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Granulation of Biochar for Soil Amendment

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A thesis submitted in partial fulfillment of the requirements for the Master of Engineering Science degree in Chemical and Biochemical Engineering

GRANULATION OF BIOCHAR FOR SOIL AMENDMENT

(Thesis format: Integrated Article)

by

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Abstract

Biochar has shown potential as a soil amendment, but is a fine powder that is difficult to handle and would be blown away if applied to soils without modifications. Wet drum granulation of cornstalk biochar using binder solutions of hydroxypropyl methylcellulose was initially investigated, establishing that biochar could be granulated into a form that would be easier to handle and apply effectively to the soil. Biochars from three different feedstocks were then tested along with three binder solutions. The biochar granules were free flowing and relatively strong with a significant yield between a size range of 1 to 4 mm. The binder concentration, total binder solution volume and drum rotational speed affected both the optimal granule size yield and granule strength to different extents depending on the biochar and binder combination. The research showed that biochar could be granulated using wet drum granulation with adjustment of process parameters to ensure production of granules with specified properties.

Keywords

biochar, soil amendment, drum granulation, granule properties, binder solutions, hydrophobic interactions

Co-Authorship Statement

Chapter 3 is a research study that has been published in a peer-reviewed journal. Chapters 4 and 5 are research studies that will be submitted to an international peer-reviewed journal. The authors' individual contributions are stated below for each journal article.

Chapter 3: An investigation of drum granulation of biochar powder

Authors: Breanna Bowden-Green and Lauren Briens

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B. Bowden-Green conducted all experimental work including granulation and granule testing. Data analysis was conducted by B. Bowden-Green with assistance from L. Briens. Manuscript was jointly written and revised by B. Bowden-Green and L. Briens.

Chapter 4: A comparison of wet drum granulation of three different biochar powders

Authors: Breanna Bowden-Green and Lauren Briens

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Granulation of birchbark biochar powder was conducted by B. Poitras, H. Elkolaly and B. Weiler as a third year chemical engineering project. B. Bowden-Green conducted all other experimental work including granulation and granule testing. Data analysis was conducted by B. Bowden-Green with assistance from L. Briens. Manuscript was jointly written and revised by B. Bowden-Green and L. Briens.

Chapter 5: A comparison of binder solutions on the drum granulation of birchbark biochar powder

Authors: Breanna Bowden-Green and Lauren Briens

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Granulation of birchbark biochar powder with hydroxypropyl methylcellulose binder solutions was conducted by B. Poitras, H. Elkolaly and B. Weiler as a third year chemical engineering project. B. Bowden-Green conducted all other experimental work including granulation and granule testing. Data analysis was conducted by B. Bowden-Green with assistance from L. Briens. Manuscript was jointly written and revised by B. Bowden-Green and L. Briens.

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Chapter 1

1 Introduction

The world's energy consumption is increasing and primarily relies on fossil fuels. As the fossil fuel supply declines there is increasing pressure to develop alternative fuel sources. Biomass is an alternative fuel source and considered the fourth largest potential energy source in the world following coal, oil and natural gas [1]. Biomass is an attractive feedstock as it is a renewable resource. There are many processes that utilize biomass for the production of green fuels. The pyrolysis process thermally degrades biomass at high pressure under zero oxygen conditions producing gases, bio-oil and biochar which is currently considered a waste product.

1.1 Biochar for soil amendment

Biochar is a black, carbon rich powder that has physical and chemical characteristics which make it suitable for use as a soil amendment. Studies have shown that, when cultivated into soils, biochar powder can increase water retention and microbial growth and reduce nutrient and heavy metal leaching. Biochar powder is highly porous which allows for water and nutrient retention within the soil [2]. Increased nutrient retention helps promote plant and microorganism growth. Microorganisms are important within soils as they breakdown biomass residues into nutrients that can then be used by plants [3, 4]. Biochar also has surface functional groups which are believed to attach to heavy metals within the soil preventing them from being absorbed by plants [5].

