicellulose, and lignin; however, biochar shifts into the category of "charcoal" or "black carbon" but does not include typical black carbon produced from fossil fuel applications [2].

Feedstock and pyrolysis conditions are both significant factors affecting biochar properties. Biomass and pyrolysis conditions affect the molecular structure and pore size distribution of biochar and affect biochar sorption characteristics [3]. Studies found that poultry-litter biochar had a larger surface area and porosity than wheat-straw biochar, although both were produced at the same temperature of 400 °C [4]. In general, it is assumed that higher pyrolysis temperatures ultimately lead to greater biochar aromaticity and a larger specific surface area [3]. Aromaticity is defined by the stability of a cyclic carbon ring through resonance stabilization. For example, benzene is more stable than we might expect because it has two resonance structures that delocalize electrons and thus stabilize the structure [3]. Relatively stable aromatic backbones from pyrolysis create more carbon-to-oxygen groups and carbon-to-hydrogen groups, which assist in nutrient exchange sites after the oxidation process of the reaction [5]. Recent literature discovered that removing H- and O-containing functional groups by decreasing atomic ratios of H/C and O/C with increasing temperature will produce high aromaticity and low polarity of biochar [3]. With temperature playing a significant role in biochar properties. Also, other findings demonstrated that low-temperature biochars are more phytotoxic [6]. Phytotoxicity is described as a toxic effect by a compound on plant growth where it delays seed germination and prevents a plant from growing fully. As tars accumulate with other organic compounds related to phytotoxicity, they can significantly affect the growth of plants and their surrounding ecosystem [6].

2.3 Biochar Powder Properties

Biochar from biomass pyrolysis is often in the form of a fine powder. Measuring different biochar properties such as the potential of hydrogen (pH), bulk density, hydrophobicity, carbon stability, etc.…, helps determine its potential for application as a soil amendment [7].

2.3.1 Hydrophobic Properties

Once the biomass is pyrolyzed, the hydrophobic properties of biochar can vary significantly based on the type of biomass used and the pyrolysis temperature. A high pyrolysis temperature decreases the hydrophobicity of biochar and limits its water-retention capacity: aliphatic compounds abound in fresh biochar pyrolyzed at low temperatures and are thought to cause hydrophobicity [8]. Hydrophobic biochar can also influence the pathway of water in the soil and contribute to soil erosion. Biochar powders produced erosion-reducing effects due to increased organic matter content including increased saturated conductivity and higher aggregate stability [9, 10]. Also an increase in hydraulic conductivity is present in hydrophobic biochars that can lead to reduced surface runoff, which then can be influenced by soil water retention [11].

2.3.2 Stability

The stability of biochar is crucial when selecting the best biochar for application as a soil amendment. The stability of biochar can be determined with accelerated aging, which seeks to reflect the oxidative nature of biochar degradation in soil [12]. Stability is an important characteristic to determine the impact of carbon sequestration. A large difference in mass loss with aging indicates an unstable biochar. This is caused by unstable compounds created through the pyrolysis process which is then lost throughout the aging process. A biochar that is oxidized would indicate poor stability properties, while a biochar that does not react with an accelerated aging agent indicates good stability.

2.3.3 Water Retention and Porosity Properties

The porous properties of biochar are important when observing its ability to retain water in the soil. Water retention properties are crucially important in climates with little to no rainfall within parts of the year. Studies have shown that when biochar is cultivated into soils, the powder can increase water retention and reduce nutrient and heavy metal leaching. With biochar being highly porous it allows for water and nutrient retention to be possible within the soil [13]. A comparison was also made that forest derive biochar and mill derived biochar found that forestry derived biochar had more potential for water retention because of its porosity and pore volume [14]. Also, surface area plays a vital role in the retention of water within soil, with increased surface area having a positive effect on water retention [15].

2.3.4 pH Characteristics – Acidity, Alkalinity, and PAH Content

Biochar pH is essential given its strong influence on the existing pH of soil. While the effect of biochar on soil pH may be beneficial for improving acidic soils, increased pH has also been connected to micronutrient deficiencies and product reduction in the agricultural sector [16]. Its importance depends on the nature of the soil. Biochars used for soil amendment are alkaline, but biochar pH values ranging from 3.1 to 12 have been reported in the literature [17]. Studies also described carbonization as a process that removes acidic functional groups and enriches the biochar in salts of alkali and alkaline earth elements [18]. The variation of acidity can change within pyrolysis, depending on the operating conditions and feedstock source. Studies concluded that biochars with low ash content, such as woody feedstocks, generally have a lower pH value than biochars with higher ash contents, such as crop residues or manures [17]. Biochars produced under high temperatures (>400°C) are likely to have greater pH values [16]. This test can be performed simply by using deionized or distilled water through agitation and equilibration.

2.3.5 Bulk Density and Particle Size Distribution

Bulk density measurements are easily performed through a volume to mass ratio test, which provides a better understanding of the flow properties of biochar, its potential dust losses, and shipping costs. These characteristics can also be related to the particle size distribution and particle shape of biochar. In the sense of pore characteristics, the overall size, shape, and internal structure likely play essential roles in controlling soil water storage [19]. Biochar maintains two different types of pores inside each particle: intrapores and interpores [19]. Therefore, the particle or biochar size then affects the intrapore and interpores within them [19]. When looking at this application within the field, biochar particles may have different sizes and shapes than the soil particles they are interacting with. Biochar addition will change the soil characteristics (size, shape, connectivity, and volume) and affect water retention and mobility [19].

2.3.6 Ash Content – Observation of Metals

Fixed carbon properties are an essential characteristic to determine the volatile matter within biochar. Fixed carbon is the material other than ash that does not vaporize when heated in the absence of air. In the pyrolysis process, the cellulose in biomass mainly produces volatiles, while the lignin primarily forms fixed carbon [20]. Testing for fixed carbon and ash content is performed when a biochar sample is placed within a muffle furnace and heated to a high temperature (e.g., 900 ºC). This biochar is then weighed to determine the percentage of moisture, volatiles, and ash within the biochar [20].

Ash content helps determine the actual minerals in biochar. Overall, all biochars produced contain carbon; however, biochars vary significantly in their volatility component. This means that for soil amendment applications to be effective they must contain volatile aspects that are beneficial to plants. The starting biomass material has the largest effect on the ash content as seen in previous work. Studies determined that wood derived biochars have a higher carbon content and a lower ash content compared to agricultural biochars or manure based biochars [21]. Due to different biochar chemical compositions, various biochars must be used to meet the specific needs of individual soil profiles.

2.3.7 Biochar Washing

Studies identified methods to reduce biochar phytotoxicity [22]. Washing biochar with pure water significantly reduced its toxicity [22, 23]. Washing with pure water also decreased the hydrophobicity of biochar [23]. Washing with acidic water can also help improve the biochar [25, 26]. By decreasing the hydrophobicity, it is assumed that contaminants within the biochar are also diminished. Washing can reduce electrical conductivity and increase carbon stability through accelerated aging by removing contaminates off the exterior and interior portions of the biochar particles [19, 22–27].

2.4 Potential Applications of Biochar

Biochar is widely recognized as an efficient tool for carbon sequestration and soil fertility. These biochars can be produced from several feedstocks, including forestry products, various manures, agricultural waste, and urban green waste [30]. A brief discussion below reviews the main applications of biochar such as carbon sequestration, activated carbon, biocoke in metallurgical applications, biocoal, catalyst, and, lastly, soil amendment. Biochar is seen as having many applications, but this material has been primarily sought after as a soil amendment/fertilizer in recent years. With regards to biochar being a soil amendment, it can increase the water holding capacity, reduce bulk density, provide additional cation exchange sites, and serve as a source of reduced carbon compounds that may benefit microbial populations, promoting plant growth [13].

2.4.1 Biocoke for Metallurgical Applications

Biocoke is produced by applying heat and compression of biomass fuel [31]. This biocoke is used in metallurgical applications, specifically in iron production, as it provides heat for the blast furnace and acts as a reducing agent [31]. The Canadian steel industry uses 3.7 megatonnes of metallurgical coke, which amounts to 13.7 megatonnes of carbon dioxide, making this industry one of the largest carbon dioxide generators [32]. Overall, Biocoke has a significant advantage: it can be stored and combusted differently from the biomass it derives from, thanks to property transformation through these processing processes. It has a significant disadvantage: it cannot utilize all the original biomass energy because part of the carbon is consumed or released in processing the raw material [31].

2.4.2 Biochar as Biocoal

Biocoal is a higher value carbon product from biomass which is made similarly to biochar. Biocoal is human-made coal that can completely replace or be co-fired with fossil-fuel-based coal products in energy plants. In bio-coal production, biomass is torrefied in an inert (oxygen-free) environment [33]. The difference between torrefaction and pyrolysis is the process temperature (torrefaction is at a lower temperature than pyrolysis). Torrefaction is typically carried out using an indirect rotary kiln, also known as a calciner [34]. The properties of biocoal are hydrophobic to match fossil coal properties. Biocoal is used within the petroleum industry sector in a pelletized form to aid in producing various fuels. This sector focuses more on producing energy than products such as soil enhancers that pyrolysis focuses on [35]. One advantage of biocoal is that it requires less energy to make than biochar, meaning that it conserves energy and cost while still producing similar products as a pyrolysis reaction. However, one disadvantage is that there are many available fuels in the energy production industry, making it hard for biocoal to compete.

2.4.3 Biochar as a Catalyst

Biochar as a potential catalyst is a new application. Studies showed that biochar directly obtained from pyrolysis of biomass has a relatively low specific surface area and poor porosity, and limited surface functional groups [19], which can hinder some applications as useful catalysts or catalyst supports. However, activation can improve the internal porous structure [36], and therefore some potential as a catalyst can still be obtained. Some advantages of biochar as a catalyst are that biochar can act as a catalyst to increase the degradation rates of plastic or biomass wastes or be used as an adsorbent material during the post-treatment to improve the quality of the liquid oil [37]. However, some disadvantages include the inability to recover and or reuse, requiring a resource-intensive method of separation, and production of a considerable amount of waste to the environment [38]. Thus, with the newly discovered use of biochar as a catalyst, it does pose potential interest in petrochemical industries. However, it is seen as still containing disadvantages that must be overcome regarding reusability in petroleum sectors and minimizing potential waste.

2.4.4 Carbon Sequestration

Carbon sequestration is the process of capturing and storing atmospheric carbon dioxide. This method reduces the amount of carbon dioxide in the atmosphere with the ultimate goal of reducing global climate change [39]. Biochar has carbon resistant to microbial degradation, meaning that it contributes to environmental stability through carbon sequestration [40]. Pyrogenic carbon is described as a type of carbon that is stable [41]. Overall, Carbon sequestration is vital in agricultural applications because they emit almost 30% of global greenhouse gas (GHG) emissions [42]. With advancements in carbon sequestration within soil applications, we can limit our imprint on the environment and improve the soil quality and the ecosystem surrounding them.

2.4.5 Activated Carbon

Both biochar and activated carbon are viewed as carbonaceous pyrogenic materials but can function differently depending on the application. While biochar shares adsorption properties with activated carbon, it also exhibits a significant ion exchange capacity, a minimal or absent property in traditional activated carbons. The ion exchange capacity of biochar is due to the residual carboxylic acid functionalities on the biochar graphitic backbone. As the activation process removes residual side chain groups, activated carbon has limited ionic interactions [43]. The consensus is that biochar retains between 10 percent to 70 percent (average of 50 percent) of the carbon present in the original biomass [44]. However, activated carbon is not good at removing chemicals that are not attracted to carbon, such as sodium or nitrates [45]. For example, although road salt can significantly affect soil properties, activated carbon cannot adequately protect against salt contamination. Also, activated carbon is not effective against some pathogenic bacteria and viruses and can harbor bacteria, leading to bacterial growth, damaging some plants [45].

2.4.6 Soil Amendment

Biochar has excellent potential as a soil amendment as its porosity allows it to retain nutrients and water [46]. Studies reported biochar could improve soil quality and fertility by stabilizing soil pH and increasing moisture-holding capacity. At the local or field scale, biochar can enhance existing sequestration approaches. It can be mixed with manures or fertilizers and included in no-tillage methods without additional equipment. Biochar has been shown to improve soil structure and fertility, thereby improving biomass production [47]. Biochar not only enhances the retention and therefore efficiency of fertilizers but may, by the same mechanism, also decrease fertilizer runoff. This stabilization of the soil resulted in attracting more beneficial fungi and microbes, improving cation exchange capacity (CEC), and retaining soil nutrients [48]. Another significant benefit of using biochar as a soil amendment is its ability to sequester carbon from the atmosphere-biosphere pool and transfer it to soil [49]. Biochar releases nutrients for plant growth, promotes the soil structure, biological and physical health, and is a buffer against harmful substances. However, for the biochar to be applied as a soil amendment, it must be improved through granulation to be spread throughout large land sectors. A study demonstrated that an average biochar sample has a target application rate was 5.6 tonnes/hectare. Still, an estimated 30% of the material was wind-blown and lost during handling, transport to the field, soil application, and incorporation. This resulted in an estimated 3.9 tonnes/hectare biochar application [50]. Biochar granulation is, therefore, essential to efficiently deliver maximum product. The beneficial aspect of soil amendment applications is that various biochars and binders can be used in unison to create a vast variety of different fertilizers to assist different types of soils. Ultimately soil amendment is sought after to neutralize the pH levels in soil, increase microbial activity, and longevity of the soil itself. The industry surrounding soil amendment is also exponentially growing.

Soil amendment can be very beneficial to agricultural applications; however, determining the correct additive to incorporate into a specific soil and the proper amount used is also significant as it can easily affect the environment. Soil structure is greatly improved by biochar addition, as discussed earlier by the soil increased ability to hold water and increase nutrients [8]. This allows for microbes to thrive within their respective environment by increasing carbon, phosphorus, nitrogen, and potassium to the soil and consequently feeding the microbes and increasing microbial activity and growth. Soil amendments are also able to enhance soil aeration by improving its physical properties [51]. Biochar could be applied to damaged soils or low nutrient soils such as clay [51].

2.4.7 Summary of Potential Applications for Biochar

Table 2-1. Advantages and disadvantages of potential biochar applications

Applications	Advantages	Disadvantages
Biocoke – Metallurgical applications	• Large sector to tackle seeing that they produce millions of tonnes of metallurgical coke • Can be stored very easily and combusted in many different ways	• Emissions from the metallurgical industry • Can not utilize all the energy the original biomass had • Large effect to atmosphere
Biocoal	• Very appealing to the fuel industry, large sector of business to grow into • Torrefaction rather than pyrolysis – utilizes less energy to make products	• Many other sectors in the fossil fuel industry – deemed as just another industry • Does not have the ability to expand
Catalyst	• New application and tempting to many industries to pursue • Increase the degradation rates of plastic • Used as an adsorbent material during post-treatment to improve oil	• Low specific surface area • Poor porosity properties • Limited surface functional groups • Inability to recover and reuse • Too much waste created
Carbon sequestration	• Reduces global climate change by absorbing CO_2 from the atmosphere • Provides environmental stability and increases photosynthesis in plants	• Singular application • Selectivity of placing biochar – can not be in an area where there is little CO_2 to absorb
Activated Carbon	• Mimics the properties of biochar and its benefits to soil • Good ion exchange capacity	• Not good at removing chemicals that are not carbon • Pathogenic bacteria remains
Soil amendment	• Uses CO_2 through carbon sequestration to assist plant growth • Increases microbial activity in a damaged ecosystem • Decreases fertilizer use – less runoff • Water retention allows plants to maintain water in them without rain. • Neutralizes soil's pH and creates a balance within the ground • Act as a natural pesticide • Enhance soils aeration, by improving its physical properties • Vast variety of chars and binders to create a granular specific to a particular need	• Over-fertilization can create water pollution through run off with rain or wind • Must know which biochar to apply in which soil • Weak granules have the ability to damage air quality through dust generation

In conclusion to this section and Table 2-1, it seems more effective and efficient to use biochar as a soil amendment. This is due to the increasing advantages of improving its surrounding ecosystem and overall carbon capture, which improves air quality. Soil amendment is also an area of new research when combined with granulation, which demonstrates an immense amount of potential in industries and research and development in this sector.

2.5 Challenges of Biochar Powders

One of the most significant challenges of biochar applications as a soil amendment is that biochar is usually an excellent powder (1-100μm), making it difficult to handle [52]. It cannot be directly applied to soils as it would not flow easily and uniformly from spreading equipment and would then be blown away. Airborne particles less than 10μm, particularly less than 2.5μm, negatively impact respiratory health [52]. Directly applied to the soil, a significant fraction of the biochar would be entrained by wind, become airborne, and impact exposed occupants' health.

To be used as a soil amendment, biochar must be modified to minimize dust hazards. Methods that have been proposed include mixing the biochar with a liquid to create a slurry and applying using liquid spreading techniques, mixing and applying with compost, and pelletizing or granulating and applying as per solid fertilizers. A slurry of biochar and aqueous solution can be prepared and applied using liquid spreading techniques, eliminating the dust from the biochar. The liquid can contain complementary nutrients such as N, P, and K. There are, however, challenges with the slurry, including obtaining and maintaining an adequate biochar concentration in suspension. Besides, the transportation and application of large volumes of a liquid can be expensive. Biochar can be pelletized or granulated into solid particles similar to a solid fertilizer. Studies combined and then pelleted mixtures of biochar, wood flour, polylactic acid, and starch. The pellets were combined in different ratios with peat to assess potential use as a soil amendment in nurseries. As the pellets expanded when wetted while the peat volume decreased, the ratio becomes critical in ensuring that the nursery containers are filled to appropriate levels to encourage plant growth [13]. Studies pelletized biochar from wood and wheat straw and evaluated the pellets as a replacement from peat moss in nursery containers. Substitution at rates up to 15% volume for volume had positive effects on tomato and marigold plants. Possible disadvantages of biochar pellets as a soil amendment include expansion when wetted and hardness that does not allow the pellet to decompose once in the soil to provide optimal benefits to the soil [53].

The literature for biochar pellets for soil amendment is scarce as most of the research on biochar pellets has been conducted for pellets as a fuel source [54]. The desired properties and challenges of pellets as a fuel source are different from those of a soil amendment. It demonstrated that biochar could be granulated to create biochar granules that have properties like solid fertilizers. Granules can be formed to resist attrition but still allow decomposition once in soil and are therefore considered to be potentially more attractive as a form for soil amendment than biochar pellets [55, 56].

2.6 Granulation

Granulation is the process of agglomerating particles into a larger structure, a granule. Granulation is used in the pharmaceutical, food detergent, and fertilizer industries [54]. Granulation eliminates dust and segregation of particle components and enhances flowability. There are three main types of granulation: melt, dry, foam, and wet granulation.

2.6.1 Melt Granulation

Melt granulation is a type of wet granulation process in the sense that it is a enlargement process through the agglomeration of solid particles, but uses a meltable binder liquid that melts or softens at relatively low temperatures (60 °C). Ultimately, the melting is achieved by the energy created through the friction of the mixer and the heated jacket of the bowl. This can cause degradation or oxidative instability of the components added to the mixing process [57]. The main concern for a melt granulation process is that finding an appropriate binder to use is very difficult.

2.6.2 Dry Granulation

Dry granulation uses pressure to force and bind particles together. Typically, the mixture of particles is fed through a roller compactor, and then compressed material is milled to the desired sizes [58]. The combination of particles used in dry granulation is critical to achieving desired granule strength and properties. This restriction for particles means that dry granulation is not commonly used except for particles sensitive to moisture or heat and could not be wet or melt granulated [58]. As other components should be added to the biochar to optimize its potential as a soil amendment and these components would be limited by their compressive properties, dry granulation is not an attractive method for the granulation of biochar.

2.6.3 Wet Granulation

Wet granulation uses a liquid as a binder to combine particles into granules. The liquid binder is sprayed onto the particles. The bed of particles is agitated to disperse the binder and promote the formation of granules. Then, the wet granules are dried to the final granular product [59]. Wet granulation is applied widely as many different combinations of powders, and liquid binders can be used with various methods: high shear, fluidized bed, and drum granulation.

High shear granulation uses shear forces through an impeller to agitate the powder bed while the liquid binder is sprayed onto the top of the moving powder bed [60]. The shear forces the liquid binder droplets to penetrate the powder bed to form granular nuclei. The granule nuclei then collide with sufficient force to promote coalescence into granules [60]. High shear granulation is commonly used in many industries. Many different combinations of liquid binders and powders are possible. When combined with adjusting process parameters such as impeller speed and liquid binder spray-rate, granules can usually be formed. Limited or different scales and restrictions to a batch process are significant disadvantages in considering high shear methods for biochar granulation.

In fluid bed granulation, a binder liquid is sprayed over the fluidized particles to bind them together [61]. The binder droplets are in continuous contact with the particles or granules within this process. A liquid droplet spreads over the surface of any solid substrate on which it impacts until getting an equilibrium configuration [62] that ultimately depends on the characteristics of the droplet, such as size and equilibrium contact angle. The main disadvantages of using fluidized bed granulation are the complexity of the batch process and fines entrainment, which means that it is not suitable for small and light biochar particles.

Drum granulation is a batch process where small particles sit on the bottom of a large rotating drum and move as the drum rotates [63]. Drum granulation has been applied in many industrial processes. It appears to be the best choice for biochar granulation because of low capital costs, low operating costs, and easy scale-up [55]. The powder is first loaded into the drum, drum rotation is initiated, and a continuous flow of liquid binder is sprayed onto the biochar throughout multiple spargers going along the drum axis.

2.7 Granulation Mechanism

There are two very different granulation mechanisms, and these depend on the interaction of the liquid binder with the powder. If the interaction is hydrophobic then a liquid marble followed by layering for growth mechanism occurs (Figure 2-1a). If the interaction is hydrophilic then a mechanism of wetting and nucleation followed by coalescence and consolidation is followed (Figure 2-1b).

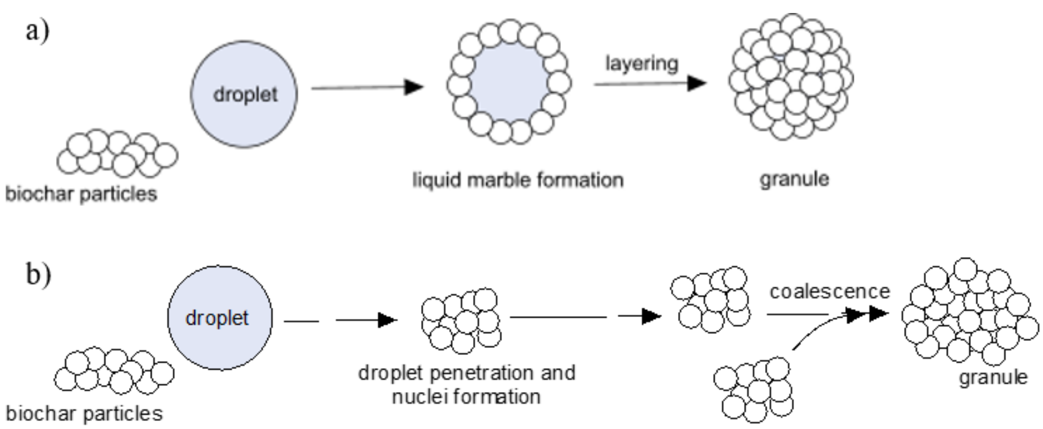

Figure 2-1. Schematic of granulation mechanisms for (i) hydrophobic powders and (ii) hydrophilic powders

A study analyzed the hydrophobic differences between three different biochar powders to understand their granulation mechanism. One biochar sample formed by layering onto the droplet due to high hydrophobic biochar properties, whereas the other biochar powders displayed less hydrophobic properties by allowing the biochar to surround itself with droplets eventually penetrated the powder bed rather than remaining on its surface. Other mechanisms demonstrated a combination of the two granulation mechanisms as represented in Figure 2-2 [56]. This indicated that although the biochars were still hydrophobic, some of the biochars analyzed had less hydrophobic properties than others. It was concluded that the granules produced from this experimentation were not to the standard strength of conventional fertilizer, deeming them to be too weak [56].

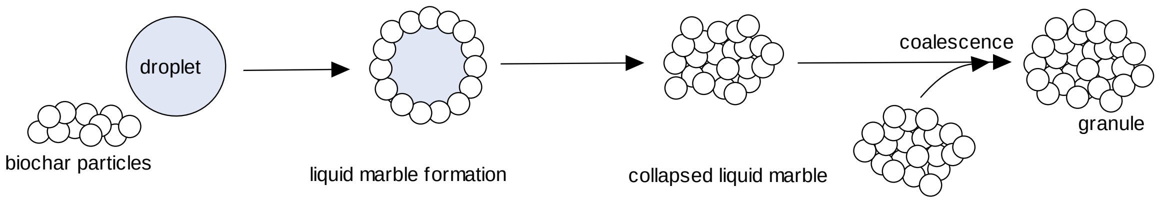

Figure 2-2. Schematic of a combination mechanism between hydrophobic and hydrophilic powders

Hydrophilic granulation of biochar powders has been minimally studied since biochar powders are conventionally hydrophobic. Studies in the past have shown various water or acid washes to improve the hydrophobicity to enhance the chemical properties of the biochar for soil amendment [21–27]. Still, such washes have not been used to facilitate granulation. To achieve hydrophilic granulation, the biochar must be pre-treated to reduce its hydrophobic characteristics so that it can allow penetration of its powder bed by a water-based binder. This can lead to oversized granules, which would be considered unacceptable for soil amendment applications.

2.8 Factors Affecting Wet Drum Granulation

2.8.1 Drum Rotation

Drum rotational speed is a fundamental parameter impacting the degree of size enlargement and the physical properties of granules. With low drum rotational speed, the powder bed will slip at the bottom of the drum with almost no movement. However, high rotational speeds can cause cataracting flow along with wall build up. A cascading flow is seen as the most desired to promote granule coalescence to occur [61].

Drum rotation can be varied and described by the Froude number [64]. Froude is defined as the ratio of centrifugal force to gravity as shown in equation 2-1, where ω, R, and g are the drum rotation speed, drum radius, and gravitational acceleration, respectfully.

$$F_r = \frac{\omega^2 * R}{g} \tag{2-1}$$

The purpose of this equation exemplifies that the equilibrium of forces is achieved when the Froude number is equal to one, and the corresponding rotational speed is well known as the critical rotational speed of centrifuging [64]. As well as the change in flow from cascading to cataracting can vary significantly through increased rpm. Critical Froude number is used to introduce the cascading flow that is recommended for granulation. This flow regime is recommended for hydrophilic granulation to ensure enough energy during a collision of two nuclei to result in coalescence [61].

On the other hand, if the flow is too far beyond cataracting, it will result in centrifugal flow, resulting in no granulation. If in cascading flow, the surface does not renew at a sufficient rate and would become overwetted and lead to caking rather than granulation.

2.8.2 Binder Concentration

Binder concentration in the sprayed liquid that is important for the formation of granules. It can affect coalescence and consolidation of granules. By increasing the binder concentration inhibits the movement of binder through the powder capillary pores of the biochar. This will result in reduced particle wetting and granule deformation due to decreased movement through the powder pores [61]. Thus, by reducing the granule deformation there is a reduction in successful coalescence due to granule collisions resulting in smaller and weaker sized granules.

2.8.3 Binder Solution Volume

The volume of applied binder solution can play a vital role in the physical and chemical characteristics of granules, depending on whether they are hydrophobic or hydrophilic. In hydrophilic granulation, there must be enough solution to form liquid bridges between particles. If a powder contains hygroscopic features, such as microcrystalline cellulose

(MCC), more liquid is required, which in turn results in granular growth being delayed [65]. Adding a large amount of liquid can also create a slurry within the granulation drum, which will destroy the powder chances to agglomerate and form nuclei. For hydrophobic granulation to be affected by binder solution, increasing the amount of liquid means more droplets, and each droplet becomes a marble

2.8.4 Breakage and Attrition

Granules used in soil amendment applications must be able to withstand collision amongst the granules themselves when being transported or processed through spreading equipment and the pressure placed on themselves. Studies discovered that the attrition of granules happens when granules collide and do not break but instead fall off or apart from the nuclei and suffer surface wear due to the friction between the granules [66]. The rotational speed of the drum and weight percentage of the binder solution can also be varied to study granular strength [13]. For wettable powders a higher rotational speed and higher weight percentage of binder solution increase the granule strength [55]. The reason for this is due to binder solution wetting particle-particle contacts reducing interparticle friction. Thus, an increase in binder solution causes an increase in the coalescence of granules [61].

2.8.5 Biochar Shape and Size

Biochar size and shape affect overall flowability, and biochar must flow well enough inside the drum to achieve cataracting flow. The issue in research has been the diameter of granules not meeting requirements (1-4 mm) and cohesiveness of biomass creates issues with spreading and achieving spherical granules. A study observed the size and shape distributions of all granules collected. The granule shape was determined by calculating the aspect ratio (AR), which represents granule elongation. It is the ratio of the length of the minor and the major diameters of the granule. The aspect ratio varies below 0.5 for elongated, needle shape particles to 1 for perfect spheres. On the other hand, particle size was calculated using standard reference indices and through an algorithm based on Mie's optical theory [67].

In both hydrophilic and hydrophobic granulations, size is the most critical factor. In hydrophilic granulation, the size must be small relative to the droplet size to form individual granule nuclei, leading to better growth control of granulation. In hydrophobic granulation, marbles will not form if the size is too large. A recent discovery found that the formation of a liquid marble varied with the biochar type. The cornstalk biochar particles completely covered the liquid binder droplet before penetration into the bed. In contrast, the other two biomasses tested (birchbark and miscanthus) did not immediately and completely cover through the bed of biochar [56].

2.9 Binders

Binders are used in wet granulation as a formulating component, ensuring the appropriate surface wetting ability and ensuring adhesion/cohesion between the biochar placed within the drum. Binders also ensure excellent plasticity, compactness, and binding capacity of various chars. This agent must be non-toxic and soluble with the feedstock as it is mixed with other soil amendment features that will be discussed further in the following table. Many different binders are available, ranging from ones that already exist as waste, such as lignin, to molasses binders used in agricultural sectors.

2.9.1 Additives to Binders for Granular Improvement

Additives incorporated into binders and feedstocks are to enrich soil quality and improve the ecosystem of the surrounding soil. These additives can increase root growth, water retention and overall enhance the soil amendment. The possibility of incorporating other additives to biochar, such as pesticides and fertilizers, allows the granules produced from granulation to be increasingly more effective on damaged soils. Additives to binders have been studied and concluded that soil conditioners, such as composted horse manure, improve soil structure by binding soil particles into larger aggregates. Therefore, this caused increases in pore space, enhancing air exchange, water movement, and root growth [68].

2.9.2 Review of Possible Binders Used in Granulation

2.9.2.1 Lignosulfonates

Lignosulfonates are known as being a by-product of sulfite pulping processes but have been known as being a potential binder in pelletizing of various biomasses. A study used lignosulfonates as one of the binders in pelletizing spruce wood shavings and wheat straw biomass [69]. It was determined that the binder displayed limitations in characteristics of durability, strength, and attrition resistance [69]. Some issues faced with this binder are the problem with sulfur contamination and how it is affecting its potential as a binder. Lignosulphonate may behave as an anionic surfactant, which contains both hydrophilic (e.g., sulphonic and phenolic hydroxyl) and hydrophobic (i.e., carbon chains) groups and thus possesses a certain degree of surface activity. More than 50 megatons of lignin are globally produced annually, of which only 10% is utilized [69]. This new lignosulphonate component needs to be ultimately treated to prevent environmental risks, which is undesirable to many industries as a form of required pre-treatment.

2.9.2.2 Lignin

Lignin as a binder overall displays beneficial qualities due to it being waste from pulp and paper industries and other petroleum industries. Lignin-based products usually are an organic material with low solubility in water but a highly biodegradable binding agent. This binder enhances the granular hardness, which aids in being an excellent dust suppressant [70]. The other beneficial aspect of lignin is that it is a natural pesticide. It defends against pests and diseases because its polyphenolic nature provides antioxidant, bactericidal, and antifungal properties [71]. Studies also were able to use melted lignin with wheat straw biomass to produce thermoplastic composites. It was concluded that lignin aided in improving the mechanical characteristics of these plastic composites and enhance their physical properties. As well as the melt index of the composite prepared with the optimum proportion was 2.07 g/10 min, which indicated that the composite had an excellent processing flowability [72]. The consensus is that lignin is seen as more of waste by industries, thus making it an abundantly available product to use within granulation processes. However, lignin does not appear to have been used in any previous literature about biochar granulation deeming it promising in research, but unaware of the potential disadvantages in applying to soil.

2.9.2.3 Hydroxypropyl Methylcellulose

Hydroxypropyl methylcellulose is more commonly used as a binder in pharmaceutical applications but has been previously tested on biochar powders. A study incorporated HPMC as a binder used in biochar granulation to produce granules used in soil amendment applications. Results demonstrated that HPMC was dropped onto the cascading biochar bed surface and rolled down the inclined bed instead of penetrating the bed quickly, accumulating particles on the droplet surface through adsorption. The liquid marble structure began penetrating the bed, where it then collapsed. Granule growth throughout this process occurred primarily through collisions and coalescence of the granule nuclei formed from collapsed liquid marble of HPMC. This demonstrated good solubility of the binder, flowability, and attrition resistance. As the attrition resistance of the granules was high, the viscosity of the binder solution permitted capillary forces to bind particles together into solid granules. The weight percentage of HPMC used was between 3-9% [55], which is essential because HPMC has the potential as a binder for biochar if the appropriate weight percentage and amount could be identified since this type of binder is more costly compared to other binders analyzed in the literature. HPMC powders have inferior flow properties and tend to be cohesive. However, further work concluded the granules flowability, fundamental in powder handling processes, was evaluated by measuring the bulk and tapped densities.

2.9.2.4 Molasses

Molasses as a binder appear to be a good binder to use in granulating biochar in the application of a soil amendment. Molasses in various forms (cane, corn, and beat) can supply plants with potassium, nitrogen, magnesium, phosphate, and calcium, along with being non-toxic [73]. Studies described sugar beet molasses as being viscous and sticky. Therefore, it was stated that a thermal or another form of pre-treatment should be required to ensure its uniform distribution in the biomass powder. To avoid pre-treatment and to reduce the consumption, its mixture with different proportions of water was prepared. It was concluded that moisture content, ash content, and volatile matter were sensitive to changes to molasses concentration of their pellets [74]. The presence of volatile matter is related to the calorific value, signifying the importance of carbohydrate content in raw molasses. Highly viscous components in molasses structure form bonds between the particles that assist the durability and bulk density of biomass pellets as the binder is added [75]. Other work also tested molasses on different biochars. It concluded that molasses provided a weak attrition resistance with a high binder concentration. It produced granules that were not adequately in size for soil amendment applications than HPMC [76]. Molasses have also been shown to improve the aeration in clay soils and reduce nematode reproduction [51]. Thus, molasses as a binder represent a substantial impact on being beneficial to plants through microbial growth and acting similarly to a natural pesticide. Overall, binder properties of molasses (type, concentration, and amount) significantly affect the properties of granules and their respective tests to determine their effectiveness within the soil. Still, granular strength is a big factor to overcome when using molasses as a potential binder.

2.9.2.5 Ammonium Nitrate

Seeing that fertilizers produced today consist of variations including nitrogen, potassium, and phosphorous, a possible binder can then consist of one or more of these compounds to create a binder for biochar granulation. With these compounds being vital to plant growth, they can enhance the soil surrounding them. However, these components have difficulty submerging into a bed of biochar due to hydrophobic properties with water. As well a study showed that when using ammonium nitrate as a binder, the weight percentage of binder used is quite large (<30 wt%) [76]. A study examined the use of ammonium nitrate as a binder and determined the granules to be relatively weak unless the wt% of the binder was between 30-35% [77]. Thus, if the granules are too challenging to compact together before spreading, too much of these compounds can cause the reverse of their original purpose and damage air quality through biochar dust. Plants are known to absorb nitrogen in the form of either nitrates or ammonium through their roots. Ammonium nitrate has been described as a supplier of sulfur and nitrogen; ammonium sulfate fertilizer enables strong crop growth and high yields [55].

Similarly, other work attempted to use ammonium nitrate as a binder to create granules, but as in other literature, it employed over 30 wt% of binder to create granules. Their research showed that ammonium nitrate never fully penetrated the biochar bed, meaning that it could not adsorb the biochar to develop a suitable granule [76]. Overall, ammonium nitrate is a binder that is low in solubility and granular strength, making this binder difficult to pursue amongst the rest. Lastly, ammonium nitrate has been a very popular fertilizer for many agricultural uses around the world. However, transporting and storing this product has become problematic because it absorbs moisture very quickly and efficiently, thus deteriorating the quality of the product and limiting its value to many farmers and agricultural users worldwide.

2.9.2.6 Sodium Silicate with PEG Wetting Agent

Above granular properties were discussed as being a crucial element to the success of soil amendment. Studies have shown success in achieving high attrition, good flowability, and shape of the granule using sodium silicate [45]. Good density and water resistance were also obtained throughout producing granules to decrease the cost spent on transportation and time spent on drying granules after being placed within the drum granulator. This ultimately assisted in utilizing these granules in humid and wetter climates and storing them for later use, which increased the granules life span while transported and placed within the soil as well [45]. Sodium silicate was tested at various weight percentages (1%, 3%, 5%, 7%, and 9%) with distilled water and 0.5 wt% of polyethylene glycol with a binder to solid ratios of 0.77-0.90. Multiple tests and analyses were performed (proximate analysis, size distribution, compressive strength, bulk density, granular density, ash melting point, and water resistance) to ensure a good batch of granules were produced. Throughout their results, the particle size distribution of granules was between 3-14 mm, which can be utilized and converted to a soil amendment application with various attrition tests to lower the particle size distribution of the granules. The moisture content of the granules was determined as being high; it had good water retention qualities, and an increase in moisture content also increased the compressive strength of the granules, which ranged from 0.45-0.97 MPa [45]. This study was for a fuel and combustion study; however, it represents the amount of binder used to granulate biochar and the properties study of the granules concerning their potential use for soil amendment regarding compressive strength, particle size distribution, and water retention capabilities.