Studies have shown that biomass feedstock and processing have an effect on the chemical and physical characteristics of biochar powder [6-10]. Biochar produced from forest residues was found to have increased porosity and pore volume compared to biochar produced from mill residues [10]. Increased process temperatures were found to increase the number of mesopores and micropores within biochar particles [11]. Kloss et al. found that increased process temperature also increased the biochar carbon content, aromatic compounds content and surface area [3]. As biochar properties can be adjusted, it has also been proposed that biochar can be fine-tuned for specific soil needs. For example, biochar derived from a glucose source stimulated Gram-negative bacteria growth, while yeast derived biochar promoted fungi growth [4].

The application of biochar for soil amendment purposes is currently limited by the fineness of the powder whose particle size ranges from 1-100 microns. During cultivation into soils, using standard farming equipment, an estimated 30% of biochar powder is lost when it becomes airborne [12]. Biochar powder losses are not only a loss in product, but can be potentially harmful if inhaled [13]. Current cultivation techniques include the on-site addition of water to dampen biochar powder, the formation of a biochar and water slurry and pelletization.

Although these techniques reduce dust and health issues, additional manual labour is required along with changes to standard application techniques and equipment [14]. A possible solution to the biochar cultivation issues is particle size enlargement. Increasing the size through granulation would increase the mass minimizing the potential for the biochar to become airborne [15].

1.2 Granulation

Wet granulation is the process of size enlargement through the addition of a liquid binder solution to a powder. The binder solution is typically sprayed onto the powder surface which is being agitated using a mechanical mixer or through fluidization. The binder solution droplets usually penetrate into the powder surface and form granule nuclei. Collisions between nuclei cause coalescences and consolidation of the nuclei into larger granules. Continued collisions with other granules and the equipment cause attrition and breakage of the granules.

Drum granulation is a type of wet granulation process in which agitation of the powder bed occurs through the rotation of the drum. In the case of hydrophilic powders, when the binder solution is sprayed onto the tumbling powder surface, granule nuclei are formed and grow through collisions into large granules [16, 17]. Drum granulation is currently used in the fertilizer industry to make granular nitrogen, phosphorous and potassium (NPK) and diammonium phosphate granules. Its ability for scale up to process large amounts of material makes it the best option for the granulation of biochar compared to other granulation processes such as high shear granulation or fluidized bed granulation.

Three main drum granulation process parameters that affect granule properties are rotational speed of the drum, binder concentration and the amount of binder solution. All of these granulation parameters can affect granule coalescence and consolidation which in turn affects granulation size and strength. Granule coalescence occurs when two deformable granules collide to form one larger granule [18]. Granule consolidation occurs through continued granule collisions and deformation causing the granule to become more compact which reduces porosity and increases strength. Not only do granules need to be deformable they must also have enough kinetic energy for the deformation to occur.

Granule growth by coalescence for wettable powders is affected by drum rotational speed. Rotational speed of the drum affects the amount of powder agitation within the granulator, and increasing the rotational speed increases the frequency and kinetic energy of collisions [19]. Therefore, a larger number of collisions will result in the successful coalescence of granules and an increased average granule size overall. High kinetic energy collisions also reduce granule porosity as the extent of consolidation increases. Granule porosity is directly related to granule strength; as granule porosity decreases granule strength increases.

Binder concentration can affect coalescence and consolidation of granules. Increased binder concentration and viscosity generally inhibits the movement of binder through powder capillary pores. Decreased movement through the powder pores reduces particle wetting, granule deformation and the overall coalescence of granules. Therefore, reduction in granule deformation reduces the probability of successful coalescence from granule collisions resulting in a smaller average granule size and weaker granules due to increased granule porosity [17].