2.9.2.7 Corn Steep Liquor

Corn steep liquor (CSL) is a liquid co-product of corn bioprocessing. It is a possible binder to agglomerate feedstock together to create granules used in various industries. These products are derived from the wet milling process, where condensed fermented corn extractives are produced. Corn products contain nutrients such as nitrogen in the form of amino acids, peptides, and vitamins. CSL was used in a study for binding mineral rock fines. It was concluded that corn steep liquor as a binder performed well in the sense of high dry crushing strength, low wet attrition loss, ease of pelletizing, and low moisture content out of the seven binders tested. It was also found that the use of Corn Steep Liquor as a binder not only results in a durable abrasion-resistant pellet that can withstand rough handling but also has the added benefit of being a food grade environmentally friendly, inexpensive, widely available [78]. CSL can help microbiological growth, meaning that these nitrogen components are readily available to the plant and not dependent on microbial activity for digestion and release. As well, another study identified issues such as poor flowability and poor dispensability. Past experiments discovered that large particle sizes of corn stover compared to fine powders that were initially set within the drum [79]. Mixing the viscous co-products with corn stover under high shear was necessary to ensure that the co-products had been uniformly before proceeding to the granulator [79]. The drying time of granules takes anywhere from a few days to a few weeks at room temperature, increasing the production time of processing granules from feedstock to final granule form. Corn products have shown excellent solubility with water and granule strength but struggle with cohesion when spreading the granules.

2.9.2.8 Overall Comparison of Binders

Table 2-2. Comparison of binders for wet drum granulation

Type of Binder	Solubility	strength	Flow properties	**IN or OUT**	References
Lignosulfonates	Contains hydrophilic and hydrophobic groups – contains surface activity, but limited	Stated as limited in granular strength and attrition resistance	No research involving the granules used in spreading equipment	**OUT -** stated as having difficulties with the physical properties of granules created	[69]
Lignin	Difficulty with solubility into a bed of powders	Stated as aiding in improving mechanical characteristics/ physical properties	Described as having good processing flowability	**OUT -** all requirements met – concerned about solubility	[70-72]
Hydroxypropyl methylcellulose	Good solubility	Demonstrated good attrition, but lacked in granular strength	Seen as having poor flow properties	**OUT -** overcoming flow properties and granular strength could be a difficult	[55]
Molasses	Good solubility to producing granules with good surface area qualities	Weak attrition resistance and granular hardness	No research of granules in spreading equipment	**IN -** all requirements are good – improve granular strength	[51, 73–76]
Ammonium Nitrate	Poor solubility – never fully submerge in a bed of biochar (time-sensitive)	Poor granular strength – requires an immense amount of binder concentration	No current research involving the granules used in spreading equipment	**OUT -** solubility into a bed of particles is slow and the attrition vs granular strength is hard to balance	[76, 77, 55]
Sodium Silicate with PEG wetting agent	Assuming good solubility – not tested in fertilizer applications but more in the petroleum industry	Excellent attrition and great granular strength	Good flowability of granules from research – spherical shape granules	**OUT -** must test for solubility to be sure however every other field is acceptable	[45]
Corn Steep Liquor	Shown great solubility in previous experiments when heated	Great granular strength – good crushing strength from alternative granulation method however no mention of attrition	Poor flowability due to cohesiveness – must be heated so "ease of pelletizing is possible	**OUT -** good attrition and solubility but the possible difficulty of spreading properties in past experiments indicate issues	[78, 79]

2.9.2.9 Conclusion

After analyzing seven binders used in past research, molasses were selected as the binder for this study. The following steps would investigate the different types of granules produced through the characteristics set out in section 2 to determine the most effective granule to use in soil amendment.

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Chapter 3

3 Impact of Post-Pyrolysis Wash on Biochar Properties

3.1 Introduction

Biochar has been acknowledged as a promising carbon-filled porous material for soil amendment [1, 2]. Biochar, when used as a soil amendment, reduces the need for irrigation and chemical fertilizers, cuts down on greenhouse gases emissions, and sequesters carbon. However, biochar may contaminate soils with biochar impurities such as heavy metals or polyaromatic hydrocarbons (PAH), can negatively alter soil hydraulics, and its application to soils may result in dust emissions.

With most soil types, the addition of biochar increases the water retention capacity of the soil [3–10]. Neutron imaging studies have shown that water retained within the biochar particles becomes available to plants under drought conditions [7], thus reducing the need for irrigation. The most important biochar properties for water retention are hydrophilicity[7, 11] and porosity [4, 5, 10–13]. The ability of soils to release water to plants under drought conditions depends primarily on the internal porosity of the biochar particles rather than the inter-particle porosity [7, 12]. Biochar hydrophilicity depends on the original biomass and its pyrolysis conditions [7]. Biochar tends to be more hydrophilic if created at high pyrolysis temperatures [14–18]. High pyrolysis temperatures increase the surface area and porosity which allows physical adsorption of water. Tars formed during pyrolysis can deposit on the surface and within the pores of the biochar creating aliphatic groups on the biochar that reduce hydrophilicity or promote hydrophobicity. The tars are vaporized at higher temperatures, thus reducing the number of aliphatic groups [12, 18, 19].

Biochar can help cut pollution by reducing the use of chemical fertilizers. Most of the chemical fertilizers not used by the plants end up in waterways, polluting them; for example, 80 % of nitrogen added to agricultural systems in the USA is wasted [20]. Fertilizer runoff is responsible for algae blooms and hypoxic marine “dead zones” in regions ranging from the Gulf of Mexico to the Baltic sea [20, 21]. The addition of biochar promotes the growth of beneficial microorganisms within the soil, thus reducing the need for chemical fertilizers [22–30]. A possible strategy is to compound biochar and chemical fertilizers, reducing fertilizer application rates and runoff by enhancing plant nutrient uptake [31–33]. The ability of biochar to promote growth depends on its original biomass and its pyrolysis conditions [34]. Biochar properties that affect microorganisms growth are the porosity of the biochar particles, as the pores act as refuge for beneficial microorganisms [24, 28, 30], the water retention capacity [28, 30], and the enhancement of sorption and degradation of soil contaminants to reduce their toxicity to microorganisms [23, 30]. To enhance the growth of beneficial microorganisms, biochar particles should, thus, have a high porosity, a high hydrophilicity and a high sorption ability.

The application of biochar as soil amendment can greatly reduce greenhouse gas emissions. It reduces the use of chemical fertilizers, cutting emissions of greenhouse gases during their manufacture. In addition, chemical fertilizer application to soils leads to the emission of strong greenhouse gases, such as methane and nitrous oxide, from both land [20, 35] and hypoxic marine zones [36]. On the other hand, adding biochar to soil reduces emissions of methane and nitrous oxide from the soil [37, 38]. Converting biomass to biochar also prevents the emission of strong greenhouse gases, such as methane and nitrous oxide, during the natural degradation of biomass [35].

Biochar stability is important as it determines how long its carbon will remain sequestered and how long the biochar will provide benefits to the soil [39]. Carbon sequestration by the biochar removes from the atmosphere the carbon originally absorbed by plants, providing a tool to potentially reverse the recent increase in greenhouse gas concentration in the atmosphere [39–44]. Pyrolysis conditions affect the biochar stability: increasing the heating rate provides a more stable biochar [45] and raising the pyrolysis temperature increases the biochar stability [45–48] although, since the biochar yield decreases with increasing temperature, pyrolysis temperature does not greatly affect the yield of stable biochar [49, 50]. Biochar stability is affected by the original biomass feedstocks, but since it is difficult to relate stability to easily measured biomass properties, direct testing of the biochar stability is important [45, 47, 50, 51]. Testing within soils is most relevant, but lengthy, while accelerated chemical oxidation of the biochar provides quicker results [47, 52–54]. An advantage of accelerated oxidation methods is that they provide easily reproducible results [47].

Contamination of soils by heavy metals from biochar is considered to be the most negative environmental impact from the use of biochar as soil amendment [55]. Heavy metals are toxic to soil microorganisms [30] and to the human and livestock consumers of the plants. Usually, pyrolysis concentrates the heavy metals present in the original biomass in the biochar [56–58], but makes them less bioavailable [56–59]. The bioavailability of heavy metals decreases with increasing pyrolysis temperature [57, 60–62] and with increasing pyrolysis heating rate [63]. Bioavailable heavy metals in biochar are usually evaluated with a variety of leaching methods [56, 58, 61, 62]. Much of positive crop response from biochar application cannot be directly attributed to nutrient content of biochar [55], so it is best to reduce the leachability of minerals from biochar.

Organic compounds are another type of contaminants from biochar. The two main types of organic contaminants are VOCs (volatile organic compounds) and PAHs (polyaromatic hydrocarbons) [58]. Although both types are toxic to soil microorganisms [23, 30, 58], PAHs are carcinogenic, mutagenic and teratogenic [23]. PAHs concentration in biochar depends on the original biomass [58, 64–66] and pyrolysis conditions. PAHs concentration is highest at pyrolysis temperatures of 400-500 °C [58, 67, 68] but the PAHs released from biochar produced at higher temperatures are less volatile and might have a different toxicity [69]. The use of a sweep gas during pyrolysis helps vaporize organic compounds and reduces their concentration in the biochar, but may be costly to implement [58]. PAHs concentration in the biochar is typically measured with solvent extraction [67, 70, 71]. Some measurement methods have also been developed to determine the concentration of bioavailable PAHs [65]. Measuring the leaching kinetics of PAHs is also important, as soil microorganisms can degrade PAHs if they are not overwhelmed by rapid leaching [23, 30, 72].

Dust emissions from biochar represent a serious health concern, either during its initial application or during subsequent tilling [73–77]. Dust emissions are enhanced by abrasion of the biochar particles within the soils [74]. Biochar dust would add to existing agricultural dusts that are already a serious health issue for agricultural workers [78, 79]. The PAH content of biochar dust greatly enhances its toxicity [74, 80]. Biochar dust is highly flammable and represents a serious explosion risk [76]. Another potential issue with biochar dust is that it may accelerate global warming: when deposited on snow and ice, it promotes solar radiation absorption, and when suspended in the atmosphere, it absorbs short-wave radiation, reemitting more problematic long-wave radiation [81]. A possible solution is to pelletize or granulate the biochar using a liquid binder [74, 82]. Safe, green binders are water-based and granulation is easier to optimize and control with hydrophilic biochar [82].

Adding hydrophobic biochar to hydrophilic soil can change soil hydrophobicity which influences the hydraulic properties of the amended soil. A uniform distribution of the biochar within soil is not practically possible. Water will therefore flow through the amended soil in preferential pathways; the more hydrophobic regions will be excluded and become dry while the more hydrophilic regions will contain the flow pathways. These pathways can become overwhelmed which increases the risk of soil erosion and transport of contaminants from the soil surface into the deep layers and possibly aquifer [83].

For use as soil amendment, important biochar properties are porosity and hydrophilicity. The current study is based on the speculation that a simple, cost-effective wash could remove oil and tars from both surface and pores of biochar particles, greatly improving their porosity and hydrophilicity. It is also speculated that the removed oils and tars would contain a major fraction of the bioavailable heavy metals and PAHs, and that the wash would, thus, greatly reduce the biochar toxicity.

Biochar can be washed to modify its properties for specific applications. A pure water wash can remove adsorbed toxic compounds to improve germination and plant growth [84]. Washing with water can also remove tars from the surface and pores thereby increasing porosity and hydrophilicity [14], improve macronutrient availability and cation exchange capacity [85], and ammonium adsorption [86]. Acid washes can also remove tars from pores [87] and remove metals [88]. Oxidizing washes have been found to increase the adsorption of ammonium thereby reducing its leaching from soil [89, 90].

Biochar can also be modified or activated through other techniques to increase surface area and porosity. For gaseous activation, the biochar is exposed to steam, ozone, carbon dioxide or air at temperatures of 700 – 900 ^{o}C [91]. This volatilizes some remaining compounds in the pores to increase surface area and porosity [92, 93], and with the oxidizing ozone or air, creates or modifies surface functional groups [93]. High temperature thermal treatment of biochar changes its structure to a more ordered form. The heat can be applied conventionally through convection and conduction, but also through application of microwave energy. Recently developed activation techniques include ultrasound, plasma and electrochemical modifications [91]. When compared to these methods, an inexpensive wash would be much more cost-effective.

3.2 Methods and Materials

3.2.1 Biomass

Three biomass feedstocks were selected: softwood woodchip (WCP) biomass that has been extensively studied in the literature, digestate from Bayview Flowers Greenhouse (BFD) in St. Catherines (Ontario, Canada) that contained mostly flower waste, and digestate from Storm Fisher Environmental (SFD) that is a food waste anaerobic digestion facility in London (Ontario, Canada). A summary of the biomass properties is given in Table 3-1.

Table 3-1. Summary of original biomass properties

Properties	WCP	SFD	BFD
Moisture content (wt%)	10	9	3
Sieve diameter through which 10 wt% passes, dp_{10} (mm)	0.4	0.3	0.1
Sieve diameter through which 50 wt% passes, dp_{50} (mm)	1.6	1.4	0.7
Sieve diameter through which 90 wt% passes, dp_{90} (mm)	3.5	2.3	2.7
Bulk density (kg/m^3)	180	700	590

3.2.2 Pyrolysis

Pyrolysis was carried out in the Pyrolytic Shaker Reactor (PSR). As shown in Figure 3-1, agitation was provided by a dedicated electric shaker and an induction system allowed rapid heating of the biomass feedstock, ensuring intermediate pyrolysis conditions. No sweep gas was used [94].

The reactor vessel was filled to 2/3 of its volume with biomass and the mass of biomass recorded. The vessel was then sealed and secured into the shaking device. Agitation and induction heating were started. When the bed temperature reached the target value of 400 ^{o}C, the agitation and heating were turned off. The reactor and its contents cooled to room temperature before the biochar was recovered from the vessel. The recovered biochar was milled and then sieved to a particle size below 710 μm for further processing and testing.

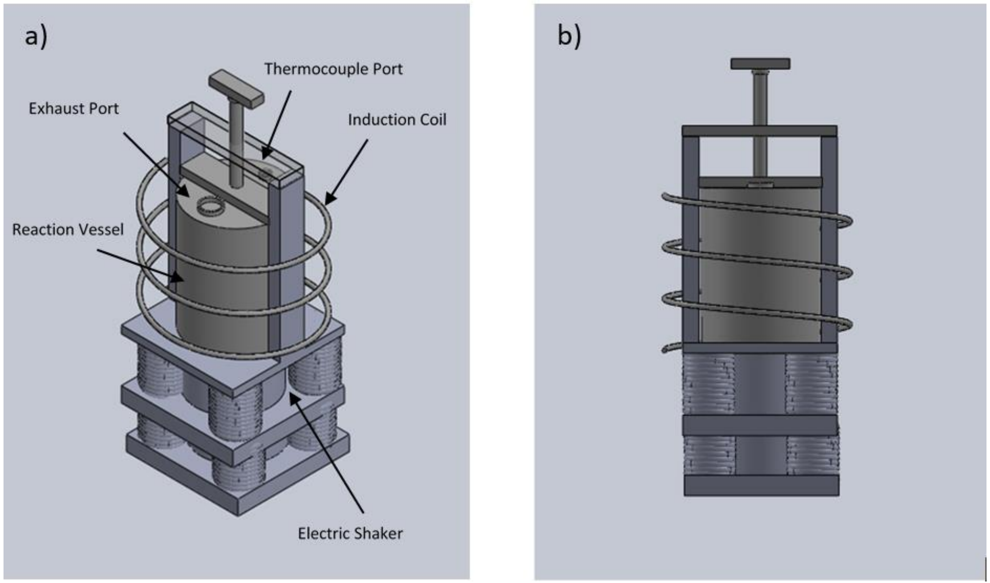

Figure 3-1. Schematic drawing of the pyrolysis shaker reactor showing (a) trimeric view and (b) front view

3.2.3 Biochar Washing

The biochar was washed with different solutions and combinations according to Table 3-2 in a ratio of 24 mL of washing solution per gram of biochar [95]. The degreaser was a mixture of 10 vol% Zep and 90 vol% deionized water as the wash liquid; Zep contains ethoxylated C9-11 alcohols and Sodium C14-16 olefin sulfonate as emulsifiers [96]. Triton X-100 (Triton) is a polyethylene glycol tert-octylphenol ether, a non-ionic surfactant and emulsifier that can be used as a mild detergent. Sodium dodecyl sulfate (SDS) is an anionic surfactant. Both Triton and SDS wash solutions were 1 g of surfactant per 100 ml of deionized water and then used as 24 ml of washing solution per gram of biochar. Hydrogen peroxide, H_2O_2, is an oxidizing agent and was added in a ratio of 2.43 g of H_2O_2 solution (7% molar concentration) per 10 g of biochar.

10 g of biochar along with the specified washing solution was vigorously mixed for 10 minutes. The washed biochar was then separated from the washing solution by filtration using Fisherbrand® Filter Paper, CS-32, Quantitative Q5, Porosity – Medium, Flow Rate – Medium. The filtered and washed biochar was then rinsed with approximately 45 ml of

deionized water. The biochar was finally dried in an oven at 105 ^{o}C for approximately 16 h.

Table 3-2. Summary of wash solutions used to wash biochar powders

Wash Solution	Components	Supplier
1	Deionized water	Snyder Industries
2	Deionized water and H_2O_2	Snyder Industries, Sigma Aldrich
3	10 vol% degreaser in deionized water	Zep [96]
4	10 vol% degreaser solution and H_2O_2	Zep, Sigma Aldrich
5	Sodium Dodecyl Sulphate (SDS)	Ward's Science
6	SDS and H_2O_2	Ward's Science, Sigma Aldrich
7	Triton	Electron Microscopy Sciences
8	Triton and H_2O_2	Electron Microscopy Sciences, Sigma Aldrich

3.2.4 Biochar Testing

The biochar was examined to determine the effects of the washing: colour imaging of the biochar to estimate the removal of any components on the surface of the biochar, drop penetration test and molarity of ethanol droplet (MED) test to estimate the hydrophobicity of the biochar, accelerated aging to estimate the stability of the biochar, methylene blue adsorption to estimate the biochar adsorption, leaching of the biochar using a Soxhlet extraction procedure and then analysis of the leachate for both inorganic and organic compounds, and specific examination of any leaching of polyaromatic hydrocarbons (PAHs) from the biochar. Further tests were then developed to investigate kinetics of the removal of any compounds from the biochar.

3.2.4.1 Biochar Colour

The biochar was examined using ZEISS Axiocam 105 colour microscope and associated software. The software analyzes each pixel of the image and assigns a Red, Green and

Blue (RGB) intensity between zero and 255: pure black corresponds to a combination of intensities of 0 for Red, Green and Blue while pure white a combination of intensities of 255 for Red, Green and Blue. It was hypothesized that, if a wash removed components that coated the biochar particles, then the colour of the biochar would change with washing.

3.2.4.2 Biochar Hydrophilicity/Hydrophobicity

The MED test was used to estimate the hydrophobicity of the unwashed biochar. The MED (molarity of ethanol droplet) test examines the penetration of an aqueous ethanol solution into a prepared bed of biochar powder. Ethanol solutions (Fisher Chemical) of increasing concentrations were created. A droplet of each solution was carefully placed onto the biochar powder bed surface [97]. The time required for the droplet to penetrate the bed was recorded. A higher required ethanol concentration to achieve drop penetration within 10 s indicated a higher degree of hydrophobicity [15].

Drop penetration tests with water were also used to estimate the hydrophobicity of the washed biochar. A droplet of deionized water was carefully placed onto the bed of washed biochar [97]. The time required for the droplet to penetrate the bed was recorded. Long droplet penetration times indicated a high degree of hydrophobicity.