Granule coalescence and consolidation can also be affected by the amount of binder solution. Binder solution wets particle-particle contacts reducing interparticle friction [20]. Therefore, an increase in the amount of binder solution increases granule deformation and the coalescence of granules. As stated previously, increased coalescence results in larger granules with increased strength.

Studies have shown that some powders and powder formulations do not form granule nuclei as expected. Aqueous liquid binder droplets quickly penetrate into hydrophilic powder beds forming granule nuclei that then grow through coalescence and consolidation. In contrast, binder solution droplets on hydrophobic powders do not penetrate quickly. Instead, the droplets sit on the powder surface and pull powder particles up and around them forming liquid marbles [21]. Many studies have been conducted to examine drop penetration into static beds of hydrophobic powders [21-24]. Increasing hydrophobicity resulted in longer drop penetration times and decreased particle size [21, 22]. Mechanisms that have been proposed to explain the formation of liquid marbles include a solids spreading coefficient, bulk motion due to a droplet impacting a powder surface and convection driven flow within the droplet [25-27].

Some granulation studies have been conducted on hydrophobic powders using high shear and twin-screw granulation processes [28-32]. These processes have high agitation rates which help to distribute the liquid evenly throughout the hydrophobic powder so granulation occurs much like it would for hydrophilic powders. High shear granulation can be used to form hollow granules [32]. No studies have been conducted on the wet drum granulation of hydrophobic powders.

Fertilizers usually contain three macronutrients to stimulate plant growth: nitrogen, phosphorous and potassium [33]. Multicomponent granular fertilizers, such as NPK or diammonium phosphate, are produced through wet drum granulation.

Important fertilizer granule properties include granule size, flowability and strength. A specified granule size range must be maintained to ensure granules can be used in standard fertilizer equipment. Granule size is also important for even distribution of fertilizer nutrients during cultivation. If the fertilizer nutrients are not evenly distributed, some plants can receive fertilizer burns from over fertilization or a lack of growth from under fertilization. Granule flowability is important in the processing and distribution of fertilizers on soils [34]. Granule strength is important to ensure granules are not crushed during storage and transportation [35].

Fertilizer granule properties have also been found to be affected by granulation parameters [36]. Walker et al. found that increased rotational speed of the drum increased the granule size of NPK fertilizers [34]. Increased binder solution volume was also found to increase the granule size and strength of fertilizers.

1.3 Thesis Objectives

The overall goal of granulating biochar powder would be to produce biochar granules that would be very similar to granular fertilizers and could potentially replace fertilizers. Current research has only proposed that biochar powder could be used as a soil amendment or supplement to fertilizer. However, the use of biochar as a supplement would require the application of both biochar and fertilizer to soils which would not necessarily be cost effective or timely. Ideally, biochar powder would be modified into a form that would enhance its soil amendment properties and contain the required plant nutrients for it to function as a fertilizer. The first steps towards this end goal are a better understanding of the granulation process and optimization of granule properties.

The overall objective of the research presented in this thesis was to investigate the potential for drum granulation of biochar into a form that could be applied as a soil amendment. The complex interaction between biochar powder, binder solutions and granulation parameters indicated the need for a better understanding of the influence of process parameters and liquid-powder interactions of wet drum granulation on the granulation of biochar.

Operational parameters effect coalescence and consolidation of granules during granulation and must be optimized to produce granules with specified properties. The variation in biomass feedstocks results in chemical and physical differences in biochar powders that affects liquid-powder interactions. Binder solution properties also affect liquid-powder interactions and the overall granulation process. Therefore, specific goals included the evaluation of the effect of operational parameters (drum rotational speed, binder concentration and liquid binder solution volume), biochar produced from various biomass feedstocks and liquid binders on the drum granulation of biochar.

1.4 Thesis Overview

Chapter 2 presents a literature review summarizing the properties of biochar that demonstrates its ability to be used as a soil amendment. This chapter also includes a literature review on drum granulation focusing on granule formation, the effect of process parameters on granule properties and hydrophobic powders.