3.2.4.3 Biochar Stability

Biochar will react within soil over time. To estimate this aging, the biochar was subject to an accelerated aging process [98] that uses hydrogen peroxide to oxidize the biochar. A 35 ml solution which included 1.7 g of H_2O_2 in deionized water (5 wt% concentration) was added to 0.5 g of biochar in test tubes. These samples were placed in a bath at 80 °C for 48 h while mixing the samples 4-6 times over 48 h. The samples were then placed in an oven at 105 °C for approximately 16 h for further drying before final weighing to compare the difference in biochar mass pre and post aging [99]. The oxidative stability of biochar was characterized from the change in biochar mass during the accelerated aging process.

the stability index (SI) was defined as:

$$SI = \left(1 - \frac{biochar\ mass\ pre\ aging - biochar\ mass\ post\ aging}{biochar\ mass\ pre\ aging}\right) \times 100\% \qquad (3\text{-}1)$$

A biochar that was not oxidized would, thus give stability of 100% while a biochar that was completely oxidized would give a stability of 0%.

3.2.4.4 Biochar Adsorption

Methylene blue adsorption was used to estimate biochar adsorption [100]. 0.2 g of biochar was combined with 15 ml of 400 ppm methylene blue in deionized water solution in a test tube. The mixture was agitated for 48 h in a BioNexus™ Thermo Incubator Shaker. The solid biochar was then separated from the liquid by filtering through Fisherbrand® Filter Paper, CS-32, Quantitative Q5, Porosity – medium, Flow Rate – Medium. The filtrate was diluted with deionized water at a ratio of 1:7.5 and then analyzed with a spectrophotometer (Thermo Scientific – Evolution 220: UV-Visible Spectrophotometer). Calibrations and mass balance calculations allowed the amount of methylene blue that was adsorbed by the biochar to be determined.

3.2.4.5 Biochar Leaching

When biochar is used as a soil amendment, it is important to know and usually to minimize the leaching of any components from the biochar into the surroundings. Biochar leachate was created using a Soxhlet extractor and a procedure modified from EPA Method 3540C [101]. A Soxhlet extractor using deionized water as a solvent was used to continuously wash the biochar over 16 h [99].

The biochar leachate from the Soxhlet extraction was analyzed for organic and inorganic compounds. Organic compounds in the leachate were estimated by measuring the absorption differences within 600 – 190 nm using a spectrophotometer. Inorganic compounds in the leachate were estimated by measuring the electrical conductivity of the leachate using a High Range Hanna Instruments Combo pH/Conductivity/TDS tester.

3.2.4.6 Leaching of PAHs (Polyaromatic Hydrocarbons)

Biochar leachate was created using toluene as a solvent (Fisher Chemical); 10 ml of toluene was combined with 0.1 g of biochar and the mixture agitated for 5 days. The solid biochar was separated from the toluene leachate by filtering through Fisherbrand® Filter Paper, CS-32, Quantitative Q5, Porosity – medium, Flow Rate – Medium. The toluene leachate was examined for PAHs using a gas chromatograph – mass spectrophotometer (GC-MS). A DB-5ms column (30 m x 0.25 mm ID x 0.25 um) equipped with a guard column (5 m x 0.25 mm ID x 0.25 um). The program rate used for the analyses was 50 °C / 1 min. hold / 20 °C / min. / 100 °C / 0 min. hold / 5 °C / min. / 300°C / 7.5 min. hold. Analytical standards were prepared [102]. There were 16 targeted PAHs [103] with 15 of these identified as having negative impacts on human health [104].

3.2.4.7 Removal of Components from Biochar

The leaching of compounds from the biochar over time was studied. 0.1 g of biochar was mixed with 10 ml of toluene and agitated for 1, 2, 24, 48, 72 and 120 h. Following the mixing and agitation, the solid biochar was separated from the toluene leachate through filtering and the absorbance of the leachate examined over 600 – 190 nm using a spectrophotometer. The absorbance curves were analyzed to estimate the reduction in exterior and interior compounds from the biochar after washing.

The area Y under the curve (spectrophotometer absorbance vs. wavelength) was determined and normalized values were found in terms of Y in the following equation:

$$Z = \frac{Y - Y_0}{Y_\infty - Y_0} \tag{2-2}$$

Z can be viewed as the fractional removal of tars from the biochar, with a value of zero before leaching and one for an infinitely long leaching.

Compounds can be removed from the surface of the biochar particles, which is controlled by external compounds, and from within the particles, which is controlled by internal compounds:

$$Z = Z_e + Z_i \tag{3-3}$$

where Z_e is the contribution from external compounds and Z_i is the contribution from internal compounds.

The removal of the internal compounds can be obtained with Crank's model assuming a perfectly spherical particle: [16]

$$Z_i = \left(\frac{M_t}{M_\infty}\right) \tag{3-4}$$

where the ratio of the mass M_t of compounds removed at time t to the mass M_∞ of compounds removed at an infinite time can be calculated [16].

Therefore, by finding a regression for data at time, t, then the equation will be completed by:

1) Assuming Z_e

2) Fitting: $Z_i = (Z - Z_e) = \frac{M_t}{M_\infty}$

3) Solving for $Z = Z_e + Z_i(t)$ and using different values of Z_e that minimize the error to obtain the best fit between measured and calculated Z values.

Washing the biochar can remove some compounds. This method provides the fraction of the external and internal compounds removed by washing. Details can be found in Appendix A.

3.2.4.8 Dilution Testing

Biochar leachate was created using a Soxhlet extractor and deionized water as described in Section 3.2.4.5. The leachates were diluted by various factors and each dilution analyzed with a spectrophotometer (Thermo Scientific – Evolution 220: UV-Visible Spectrophotometer) to estimate organic compounds and with a High Range Hanna Instruments Combo pH/Conductivity/TDS tester to measure the electrical conductivity to estimate the inorganic compounds. Calibrations combined with comparison of the leachates from unwashed and washed biochar provided an estimate of the reduction in compounds from the biochar with washing.

3.3 Results

Unwashed biochars were hydrophobic, with drop penetration times larger than 900 s for pure water. The MED test was therefore used to estimate the hydrophobicity of the unwashed biochars. The lowest molarity required for drop penetration within 10 s for the unwashed biochars ranged from 1.00 mol/l to 1.25 mol/l to 1.75 mol/l for the biochar from WCP, BFD and SFD, respectively. Biochar from SFD was the most hydrophobic or least hydrophilic. Visual observations and RGB colour analysis also indicated that biochar from SFD was the darkest in colour.

Washing resulted in biochar that was lighter in colour than the untreated biochar (Figure 3-2). Washes that contained SDS or Triton were the most effective at lightening the colour of the biochar. The addition of hydrogen peroxide to the wash solution had only a small impact on its effectiveness. The largest change in colour was observed for the biochar from SFD.

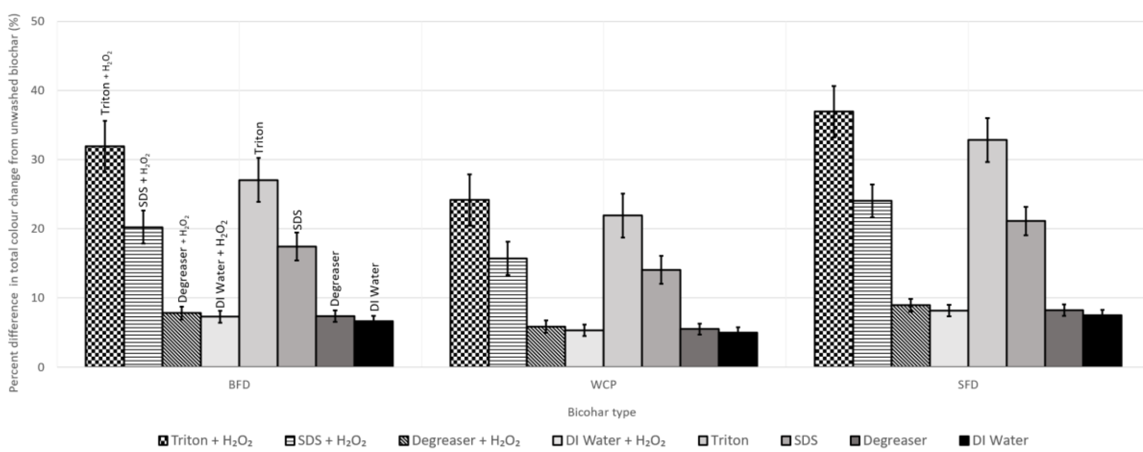

Figure 3-2. Difference in colour using RGB microscopic analysis relative to unwashed biochar. Error bars represent the range of duplicate values

Table 3-3 shows the drop penetration test results for the washed biochars. Biochars washed with only deionized water remained very hydrophobic with very long drop penetration times. The other washes significantly reduced the biochar hydrophobicity with the most effective wash being Triton combined with hydrogen peroxide. Biochar from SFD exhibited the largest reduction in hydrophobicity with washing.

Table 3-3. Drop penetration times of various washing solutions on biochar powders

Wash	Components	Penetration time (s)		
		BFD	WCP	SFD
1	Deionized water	> 900	> 900	> 900
2	Deionized water and H_2O_2	110	55	185
3	10 vol% degreaser in deionized water	47	15	65
4	10 vol% degreaser solution and H_2O_2	28	15	50
5	Sodium Dodecyl Sulphate (SDS)	29	10	44
6	SDS and H_2O_2	13	6	30
7	Triton	13	6	28
8	Triton and H_2O_2	8	3	15

Figure 3-3 shows that washing improved the mass loss of the biochar, which ultimately improved its stability. The greatest improvement was for biochar from woodchips washed with a solution of Triton and hydrogen peroxide.

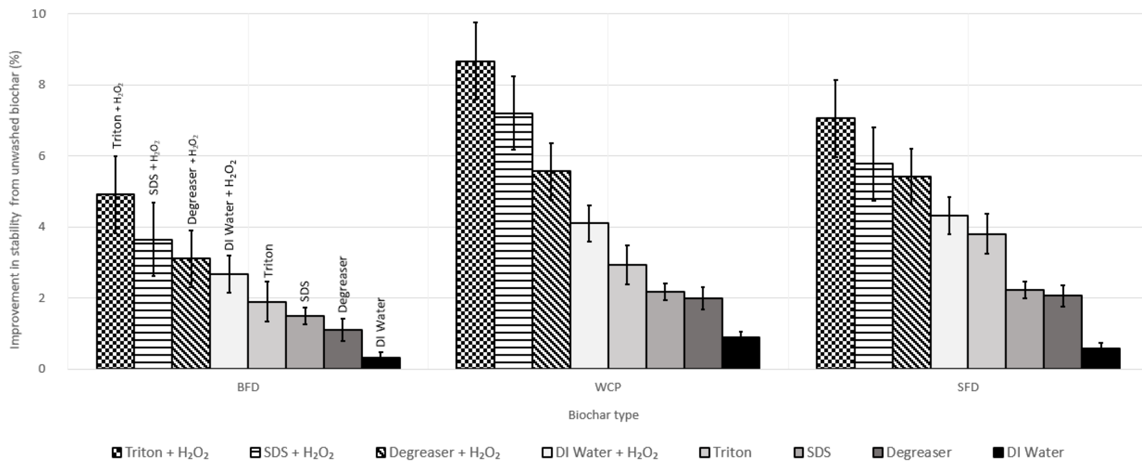

Figure 3-3. Improvement in biochar stability relative to unwashed biochar using an accelerated aging technique to measure the difference in mass loss. Error bars represent the range of duplicate values

The adsorption capacity of the biochar was estimated by measuring the adsorption of methylene blue. Figure 3-4 shows that the adsorption capacity of the biochar increased after it was washed. Washes with hydrogen peroxide were especially effective for the biochar from Bayview Flowers Digestate.

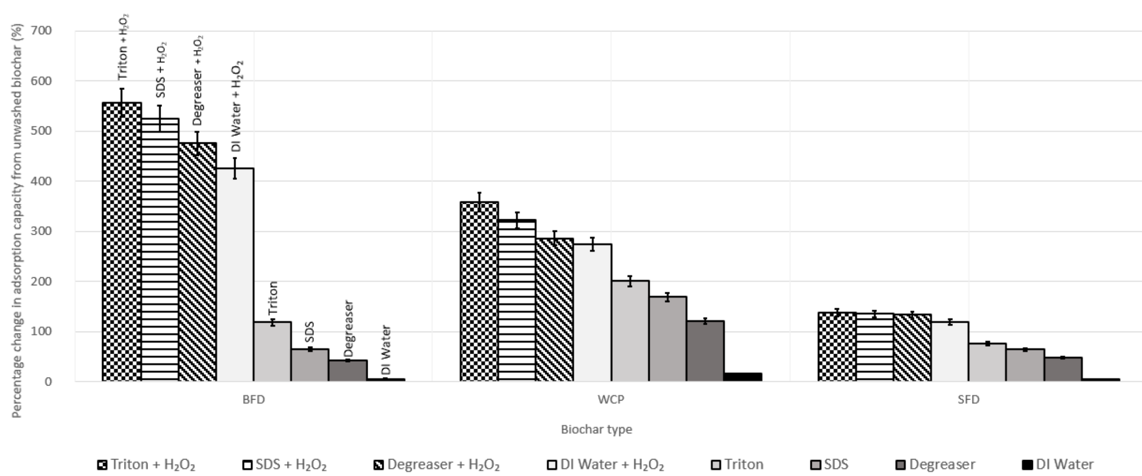

Figure 3-4. Increase in adsorption relative to unwashed biochar using a methylene blue adsorption analysis from 600 – 190 nm. Error bars represent the range of duplicate values

Washing removed compounds from the biochar. This reduced compounds that could be leached from the washed biochar; biochar leachate was created using a Soxhlet extractor with deionized water as the solvent. Figure 3-5 shows the reduction in organic compounds in the leachate from unwashed biochar. Figure 3-6 shows the reduction in washed inorganic compounds that contribute to the electrical conductivity of the leachate. For biochar from woodchips and SFD, the reduction in leachable organic compounds was slightly higher than the reduction in leachable inorganic compounds. Reduction in inorganic leachable compounds was very high for biochar from BFD, reaching almost 70%.

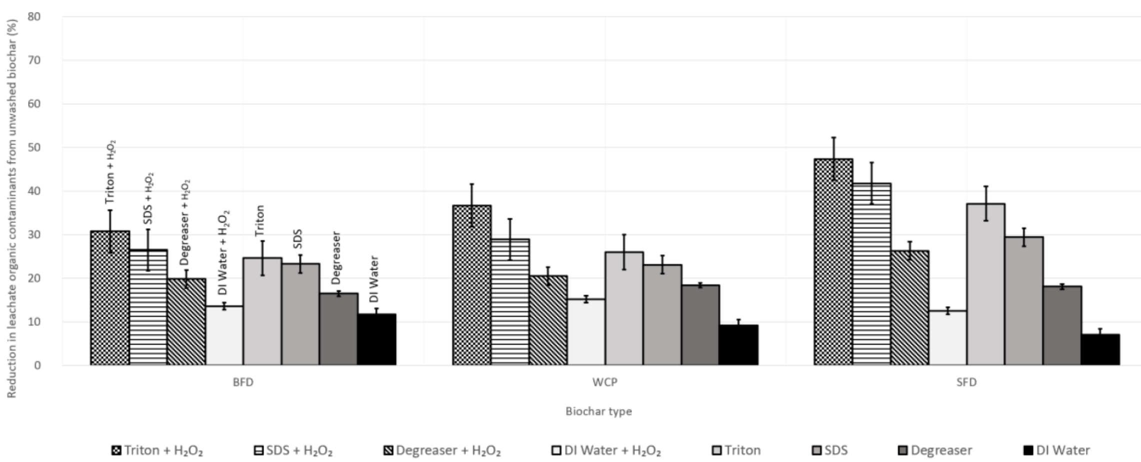

Figure 3-5. Reduction in leachable organic compounds relative to unwashed biochar by measuring the absorbance from 600 – 190 nm of the Soxhlet leachate liquid. Error bars represent the range of duplicate values

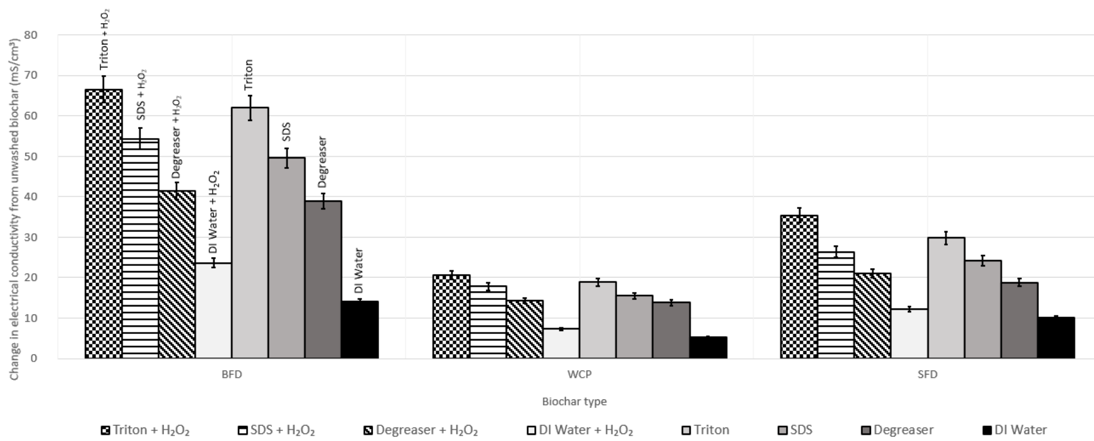

Figure 3-6. Reduction in leachable conductive inorganic compounds relative to unwashed biochar by measuring the electrical conductivity of the Soxhlet leachate liquid. Error bars represent the range of duplicate values

Measurements were taken to determine if any PAHs were present in the biochars and then if these PAHs were removed during washing. Figure 3-7 shows a comparison of the GC-MS scan of the toluene leachate from biochar from SFD unwashed and then washed with the degreaser solution. The peaks in the absorbance spectrum indicated the presence of PAHs within the biochar and their reduction following washing.

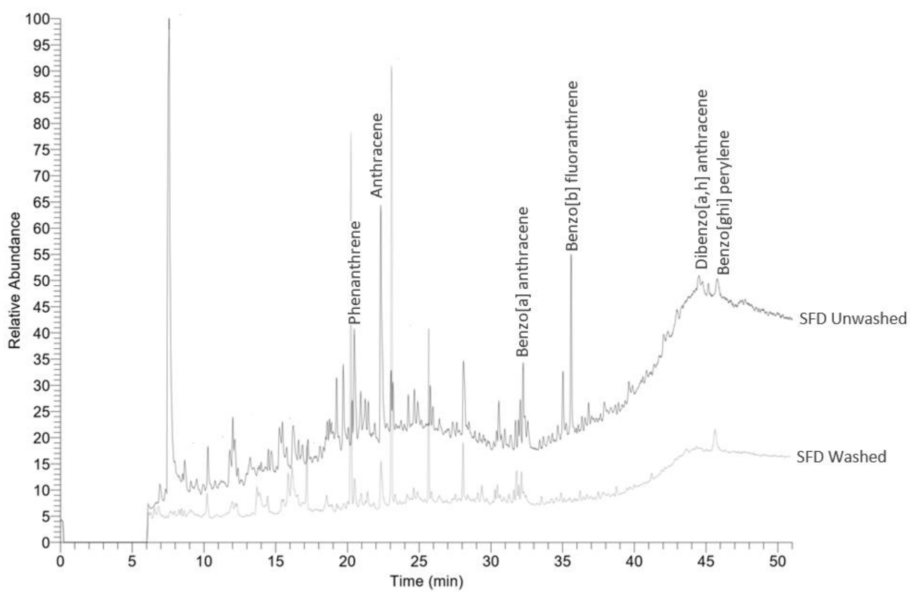

Figure 3-7. GC-MS scan comparison of two toluene extract solutions with unwashed and washed (degreaser solution) biochar powder from SFD

Biochar was soaked in toluene to create a leachate that was then tested at various time intervals for general compounds using a spectrophotometer. The absorbance curves were analyzed to estimate exterior and interior compounds from the biochar. Table 3-4 compares the removal of compounds from the exterior (Z_e) and interior (Z_i) of the biochar particles. Washing the biochar decreased the relative amount of external compounds. Over time, the relative amount of removed internal compounds increased and this effect was more pronounced with washed biochar.

Table 3-4. External and internal compounds in various biochar powders using a toluene solvent extraction

	BFD			WCP			SFD		
	Time (hr)	Z_e (%)	Z_i (%)	Time (hr)	Z_e (%)	Z_i (%)	Time (hr)	Z_e (%)	Z_i (%)
Unwashed	1	51.7	7.80	1	44.4	9.20	1	38.2	9.50
	2	51.7	10.9	2	44.4	12.8	2	38.2	13.2
	24	51.7	31.5	24	44.4	36.7	24	38.2	38.5
	48	51.7	39.3	48	44.4	45.8	48	38.2	48.6
	72	51.7	43.3	72	44.4	50.3	72	38.2	54.1
	120	51.7	46.8	120	44.4	54.1	120	38.2	59.1
Washed - Triton	1	41.7	12.7	1	35.1	10.2	1	35.8	10.7
	2	41.7	14.4	2	35.1	14.7	2	35.8	18.6
	24	41.7	33.3	24	35.1	38.2	24	35.8	40.4
	48	41.7	41.4	48	35.1	46.6	48	35.8	50.6
	72	41.7	45.5	72	35.1	51.3	72	35.8	54.9
	120	41.7	49.6	120	35.1	57.7	120	35.8	65.5
Washed - Triton + H_2O_2	1	33.6	15.5	1	23.7	12.7	1	12.3	13.4
	2	33.6	19.5	2	23.7	15.4	2	12.3	20.7
	24	33.6	37.7	24	23.7	39.4	24	12.3	44.4
	48	33.6	42.9	48	23.7	48.2	48	12.3	52.3
	72	33.6	46.6	72	23.7	54.7	72	12.3	60.2
	120	33.6	51.2	120	23.7	61.8	120	12.3	69.9

3.4 Discussion

Biochar that is hydrophilic could have advantages for soil amendment. The MED test was used to estimate the hydrophobicity/hydrophilicity of the unwashed biochars. The results confirmed that the unwashed biochar was not hydrophilic (Table 3-3). There was a general correlation between the colour of the unwashed biochar and the hydrophilicity: unwashed biochar that was dark in colour was less hydrophilic with biochar from SFD as the darkest and least hydrophilic. This suggested that hydrophilicity could be negatively impacted by components such as tars deposited on the biochar surfaces.

The change in colour of the biomass confirmed that components were removed from the biochar with washing (Figure 3-2). As the washes lightened the colour of the biochar, it was hypothesized that the washes removed tars deposited on the biochar surfaces and possibly also within the pores of the biochar. The colour change was small for washes of deionized water and degreaser and larger for the washes containing SDS and Triton. The addition of oxidizing hydrogen peroxide to the washes had only a small impact. Therefore, washes containing surfactants are required to effectively remove deposited tars from the biochar surfaces.

Tests on the washed biochar showed that the washes increased the biochar hydrophilicity (Table 3-3). This complemented the colour analysis, indicating that the washes removed tars from the biochar surfaces. The washes containing hydrogen peroxide had a positive effect on hydrophilicity although not a significant effect on colour. This difference reflects the multiple factors that influence the interactions of the biochar with water. Removal of tars with the surfactant washes from the biochar surfaces reduced the hydrophobic aliphatic groups on the surfaces. The addition of oxidant hydrogen peroxide could have modified some functional groups on the biochar surfaces, improving their interaction with water.

Adsorption is a very important property of biochar for soil amendment. It is proposed that washing could increase adsorption through displacing tars from the pores and through modification of functional groups on the biochar surfaces. Figure 3-4 showed that the adsorption capacity of biochar increased after washing. There were differences in the effectiveness with biochar source and type of wash possibly reflecting differences in the amount and location of tars.

For biochar from Bayview Flower Digestate washes with solutions containing only a detergent or surfactant were not very effective at increasing adsorption capacity while washes with hydrogen peroxide resulted in a significant increase in the biochar adsorption capacity. The change in colour of this biochar with washing combined with improved hydrophilicity indicated that tars were likely being removed from the biochar surfaces. However, as washes with only the detergent or surfactant had minimal impact on the adsorption capacity, it was hypothesized that most tars were removed from the biochar surfaces and not from the pores; if pores remained clogged with tars then available porosity would not increase and adsorption due to porosity would not change. The increase in adsorption capacity could instead be primarily attributed to oxidation from the hydrogen peroxide to increase the oxygen containing functional groups such as carboxyl groups on the biochar surfaces. A study discovered that biochar made from peanut hulls that was washed with 10% hydrogen peroxide solution showed an increase in surface carboxyl groups which resulted in enhanced sorption capacity [105]. Other studies determined that washed biochar from pinewood with hydrogen peroxide solutions of concentrations up to 30% w/w and measured the effect on many parameters including methylene blue adsorption [106]. The methylene blue adsorption increased for washes with low hydrogen peroxide concentrations (1 and 3% w/w) and then decreased and became lower than the unwashed biochar for solutions larger than 10% w/w. The hydrogen peroxide washes altered surface functional groups and the extent of this alteration affected the methylene blue adsorption.

The effect on adsorption capacity of washing varied with biochar source. For the biochar from woodchips and Storm Fisher Digestate it is hypothesized that the methylene blue adsorption was increased by a combination of tars being removed from pores and from oxidation of functional groups on the biochar surfaces.

Compounds can be leached from biochar and cause contamination in amended soils. Figures 3-5 and 3-6 showed that washing removed components from biochar, leaving behind fewer components that could be leached from the biochar into soils. It is hypothesized that biochar from SFD has large deposits of tars on its surfaces. This contributed to its dark colour and hydrophobic behavior. Washing removed significant amounts of these tars; washes containing SDS or Triton were the most effective. As large amounts of surface tars were significantly removed by washing, the reduction in organic leachate from the washed biochar was significant, approaching 50% reduction for a wash solution of Triton and hydrogen peroxide (Figure 3-5).

Some deposits of tars on the surfaces of biochar from BFD were removed with washing as shown by its changes in colour, hydrophobic behavior and reduction in organic leachate. However, it is hypothesized that washes containing hydrogen peroxide also interacted with functional groups on these biochar surfaces. This increased the adsorption capacity, but also allowed conductive ions to be released resulting in a reduction of inorganic compounds that could be leached from the washed biochar (Figure 3-6). A wash solution of Triton with hydrogen peroxide resulted in close to 70% reduction in leachable inorganic compounds from biochar from BFD.

Figure 3-7 shows, as an example, the GC-MS scans from the leachates of biochar from SFD unwashed and then washed with the degreaser solution. Six PAH compounds were specifically identified in the leachates: Phenanthrene, Anthracene, Benzo[a]anthracene, Benzo[b]fluoranthrene, Dibenzo[a,h]anthracene, Benzo[ghi]perylene. Washing the biochar reduced the amount of these PAHs in the leachate indicating that washing removed some tars that contained these compounds. Overall, the measured relative abundance in the leachate from the unwashed biochar was higher than that for the washed char. Therefore, in addition to the identified PAHs, other contaminants were present in the leachates and were reduced with washing.

Stable biochar improves carbon sequestration and the length of time that biochar provides benefits to the soil. An accelerated oxidation method estimated the interaction of the biochar within soil over time and was measured by the change in biochar mass with the accelerated oxidation procedure. As easily leachable compounds were removed through washing, washed biochar was then more stable than unwashed biochar in the sense of losing less of its mass due to oxidation (Figure 3-3). Since the mass loss was reduced after washing, this means that washing contributed to removing unstable components from the biochar to minimize its mass lost to the aging process. A large difference in mass indicates a relatively unstable biochar, which was identified in the unwashed cases, but not as much in washed cases. This study indicated a representation over hundreds of years of how biochar will interact within soil and how environmental impacts will affect its stability over time.

To better understand the effect of washing on biochar properties, experiments were developed to indicate if compounds were removed primarily from the biochar surfaces (exterior) or from the pores (interior). Table 3-4 compares the removal of tars from the particles exterior (Z_e) and interior (Z_i). Washing the biochar decreased the relative amount of compounds on the biochar exterior surfaces. There were differences between the biochars. The addition of hydrogen peroxide to the wash solution significantly improved the removal of external compounds from biochar from BFD. This complements the hypothesis that hydrogen peroxide interacted with the surface functional groups that improved adsorption and reduced inorganic compound leachability. The internal compounds from all biochars increased with time and with washing. By creating this reduction in external compounds allows for biochar to be more reliable in soils and have less effect on its hydraulic conductivity and water retention that conventional biochar powders are known to have.

Various washing solutions indicate various interaction mechanisms between the biochar powder and the washing solution mixture. Zep degreaser is chemically comprised of various alcohols, acids, and sodium olefins that form an emulsifier to attack oily components of biochar [107]. Emulsifiers contain a hydrophobic end that is attracted to the oil and fat component of materials to remove them [108]. In the case of an anionic surfactant, such as SDS, these surfactants work following ionization in water. When added to water, SDS ionizes and becomes negatively charged. These negatively charged surfactants bind to positively charged particles like oils, dirt, and clays in biochars to attack them and ultimately remove them which greatly impact hydrogen bonding and electrostatic interaction [109]. Lastly, in the case of an ionic surfactant, such as Triton, this surfactant works due to the hydrophobic aromatic group that attacks various oil components in the char making them less hydrophobic. This surfactant contains both hydrophobic and hydrophilic aspects to its chemical structure that make it effective as a surfactant to wash hydrophobic biochars [110].

3.5 Conclusions

Biochar pyrolyzed from biomass sources of two digestates and of woodchips were hydrophobic and exhibited leaching of compounds including carcinogenic PAHs. Washing the biochars improved hydrophilicity, enhanced adsorption due to increased available porosity and modified surface functional groups, improved stability and minimized leaching of various compounds. Washes with only water had minimal effect. The greatest improvement was for a wash containing Triton and hydrogen peroxide; the surfactant and emulsifier properties of the Triton were effective at removing tars from the biochar while the oxidizing effect from the hydrogen peroxide contributed to the modification of surface functional groups. Biochar differences were reflected in the effectiveness of each type of washing solution. Further research is required to optimize the concentrations of Triton and hydrogen peroxide and understand the complex interactions with the biochars. However, from these preliminary findings, washing biochars with a solution of Triton and hydrogen peroxide improves their properties for soil amendment.

3.6 References

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Chapter 4

4 An Investigation of Drum Granulation on Post-Pyrolysis Washed Biochar

4.1 Introduction

As a soil amendment, biochar has been recognized as a promising solution to the arising issues in the agricultural sector [1]. When implemented into soils, biochar has been proven to demonstrate an improvement in water retention, microbial activity and diminish heavy metals and leached nutrients in the soils [2-4]. These areas of improvement lead to reducing the need for irrigation and chemical fertilizer use, which in turn diminishes greenhouse gas emissions, and increases carbon sequestration.

Biochar, as a soil amendment, can reduce greenhouse gas emissions. Biochar soil amendment reduces the need for chemical fertilizers. Manufacturing emissions are therefore lower. Emissions of methane and nitrous oxide, two strong greenhouse gases, will be reduced [5-7]. Besides, converting biomass to biochar eliminates the emissions from natural degradation of biomass [6].

Dust generation from biochar is a crucial health issue, whether during the initial spreading onto soils or remaining on the surface of soils [8-11]. Biochar is a fine powder with particle sizes anywhere below 600 μm which could be easily blown away in many scenarios such as processing and handling, spreading, and also once in contact with the soil [12]. Biochar dust would add to the current agricultural dusts that already poses a health concern for agricultural workers [12, 13]. Another concern is the explosion risk of biochar dust [9, 11, 14]. Finally, biochar dust may contribute to global warming through radiative factors [16].

Biochar agglomeration has been shown to prevent product loss and avoid dust generation [17]. Pelletizing can compact biochar powders into small pellet shapes [18]. A study pelletized biochar to create a dense and robust product with high attrition resistance and in combination with Sphagnum peat has improved the hydraulic conductivity of the mixture [2]. However it was also determined that once placed in container nurseries that expansion at high pellet additions created problems in filling the containers [2]. Wet granulation is also a well-known process used for size enlargement of powders and improves dispersibility, flowability, and overall handling in past literature [19]. There are three main wet granulation processes which are high shear, fluidized bed, and drum granulation. Drum granulation presents itself as the best option of the three: it can be reliably scaled up to provide the large volumes required for commercial application. However, drum granulation has encountered issues in creating weak granules that tend to break before their soil application [20].

Hydrophobic granulation has been examined in past literature in the sense of high shear granulation, twin-screw granulation, and also wet drum granulation of hydrophobic powders [20, 22–25]. However, throughout the literature, hydrophobic biochar has only been wet drum granulated to produce granules for soil amendment applications. Previous findings determined that hydrophobic biochar can be wet drum granulated to produce adequately sized granules, but lack in resembling the strength of a conventional soil amendment product in the industry [20, 24, 25].

Granulation mechanisms depend on the hydrophilic or hydrophobic interactions between the liquid binder and powders. For hydrophilic granulation, the liquid binder solution penetrates quickly into the powder bed forming a granule nuclei that then progresses through coalescence and consolidation. However, for hydrophobic granulation, the liquid binder droplet sits on the powder bed surface, pulling powder particles up around the liquid droplet to form a liquid marble structure [26]. Hydrophobic biochar can be wet drum granulated into granules [20, 24, 25]; however hydrophilic biochar wet drum granulation has not yet been reported.

Biochar properties can be modified for specific applications such as soil amendment. Washing can remove adsorbed toxic components to improve germination and plant growth [27]. Washing can also remove tars from the surface and pores to increase the porosity and hydrophilicity, cation exchange capacity and adsorption characteristics [28]. Washing will ultimately create more hydrophilic biochar that will be easier to granulate within a drum granulation unit. Hydrophilic granulation can more easily handle variations in biochar characteristics. Past studies have also determined that hydrophobic biochars negatively impact the hydraulic conductivity and water retention of various soils [29], as biochar particles fill the voids among the soil particles and clog the pores of the soil. This reduces the soil hydraulic conductivity and water retention due to biochar hydrophobicity [29].

4.2 Methods and Materials

4.2.1 Biomass

Two biomass feedstocks were softwood woodchip (WCP) biomass and digestate from Bayview Flowers Greenhouse (BFD) in St. Catherines (Ontario, Canada) that contains mainly flower waste. A table summary of the two biomass properties is shown in Table 4-1.

Table 4-1. Summary of original biomass properties

Properties	WCP	BFD
Moisture content (wt%)	10	3
dp_{10} (mm)	0.4	0.1
dp_{50} (mm)	1.6	0.7
dp_{90} (mm)	3.5	2.7
Bulk density (kg/m^3)	180	590

4.2.2 Pyrolysis

The Pyrolytic Shaker Reactor (PSR) was used for pyrolysis (Figure 4-1). Dedicated electric shaker provided agitation, rapid heating by an induction system, and no sweep gas was used [30].

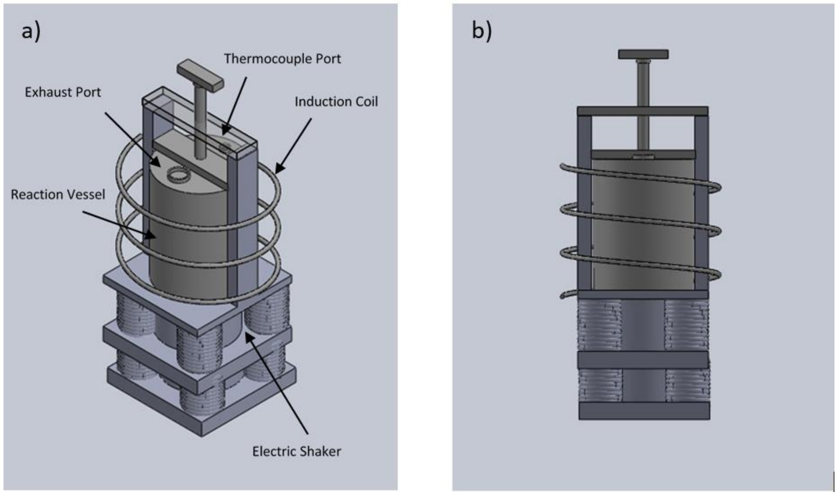

Figure 4-1. Schematic drawing of the Pyrolytic Shaker Reactor showing (a) trimeric view and (b) front view

The reactor vessel was filled to 2/3 of its volume with biomass, the vessel sealed and then secured into the shaker. Agitation and induction heating were provided until the bed temperature reached the target value of 400 ^{o}C. The reactor and its contents were cooled to room temperature. The biochar was recovered, milled, and then sieved to a particle size below 710 μm for further processing and testing.

4.2.3 Biochar Washing

A washing solution of 1 g of Triton (Triton x-100 or polyethylene glycol tert-octylphenol ether) per 100 ml of deionized water with 0.6 g of hydrogen peroxide (H_2O_2) was created. The biochar was vigorously mixed with the washing solution for 10 minutes in a ratio of 24 ml of washing solution per gram of biochar. The washed biochar was filtered using Fisherbrand® Filter Paper, CS-32, Quantitative Q5, Porosity – Medium, Flow Rate – Medium and then rinsed with large volumes of deionized water. The biochar was finally dried in an oven at 105 ^{o}C for approximately 16 h.

4.2.4 Biochar

The biochar powder was examined for hydrophobicity, particle size, bulk density shape and flowability potential.

The MED test was used to estimate the hydrophobicity of the unwashed biochar [31]. Droplets of aqueous ethanol solutions were carefully placed onto the biochar powder bed surface [26]. The time required for a droplet to penetrate into the bed was recorded. A higher required ethanol concentration to achieve drop penetration within 10 s indicates a higher degree of hydrophobicity [26].

For washed biochar, the drop penetration tests were conducted with deionized water as well as the 10, 20, and 30 wt% molasses binder solutions to be used for granulation. Long droplet penetration times indicate a high degree of hydrophobicity

Images of the biochar powders were taken and analyzed using Image-Pro. One hundred biochar powder particles were sampled from each trial randomly and placed on a white sheet of paper. This monogram image was then filtered for smoothing and the dark mode was selected to differentiate the small black individual particles from the white background. The circularity of the 100 biochar particles for each trial was calculated:

$$Circularity = \frac{4 * \pi * Area}{Perimeter^2} \tag{4-1}$$

The flowability potential was estimated through the static angle of repose (AOR). The AOR was measured using Geldart's angle of repose tester [32]. 30 g samples of each biochar were used for the measurements with trials conducted in triplicates and the average was determined.