From the literature review, a need was identified for additional research into the drum granulation of biochar. Chapter 3 examines the potential of wet drum granulation to produce biochar granules. Using a design of experiments, the effect of drum rotational speed, binder concentration and binder solution volume on the biochar granule properties was investigated. Drum granulation successfully granulated biochar and all three granulation parameters can affect biochar granule properties.

Building from the findings in Chapter 3, Chapter 4 compares wet drum granulation using biochar from three different feedstocks. It was hypothesized that differences in biochar can affect granulation and the final granule properties. A design of experiment was used to investigate the effect of drum rotational speed, binder concentration and binder solution volume on the biochar granule properties.

Chapter 5 examines three different binder solutions for wet drum granulation of birchbark biochar. A design of experiment was used to investigate the effect of drum rotational speed, binder concentration and binder solution volume on biochar granule properties. It was hypothesized that differences in the binder solutions could affect the granulation and the final granule properties

Chapter 6 provides a general discussion and overall conclusions from this research.

1.5 References

[1] A. Demirbas, Biorefineries: for biomass upgrading facilities, Biomass Feedstocks, Springer, London, 2010, p. 55.

[2] R.K. Dumroese, J. Heiskanen, K. Englund, A. Tervahauta, Pelleted biochar: Chemical and physical properties show potential use as a substrate in container nurseries, Biomass and Bioenergy, 35 (2011) 2018-2027.

[3] S. Kloss, F. Zehetner, A. Dellantonio, R. Hamid, F. Ottner, V. Liedtke, M. Schwanninger, M.H. Gerzabek, G. Soja, Characterization of slow pyrolysis biochars: effects of feedstocks and pyrolysis temperature on biochar properties, J. Environ. Qual., 41 (2012) 990-1000.

[4] S. Steinbeiss, G. Gleixner, M. Antonietti, Effect of biochar amendment on soil carbon balance and soil microbial activity, Soil Biology and Biochemistry, 41 (2009) 1301-1310.

[5] R. Bian, D. Chen, X. Liu, L. Cui, L. Li, G. Pan, D. Xie, J. Zheng, X. Zhang, J. Zheng, A. Chang, Biochar soil amendment as a solution to prevent Cd-tainted rice from China: Results from a cross-site field experiment, Ecological Engineering, 58 (2013) 378-383.

[6] H. Abdullah, H. Wu, Biochar as a Fuel: 1. Properties and Grindability of Biochar from the Pyrolysis of Mallee Wood under Slow-Heating Conditions, Energy & Fuels, 23 (2009) 4174-4181.

[7] K. Kawamoto, K. Ishimaru, Y. Imamura, Reactivity of wood charcoal with ozone, Journal of Wood Science, 51 (2005) 66-72.

[8] S. Kloss, F. Zehetner, A. Dellantonio, R. Hamid, F. Ottner, V. Liedtke, M. Schwanninger, M.H. Gerzabek, G. Soja, Characterization of slow pyrolysis biochars: effects of feedstocks and pyrolysis temperature on biochar properties, J. Environ. Qual., 41 (2012) 990-1000.

[9] Y. Wang, Y. Hu, X. Zhao, S. Wang, G. Xing, Comparisons of Biochar Properties from Wood Material and Crop Residues at Different Temperatures and Residence Times, Energy & Fuels, 27 (2013) 5890-5899.

[10] N. Anderson, G. Jones, D. Dumroese, S. Baker, D. Loeffler, W. Chung, A Comparison of Producer Gas, Biochar, and Activate Carbon from Two Distributed Scale Thermochemical Conversion Systems Used to Process Forest Biomass, Energies, 6 (2013) 164-183.

[11] A. Bagreev, T. Bandosz, D. Locke, Pore structure and surface chemistry of adsorbents obtained by pyrolysis of sewage sludge-derived fertilizer, Carbon, 39 (2001) 1971-1979.