4.2.5 Granulation

A drum granulator, shown in Figure 4-2, was used for the granulation trials [20]. The drum was made of Plexiglas and had an inner diameter of 7.5 cm, an inner length of 12.0 cm. A modified sparger allowed the binder solution to be added dropwise at three axial locations of h/L = 0.27, 0.53 and 0.80. The binder solution was added at a rate of approximately 4 ml/min. Previous work on drum granulation of biochar identified molasses as a suitable binder and a range of granulation operating parameters [32]. Table 4-2 summarizes the binder concentrations and amounts added for each trial. The drum was filled to 20 volume% with biomass, and the rotation rate was fixed at 40 rpm for all trials. The drum was rotated during binder addition and then continued for an additional 2 minutes of wet massing.

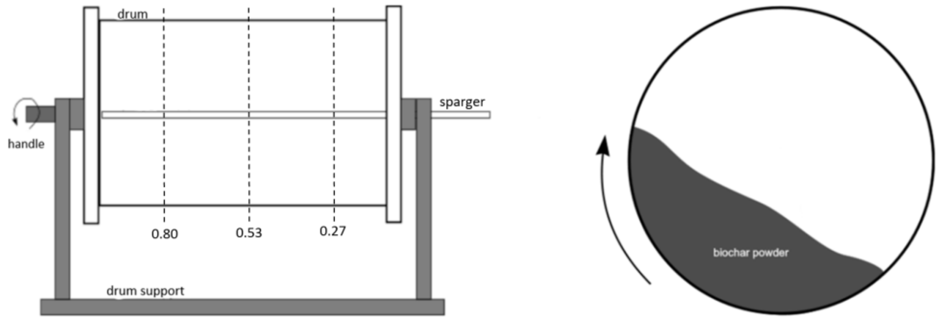

Figure 4-2. Schematic diagram of drum granulator unit used to granulate biochar powders

Table 4-2. Summary of various binder concentrations and binder solution amounts used for all granulation test trials

Binder concentration (wt%)	Binder ratios (g binder solution / g biochar)	
	WCP	BFD
10	0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7	0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7
20	0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7	0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7
30	0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7	0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7

4.2.6 Granule Characterization

Biochar granules were characterized for size, yield, skeletal density, shape, flowability potential and attrition resistance.

The granules size distribution was measured with sieves of 6.3, 4, 3.35, 3, 2.8, 2.36, 2, 1.4, 1.18, 1, 0.85, 0.60 mm sieves**.** Granules with diameters between 1 and 4 mm were defined as optimal granule size range, corresponding to conventional fertilizer granules [33]. Granules below this size range were classified as undersized (diameter smaller than 1 mm) and above this size range as oversized (diameter larger than 4 mm).

Mass-volume displacement was used to estimate the skeletal densities of granules. The mass of 25 granules and their volume displacement in acetone at 20 °C were used in the calculations.

Images of the biochar granules were taken to examine granule shape. As for the biochar granules, the images were examined using Image-pro and the circularity was calculated based on an average of 75 granules per trial.

The flowability potential of granules was estimated through the static angle of repose (AOR), measured using Geldart's repose tester angle [31]. 5 g samples of granules were used for the measurements with measurements for each trial conducted in triplicate.

Granule strength was estimated through attrition resistance testing which used a 5 g sample of biochar granules, and 50, 5 mm diameter steel beads were placed in the granulator drum [33]. The drum was rotated at the same speed used to produce the biochar granules (40 rpm) for 160 rotations, thus totaling 4 minutes per attrition trial. The granules were then separated from the steel beads and sieved with a 1 mm sieve and reweighed. The attrition resistance is defined as:

$$Attrition\ resistance\ (\%) = \frac{Mass\ of\ granules\ after\ test}{Mass\ of\ granules\ before\ test} * 100\% \qquad (4\text{-}2)$$

4.3 Results

Table 4-3 summarizes the biochar test results. There were differences between the two types of biochar; biochar from WCP was slightly smaller, and the more irregular shape contributed to a higher angle of repose. The bulk density of biochar from WCP was significantly lower than that of biochar from BFD, highlighting composition and structural differences. Hydrophobicity was the primary difference between unwashed and washed biochars. Unwashed biochars were very hydrophobic. Washing reduced the hydrophobicity significantly.

Table 4-3. Summary of various biochar powder properties for WCP and BFD

`	WCP					BFD				
Tests performed	Unwashed	Washed				Unwashed	Washed			
Molasses (wt%)	0	0	10	20	30	0	0	10	20	30
Drop penetration (s)	> 900	3	3	3.5	4	> 900	8	10	15	25
MED test (mol/L)	1.00	0				1.25	0			
dp_{10} (µm)	70	80				80	100			
dp_{50} (µm)	300	350				350	400			
dp_{90} (µm)	550	600				600	650			
Bulk density (kg/m^3)	165	170				505	520			
Circularity	0.32	0.35				0.37	0.42			
Angle of repose (°)	39.4	36.2				30.1	27.8			

Figure 4-3 shows the solids removed from the granulator drum using an example trial of 20 wt% molasses concentration and a 0.3 ratio of binder solution to biochar powder.

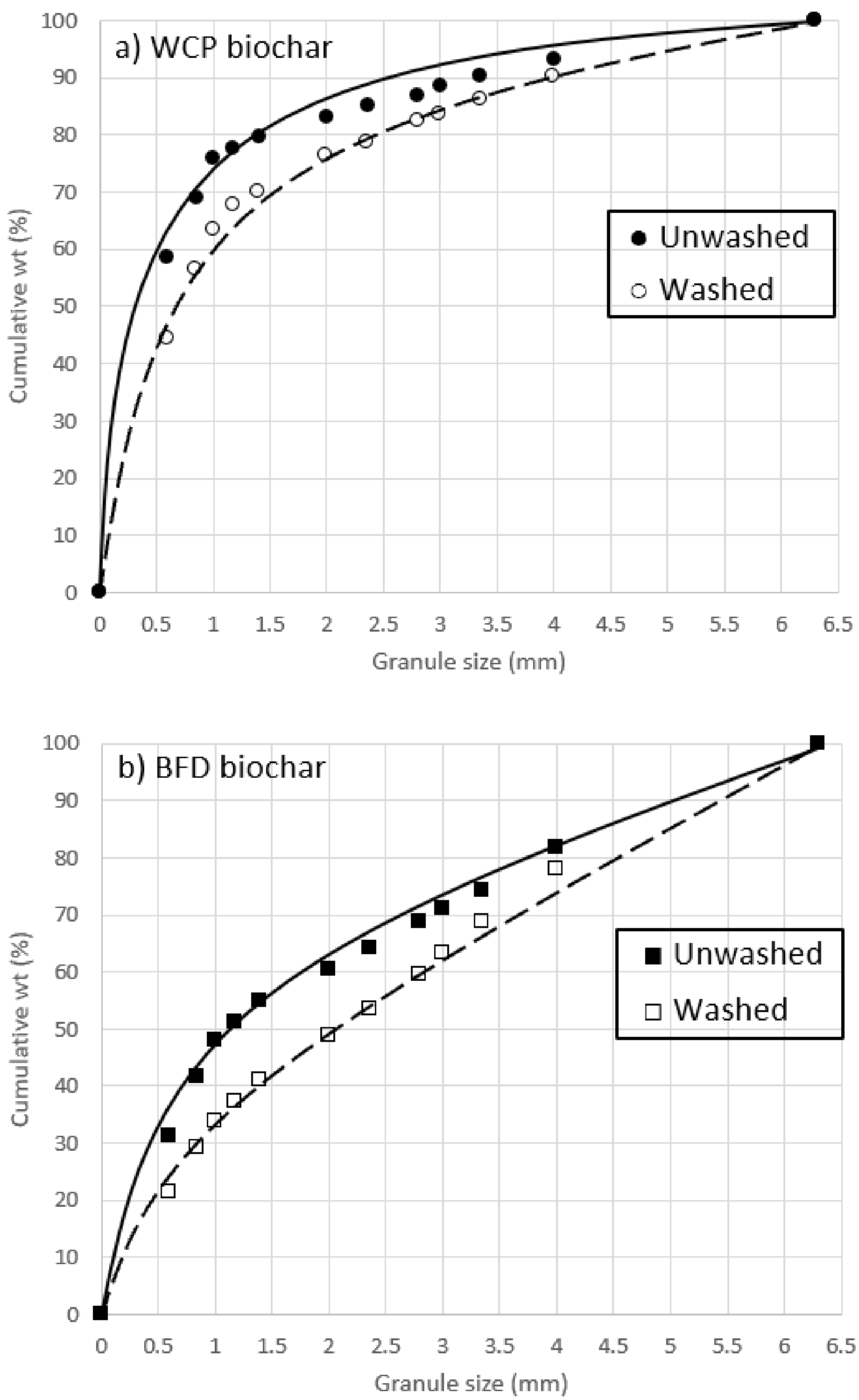

Figure 4-3. Solids removed from the granulator drum for trials of a binder solution with 20 wt% molasses added at a binder solution to biochar ratio of 0.3 for (a) WCP biochar and (b) BFD biochar

The granulator solids exhibited a range in sizes and there were differences between unwashed and washed biochars indicating overall an impact of washing on granulation; granulated washed solids were larger than granulated unwashed solids.

Increasing the binder solution to biochar ratios increased the yield of optimally-sized granules. Solids from the granulator were sieved into undersized (<1 mm), optimal range (1-4 mm) and oversized (>4 mm) fractions. Figure 4-4 shows the fractions yields for trials at a 20 wt% molasses binder solution. Appendix B analyzes the confidence interval of this trial to understand the reproducibility errors from the experiment. For unwashed biochar the yield of optimal granules increased and then reached a plateau as more binder solution was added while the yield of undersized and oversized solids increased throughout the addition of binder solution. The profiles for washed biochar were different indicating another granulation mechanism. The yield of optimal granules increased for washed biochar and then reached a plateau at a higher binder solution to biochar ratios. The fraction of oversized solids increased throughout. The fraction of undersized solids initially increased and then decreased as more binder was added for biochar from WCP.

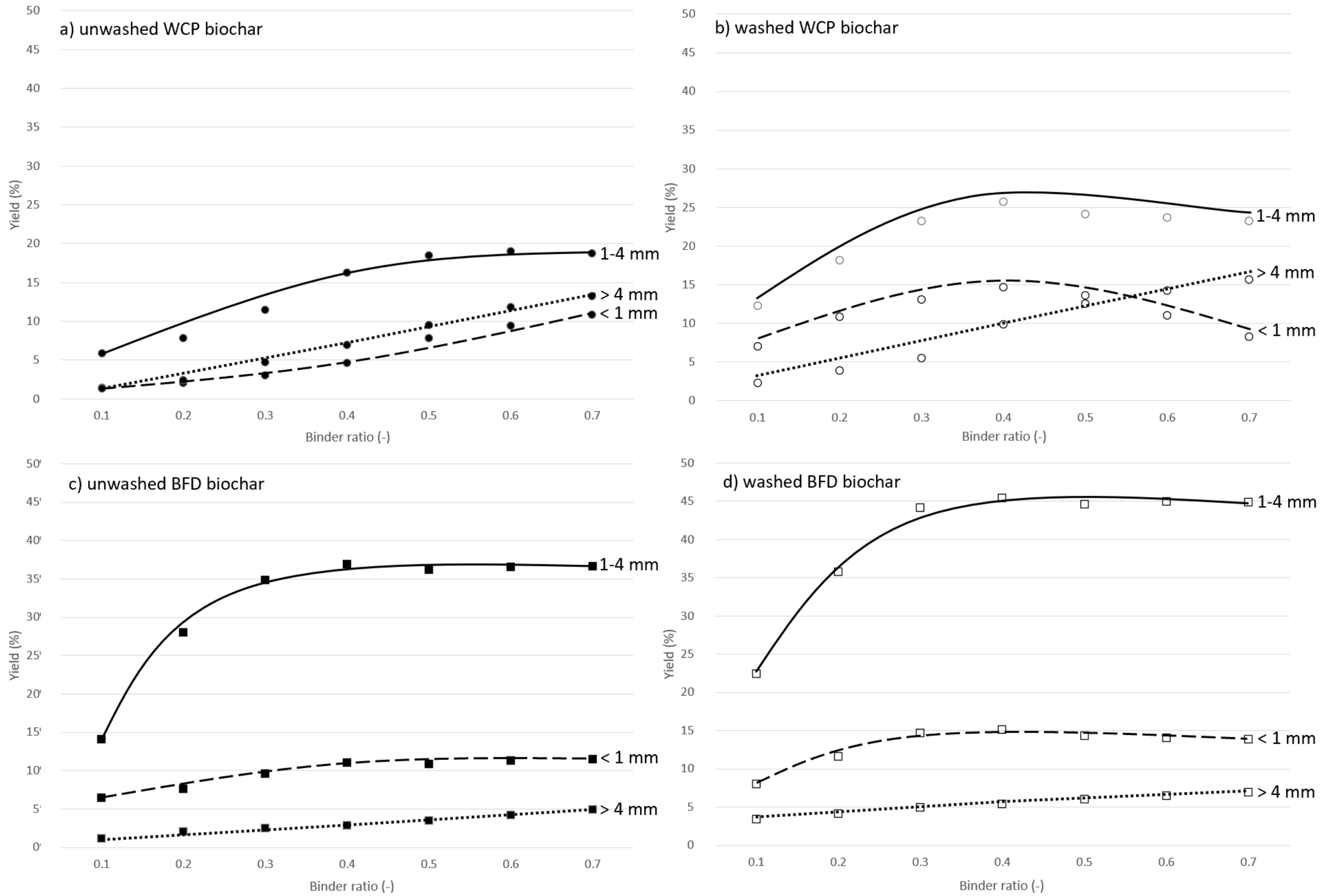

Figure 4-4. Yields of solids in undersized, optimal range and oversized fractions for (a) unwashed WCP biochar, (b) washed WCP biochar, (c) unwashed BFD biochar, and (d) washed BFD biochar

There was an optimum molasses concentration in the binder solution, for which the yield of optimally-sized granules was maximized. Figure 4-5 shows the yields for the optimal size granules. For all granulations, the yields increased with the molasses concentration in the binder solution. Granule yields initially increased but reached plateaus or decreased slightly as more binder solution was added.

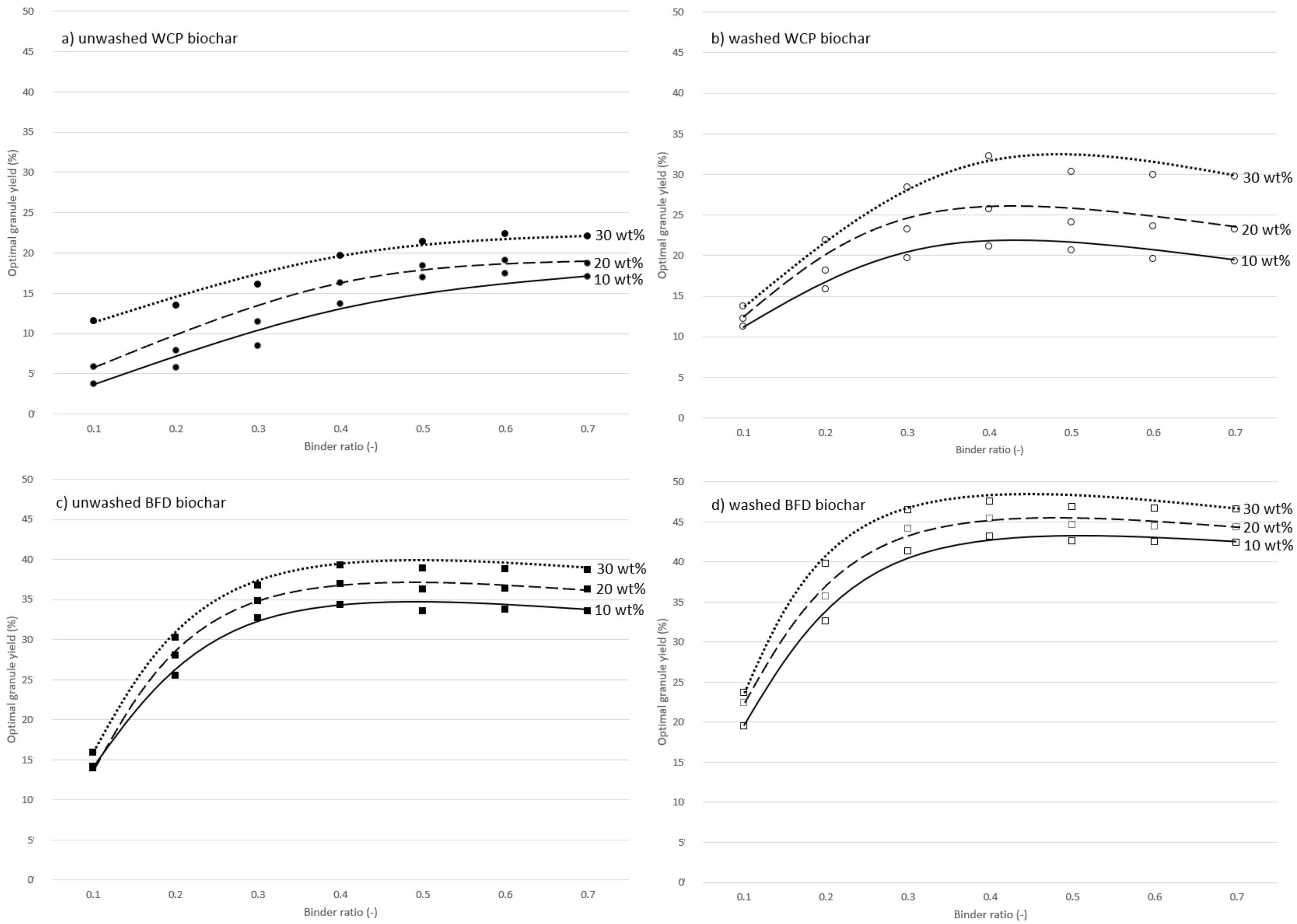

Figure 4-5. Yields of optimal size granules for (a) unwashed WCP biochar, (b) washed WCP biochar, (c) unwashed BFD biochar, and (d) washed BFD biochar

Figure 4-6 shows that adding more molasses to the binder solution increased the granules attrition resistance. Appendix C analyzes the confidence interval of 20 wt% molasses trial to understand the reproducibility errors from the experiment. The attrition resistance reached almost 95% for granules formed from washed biochar from WCP. The effect of the molasses concentration in the binder solution was significant for biochar from BFD. It showed only minor effects for biochar from WCP reflecting the biochar differences from their biomass source and their interactions with the binder solution.

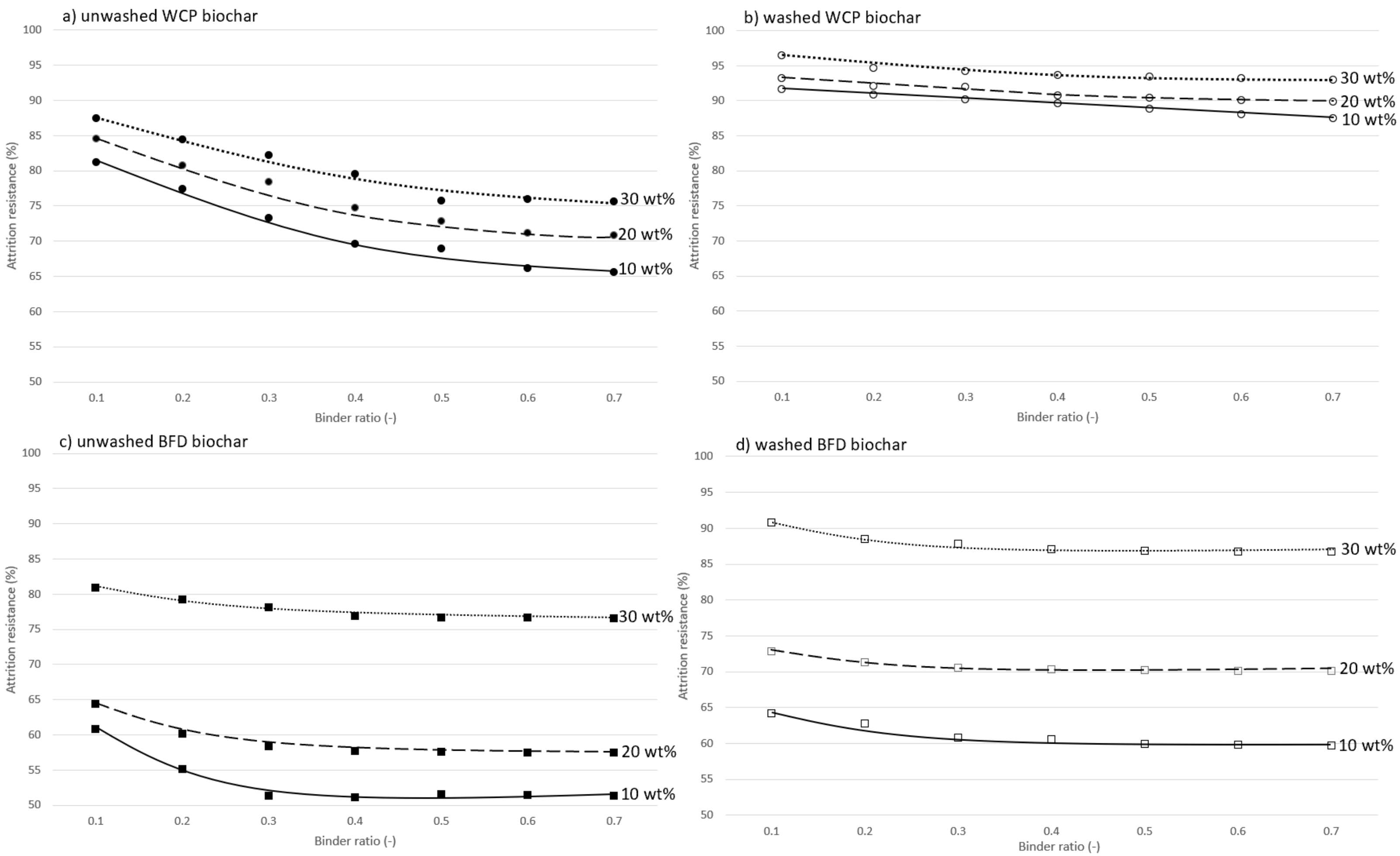

Figure 4-6. Attrition resistance of optimal size granules for (a) unwashed WCP biochar, (b) washed WCP biochar, (c) unwashed BFD biochar, and (d) washed BFD biochar

Figure 4-7 shows that granules formed from washed biochar were denser than granules formed from unwashed biochar. This indicates differences in granulation mechanisms.

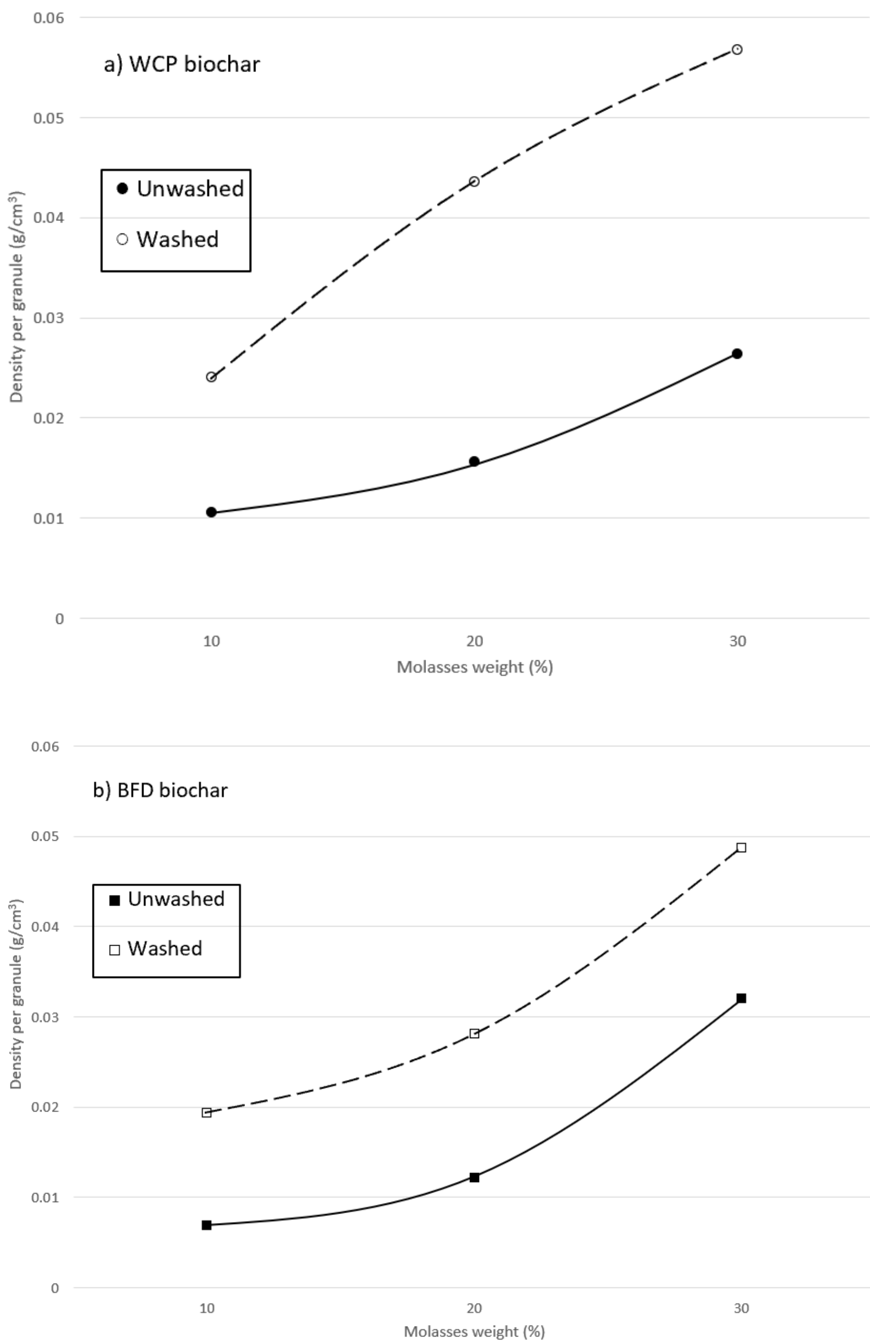

Figure 4-7. Density of optimally sized granules for (a) WCP biochar and (b) BFD biochar

Table 4-4 summaries the circularity of granules in the 1-4 mm size range. Granules from washed biochar were less spherical than granules formed from unwashed biochar. Again, this indicates differences in granulation mechanisms.

Table 4-4. Average circularity of optimally sized granules produced from three trials

Biochar powders	Circularity (-)
Unwashed WCP	0.80
Washed WCP	0.78
Unwashed BFD	0.87
Washed BFD	0.83

4.4 Discussion

Biochar powder properties are summarized in Table 4-3. Biochar particles were irregular in shape and had average diameters in the range of 300-400µm. The angle of repose indicated that biochar from WCP biomass would exhibit fair flowability at values higher than 30°, and biochar from BFD biomass would have good to excellent flowability by containing values of 30° and below [32]. Powder flowability is critical in drum granulation; a cascading flow regime is recommended for drum granulation to promote binder dispersion and optimal granule formation and growth. Cascading flow was achieved and confirmed with visual observation with the biochar powder at the specified drum rotation rate at 30 rpm.

Figure 4-3 confirmed particle size enlargement from granulation and differences in this enlargement between unwashed and washed biochar powders. Hydrophobicity was the property that showed the most significant difference between unwashed and washed biochar powders. Observations of the granule properties confirm that granulation of unwashed biochar followed a hydrophobic layering mechanism while granulation of washed biochar followed a hydrophilic coalescence mechanism or a combination mechanism.

Binder solution droplets did not penetrate the beds of unwashed hydrophobic biochar powder. Instead, the droplets rolled down the inclined powder bed, accumulating particles on the droplet surface to form a hollow marble structure. The rotating drum provided continuous agitation of the powder bed and allowed further layering of particles on the hollow marble structures. It also renewed the powder bed surface exposed to the binder addition, allowing more hollow marble structures to be created. This mechanism formed very circular granules (Table 4-4) with a low density due to the hollow structure (Figure 4-7) that started small and grew in size and number as the liquid binder was added (Figure 4-4). At high liquid binder additions, the yield of granules within 1-4 mm in diameter became constant as the growth of undersized granules to beyond 1 mm balanced the growth of granules beyond 4 mm into the oversized range.

The liquid binder solution affects the formation of the liquid marble structures. Previous research found that liquid marble structures could be more easily formed with lower viscosity binder solutions [26]. However, granule structures formed with more concentrated binder solutions may be more robust, as shown by the progressively higher attrition resistance as the molasses concentration of the binder solution was increased from 10 to 30 wt%. Although more liquid marble structures may have initially formed from the 10 wt% molasses concentration binder solution, the structures from the 30 wt% solution would have been more robust and therefore remained intact to provide slightly higher yields within the 1-4 mm range.

The surface chemistry of the powder-liquid binder system has been observed to affect the formation of liquid marble structures, although the interactions are complex and not known and understood [26]. Previous work indicated differences in the composition and surface chemistry of biochar from BFD and WCP [34]. This contributed to the observed differences in the yield and strength of granules created from unwashed biochar.

Washing the biochar, a Triton and hydrogen peroxide solution removed components such as tars and altered the surface chemistry through modification of functional groups. This changed the biochar from very hydrophobic to only slightly to moderately hydrophobic for the washed biochar from WCP and BFD, respectively [34]. As shown in Table 4-3, the molasses binder solutions penetrated the bed of washed biochar from WCP within 3 to 4 s, while the penetration times ranged from 8 to 25 s for the washed biochar from BFD. Therefore, it is proposed that washed biochar from WCP followed a hydrophilic coalescence mechanism, and washed biochar from BFD followed a combination mechanism.

The molasses binder solution droplets penetrated very quickly into the bed of washed biochar from WCP. The droplets wetted the particles to form granule nuclei. Further addition of the binder created more nuclei. The agitation provided by the rotating drum promoted coalescence of the nuclei to grow granules into the 1-4 mm optimal size range. The granules continued to grow, eventually resulting in a decrease in the number of granules less than 1 mm in diameter (Figure 4-4). The yield of granules in the 1-4 mm range plateaued as the growth of granules from below 1 mm balanced the growth of granules beyond 4 mm.

Increasing the molasses concentration of the binder solution improved both the yield and attrition resistance of granules in the optimal size range made from washed biochar from WCP (Figures 4-5 and 4-6). Increasing the molasses concentration increased the viscosity of the binder solution. For coalescence and thus growth, granules must deform with collision. Increasing the binder solution viscosity by adding more molasses reduced the rate of granule growth; viscous dissipation inhibits the required movement of liquid within the pores of the granules required for deformation for coalescence. However, higher molasses concentrations in the binder solution would have increased capillary forces to strengthen bonds between particles within a granule resulting in more robust granules with higher resistance to attrition and breakage. Therefore, although the rate of granule growth was lower for binder solutions with high molasses concentrations, the granules formed were strong and remained intact during granulation.

Granules formed from washed biochar from WCP were irregular in shape with a circularity of 0.78 (Table 4-4) and showed high relative densities ranging from 0.024 to 0.057 g/cm^3 (Figure 4-7). This is expected from a hydrophilic granulation mechanism. Coalescence results in irregular shape granules. With only a short wet massing time of two minutes and relatively low shear agitation from the drum rotation at 30 rpm, the granule consolidation to a very dense and circular shape was limited.

The granule density formed from washed biochar from WCP was higher than granules formed from this unwashed biochar. The droplet penetration to form granule nuclei provides a denser granule core compared to the hollow marble structure formed with the unwashed biochar.

The washed biochar from BFD exhibited moderately hydrophobic behavior; the molasses binder solutions had drop penetration times of 10 to 25 s (Table 4-3). It is therefore proposed that this biochar granulation followed a combination mechanism. Droplets initially formed liquid marble structures that later collapsed to form granule nuclei of particles linked through liquid bridges. The formation of nuclei increased the yield of granules within 1-4 mm compared to the unwashed biochar granulation (Figures 4-4 and 4-5). However, the delay in forming nuclei reduced the number of granules that coalesced to sizes larger than 4 mm. Therefore, the yields of granules from washed biochar from BFD were the highest obtained of all the granulation trials, reaching almost 45% yield (Figure 4-5). The granule spherical shape and strength improved from unwashed biochar, but did not reach granule values from washed biochar from WCP as the delayed nuclei formation reduced granule consolidation opportunities.

Molasses as a binder has an effect on the fertility of soil. Aside from the beneficial aspects of biochar to soil, molasses also proves to provide a source of nutrients to soils and microorganisms living within those respective soils [35]. By providing a source of potassium to soil, it improves biochar further as a soil amendment. The consumption of molasses by microorganisms allows for biochar granules to break down in soil as well as promotes and increases microbial activity and growth within this soil over time [35].

4.5 Conclusions

Unwashed and washed biochar from two biomass sources was wet granulated in a drum granulator to determine the impact of washing on granulation. Unwashed biochar was very hydrophobic, and the granulation of this biochar proceeded through a hollow marble layering mechanism. This produced spherical, low-density granules with a limited yield of granules in the optimal 1-4 mm in diameter range. Washing the biochar with a Triton and hydrogen peroxide solution significantly reduced the hydrophobicity of biochar from softwood woodchips and moderately reduced the hydrophobicity of biochar from digestate. The low hydrophobic biochar from softwood woodchips granulated through nuclei coalescence and consolidation to form dense and robust granules. The moderately hydrophobic biochar from digestate granulated through a combination mechanism wherein hollow marbles formed, collapsed and, coalesced for granule growth. Washing biochar reduced hydrophobicity and changed the granulation mechanism to produce stronger and denser granules with higher yields of granules in the 1-4 mm optimal size range.

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Chapter 5

5 Final Discussion and Conclusions

Biochar has demonstrated properties of being an effective soil amendment. When used as a soil amendment biochar displays a reduction in chemical fertilizers and irrigation thus cutting down greenhouse gas emissions and subsequently sequestering carbon. Biochar also provides water retention and increases microbial activity in soils, when applied correctly. However, untreated biochar can limit its benefits, damage soils, and generate health concerns when spread onto soils. A solution to optimize its benefits to soil is through a pre-treatment washing method using different surfactants and an oxidizing agent. The modification of chemical and physical characteristics results in maximizing its contribution to soil while removing harmful compounds and enlarging the biochar particles to diminish dust hazards. Following this, the most effective washed biochar is then wet drum granulated and compared to unwashed biochar granules to further improve dust elimination and increase granular characteristics. Minimal research has been conducted on the washing of biochars to improve its characteristics for soil amendment along with no research utilizing a surfactant and oxidizing agent wash. A study demonstrated the optimization of wet drum granulation on various untreated biochar powders for soil amendment applications using multiple binders and optimizing granulation parameters. With varying granulation parameters studied a mild conditioned granulation trial was chosen based off their findings. Therefore, the two overall objects of this research were to investigate an effective pre-treatment washing method to improve biochar powder properties and secondly, to wet drum granulate this pre-treated biochar and compare the granular differences to untreated biochar while maintaining drum granulation parameters constant.

Experiments were performed to evaluate the differences the pre-treatment washing made on the biochar powder which included: Hydrophobicity (MED test and drop penetration test), colour difference, stability, adsorption, organic and inorganic contaminants, and polyaromatic hydrocarbon (PAH) contaminants. Following this the granulation of biochar was performed in a lab scale drum granulator that used a serological pipette for liquid binder solution addition. An interval timer was used to determine the rotational speed of the drum and the binder concentrations and volume additions were constant for all granules produced. Experiments were conducted to evaluate the differences the pre-treatment washing made on the biochar granules which included: granules yield, attrition resistance, average granular density, flowability and circularity.

Three different biochars (woodchips, Bayview Flowers digestate and Storm Fisher digestate) were washed along with 4 different washing liquids (deionized water, degreaser, sodium dodecyl sulfate and Triton x-100). The same washing procedure was performed for each biochar and each solution tested. On the other hand, for granulation, two biochars (woodchips and Bayview Flowers digestate) were tested along with molasses as the binder of choice in the granulation runs. The biochar-binder solution interactions differentiated between the two biochars tested due to their hydrophobic properties which then impacted their granulation mechanisms. The granulation parameters remained constant for each run to isolate only the differences in the granules with respect to the washing done previously. The research showed that both washed and unwashed biochars can be wet drum granulated, however their physical characteristics were different. The experimental results in both studies showed the need to understand the physical and chemical attributes of the biochar powders and the physical make-up of biochar granules to be an effective product for soil amendment applications.

The washed biochars were found to decrease hydrophobicity, black pigments in the char, organic and inorganic contaminants, PAH compounds as well as increase stability and adsorption. From the previous study the drop penetration tests indicated that the washed biochar powder was less hydrophobic. Therefore, the washed biochar was successfully granulated into granules with a larger fraction being with the optimal size range (1-4 mm) then the unwashed granules. Further granule property testing found that the granules that were washed had improvements in granular strength and density but maintained a similar circularity and flowability to unwashed granules.

In concluding, by producing biochar through the pyrolysis of various biomass deems that there are multiple types of biochars that can be an effective soil amendment. The research conducted demonstrated that three different biochars were able to be pre-treated to decrease its hydrophobicity and allow wet granulation to occur. These findings allowed the modification of biochar to be possible and further increase its physical and chemical characteristics to allow the potential of any biochar becoming an effective soil amendment. Also, the research demonstrated that through this pre-treatment method that wet granulation can be successful in cultivating these biochar granules into damaged soil environments.

5.1 Future Work

In terms of future works there are multiple directions to head towards from this research: This includes (a) optimizing the washing operation in terms of concentration of the washing solution added and optimization strategy for the length of time the biochar is spent in the washing solution before rinsing and filtering. By exploiting the washing solution there are optimal parameters to be found to maximize its effectiveness on the char. This also can include further work in the addition of a second oxidizing agent or other washing solutions that can increase the chemical properties of biochar further. Secondly, (b) would be to optimize the granulation parameters used in this study to further understand which optimal rotational speed, binder concentration, and binder volume added is to produce the maximum number of granules. Stemming from this another characteristic to discover during granulation is a method to remove/sieve the granules from the granulator and continue the granulation process in order to optimize the number of granules made per run. Next, (c) the research was conducted using a lab scale granulator unit. There would be large amounts of granules needed for soil amendment applications, thus a scale up would be required and studied. Lastly, (d) only one binder was chosen in this study. In order to understand which binder is the most effective towards optimizing biochar granules as a successful soil amendment would be to utilize this study with other binders in order to enhance other properties needed for soil amendment such as microbial activity, nutrient addition and overall balance to soils.

Appendix

Appendix A: Calculation description of the external and internal compounds from toluene extraction liquid

Example: Washed (Triton + H_2O_2) BFD biochar toluene extraction for 1 hour

1. Value of Z measured was found based on the spectrophotometer reading:

$$Z_{measured} = Z_e + Z_i = \frac{Y - Y_0}{Y_\infty - Y_0} * 100\ \%$$

Z_e represents the external compound percentage

Z_i represents the internal compound percentage

Y represents the spectrophotometer reading of the toluene sample at time, t

Y_0 represents the spectrophotometer reading of the toluene sample at time = 0

Y_∞ represents the spectrophotometer reading of the toluene sample at time = ∞

$$Z_{measured} = 50.6\ \%$$

2. Using Crank's model for interior contaminants, Z_i can be calculated assuming the biochar particles are perfect spheres:

$$Z_i = \frac{M_t}{M_\infty} * 100\ \%$$

M_t represents the ratio of the mass of compound removed at time, t

M_∞ represents the mass of compounds through the particle at infinite time

$$Z_i = 15.5\ \%$$

3. Finding a regression for data at time, t by assuming values of Z_e to minimize the error of $Z_{measured}$ Vs $Z_{calculated}$

- Compared equations of fitting $Z_i = (Z_{measured} - Z_e) = \frac{M_t}{M_\infty}$ and solving $Z_{calculated} = Z_e + Z_i(t)$
- Using excel solver to find an error value as close to zero as possible for $Z_{measured}$ Vs $Z_{calculated}$

4. Calculating the error value for $Z_{measured}$ Vs $Z_{calculated}$ to be as close to zero as possible

$$Error\ value = 1.46\ \%$$

5. Find $Z_{calculated}$ based off error value

$$Z_{calculated} = 49.1\ \%$$

$$Z_{calculated} = Z_e - Z_i = 33.6\ \% + 15.5\ \% = 49.1\ \%$$

Appendix B: +/- 95% confidence interval data for granules produced in the optimal size range (1-4 mm)

Curve fitting and confidence intervals were obtained with TableCurve 2D software.

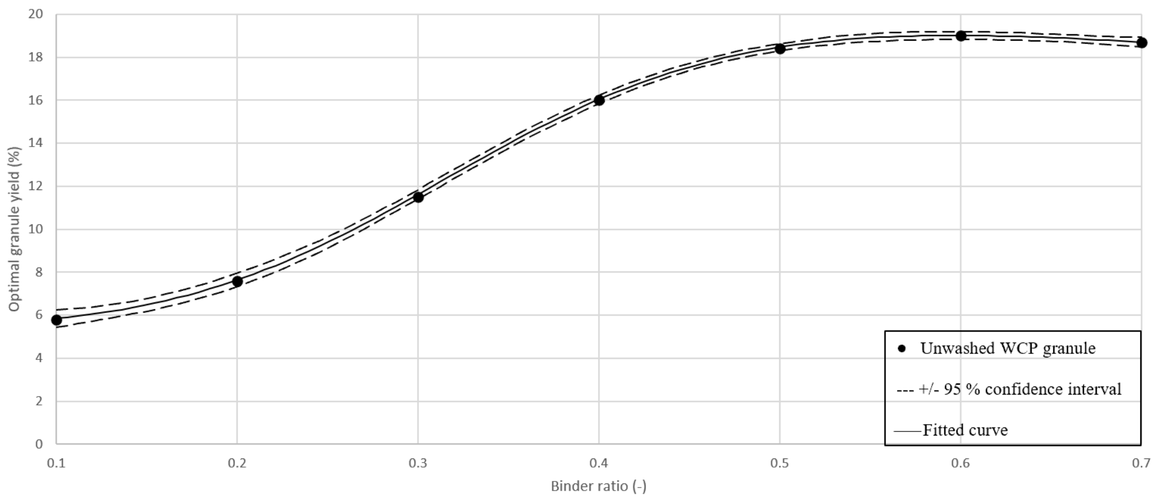

Figure B-1: Yields of optimal size granules for unwashed WCP biochar at 20 wt% molasses. Confidence intervals represent the maximum and minimum errors

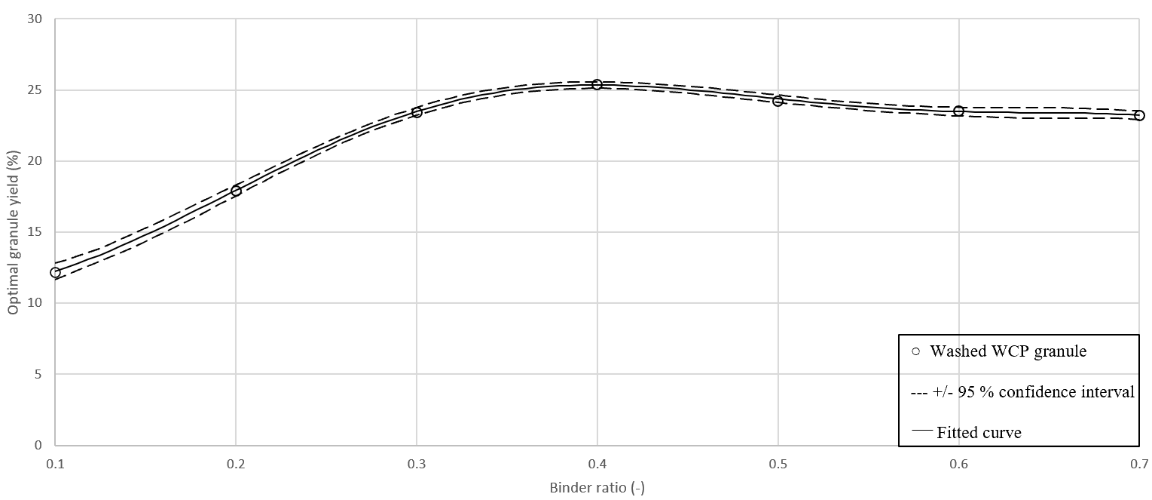

Figure B-2: Yields of optimal size granules for washed WCP biochar at 20 wt% molasses. Confidence intervals represent the maximum and minimum errors

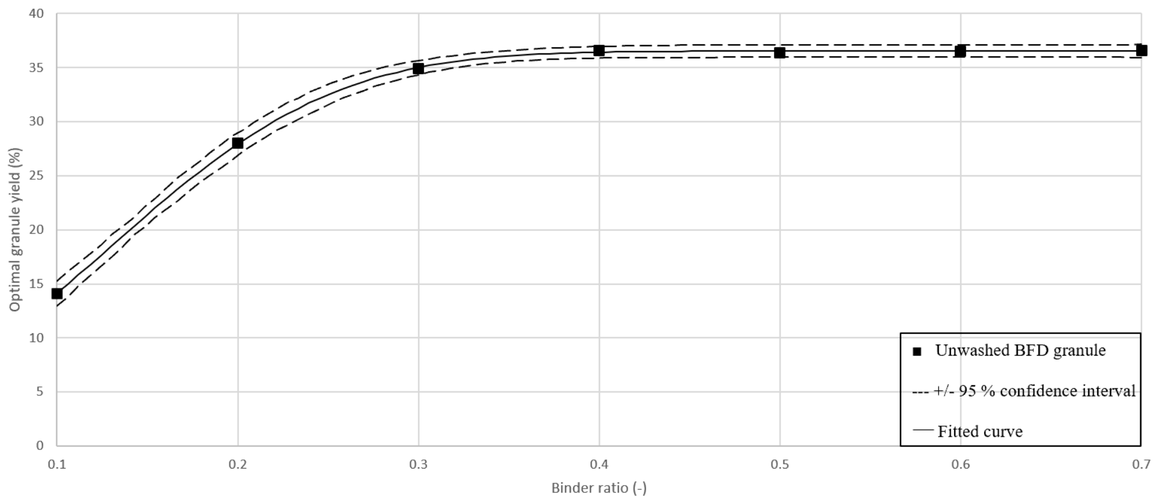

Figure B-3: Yields of optimal size granules for unwashed BFD biochar at 20 wt% molasses. Confidence intervals represent the maximum and minimum errors

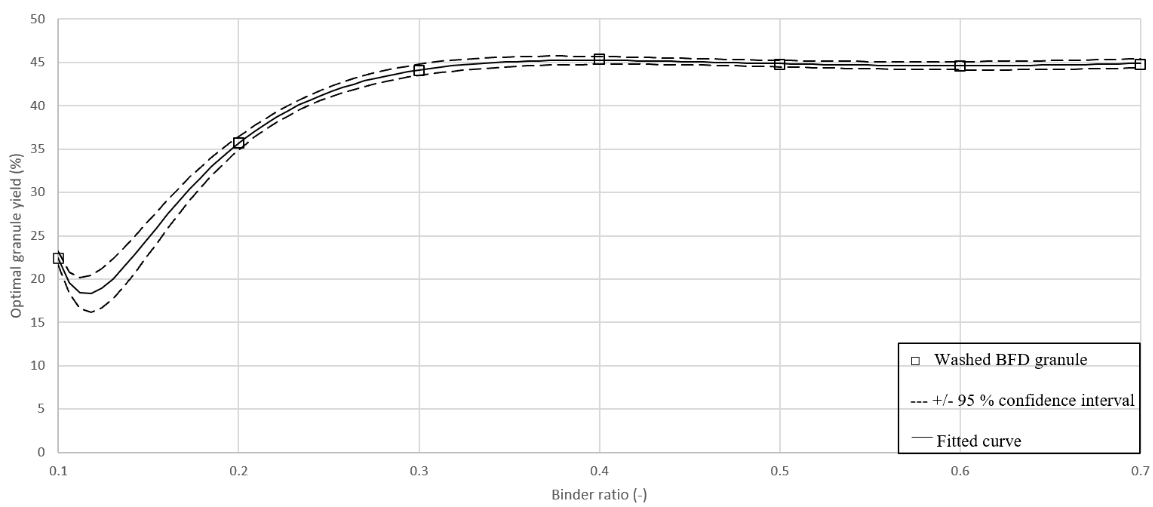

Figure B-4: Yields of optimal size granules for washed BFD biochar at 20 wt% molasses. Confidence intervals represent the maximum and minimum errors

Appendix C: +/- 95% confidence interval data of granular attrition resistance (1-4 mm granules)

Curve fitting and confidence intervals were obtained with TableCurve 2D software.

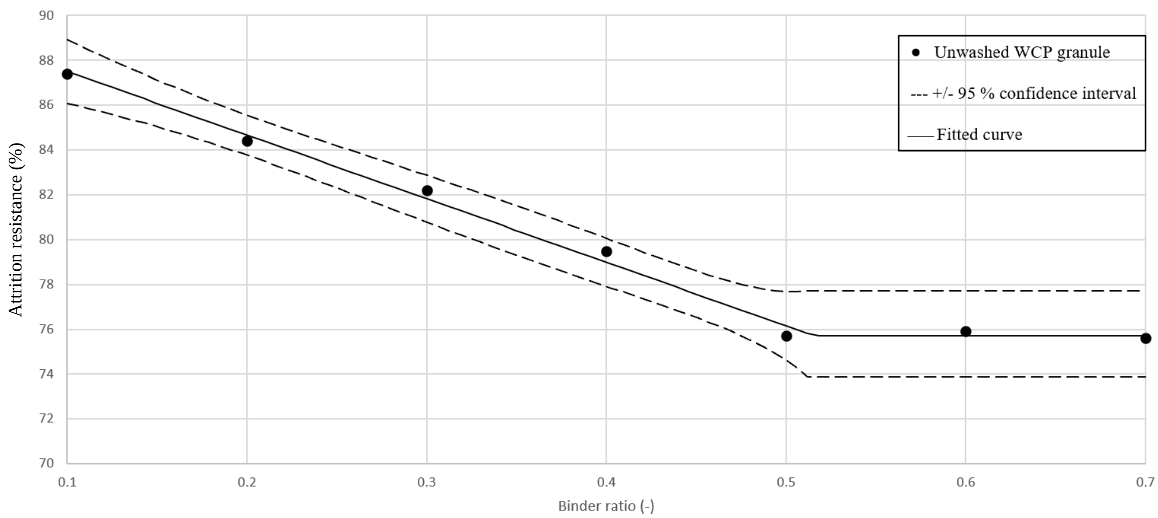

Figure C-1: Attrition resistance of optimal size granules for unwashed WCP biochar at 30 wt% molasses. Confidence intervals represent the maximum and minimum errors

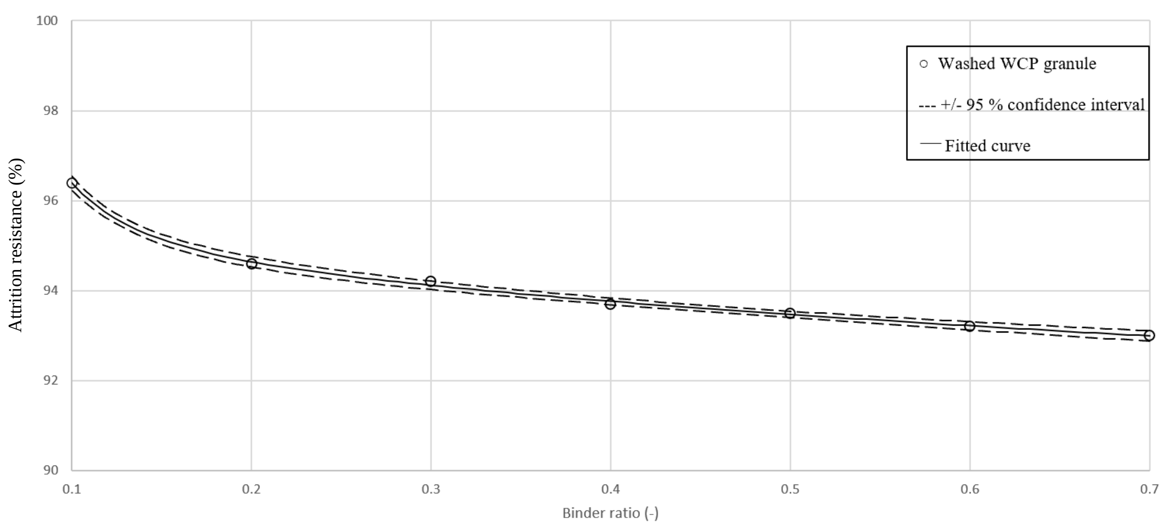

Figure C-2: Attrition resistance of optimal size granules for washed WCP biochar at 30 wt% molasses. Confidence intervals represent the maximum and minimum errors

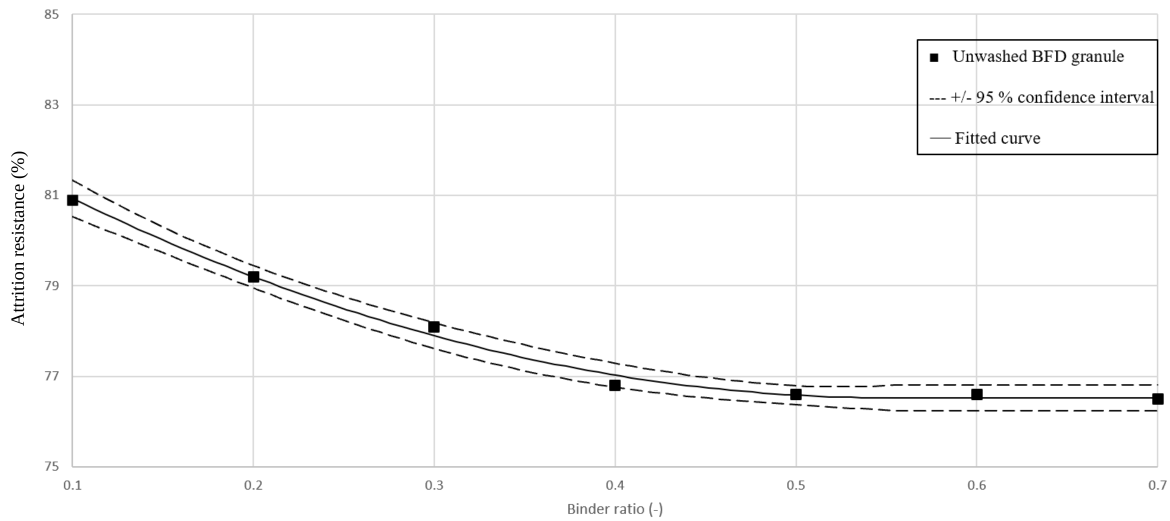

Figure C-3: Attrition resistance of optimal size granules for unwashed BFD biochar at 30 wt% molasses. Confidence intervals represent the maximum and minimum errors

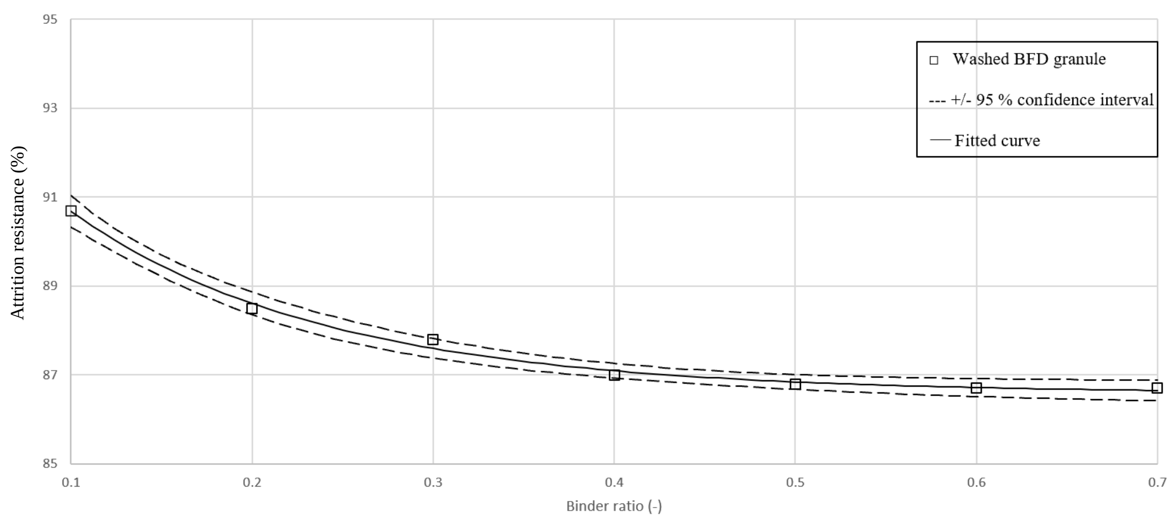

Figure C-4: Attrition resistance of optimal size granules for washed BFD biochar at 30 wt% molasses. Confidence intervals represent the maximum and minimum errors

Curriculum Vitae

Anthony Fazzalari

Post-secondary Education and Degrees:

Master of Engineering Science **2019-2021**
Chemical and Biochemical Engineering
Western University, London, Ontario, Canada

Bachelor of Engineering Science **2014-2019**
Chemical and Biochemical Engineering
Western University, London, Ontario, Canada

Honours and Awards:

Dean's Honour List **2018-2019**
Faculty of Engineering
Western University, London, Ontario, Canada

Western Admission Scholarship **2014-2015**
Western University, London, Ontario, Canada

Related Work Experience:

Teaching Assistant, Chemical and Biochemical Engineering **2019-2020**
Western University, London, Ontario, Canada

Professional Engineering Internship **May 2017 – September 2018**
FAG Aerospace – Schaeffler Group: North America
Stratford, Ontario, Canada

Summer Engineering COOP Student **May 2015 – August 2015**
Alton Farms Estate Winery
Plympton-Wyoming, Ontario, Canada