[12] B. Husk, J. Major, Commercial scale agricultural biochar field trial in Quebec, Canada, over two years: Effects of biochar on soil fertility, biology, crop productivity and quality, BlueLeaf Inc., Quebec, Canada, 2010.

[13] C.E. Brewer, Biochar characterization and engineering, (2012) 196.

[14] J. Lehmann, S. Joseph, Biochar for Environmental Management: An Introduction, in: J. Lehmann, S. Joseph (Eds.) Biochar for Environmental Management: Science and Technology, Earthscan, London & Sterling, VA, 2009, pp. 1-9.

[15] P.J. Cullen, N. Abatzaglou, C. Rielly, R. Romanach, Pharmaceutical Blending and Mixing, John Wiley & Sons, United Kingdom, 2015.

[16] J. Litster, B. Ennis, The Science and Engineering of Granulation Processes, Kluwer Academic Publishers, Dordrecht, NLD, 2004.

[17] B. Ennis, G. I. Tardos, R. Pfeffer, A Microlevel-Based Characterization of Granulation Phenomena, Powder Technol., 65 (1991) 257.

[18] S.M. Iveson, J.D. Litster, Growth regime map for liquid-bound granules, AIChE Journal, 44 (1998) 1510-1518.

[19] A. Salaman, M. Hounslow, J. Seville, Granulation, Elsevier, Amsterdam, The Netherlands, 2007.

[20] S.M. Iveson, J.D. Litster, B.J. Ennis, Fundamental studies of granule consolidation Part 1: Effects of binder content and binder viscosity, Powder Technology, 88 (1996) 15-20.

[21] K.P. Hapgood, J.D. Litster, S.R. Biggs, T. Howes, Drop Penetration into Porous Powder Beds, Journal of Colloid and Interface Science, 253 (2002) 353-366.

[22] K.P. Hapgood, B. Khanmohammadi, Granulation of hydrophobic powders, Powder Technology, 189 (2009) 253-262.

[23] C.P. Whitby, X. Bian, R. Sedev, Rolling, penetration and evaporation of alcohol–water drops on coarse and fine hydrophobic powders, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 436 (2013) 639-646.

[24] N. Eshtiaghi, J.J.S. Liu, K.P. Hapgood, Formation of hollow granules from liquid marbles: Small scale experiments, Powder Technology, 197 (2010) 184-195

[25] R.C. Rowe, Binder–substrate interactions in granulation: a theoretical approach based on surface free energy and polarity, International Journal of Pharmaceutics 52 (1989) 149–154

[26] D. Zhang, J.H. Flory, S. Panmai, U. Batra, M.J. Kaufman, Wettability of pharmaceutical solids: its measurement and influence on wet granulation, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 206 (2002) 547-554.

[27] D. Leighton, A. Acrivos, Viscous resuspension, Chemical Engineering Science, 41 (1986) 1377-1384.

[28] P. McEleney, G.M. Walker, I.A. Larmour, S.E.J. Bell, Liquid marble formation using hydrophobic powders, Chemical Engineering Journal, 147 (2009) 373-382.

[29] M. Banks, Studies on the fluidized bed granulation process, School of Pharmacy, Leicester Polytechnic Leicester, 1981, pp. 265.

[30] Z. Belohlav, L. Brenková, J. Hanika, P. Durdil, P. Rapek, V. Tomasek, Effect of Drug Active Substance Particles on Wet Granulation Process, Chemical Engineering Research and Design, 85 (2007) 974-980.

[31] K. Jaiyeoba, M. Spring, The granulation of ternary mixtures: the effect of the wettability of powders, Journal of Pharmacy and Pharmacology, 32 (1980) 386-388.

[32] H. Charles-Williams, R. Wengeler, K. Flore, H. Feise, M. Hounslow, A. Salman, Granulation behaviour of increasingly hydrophobic mixtures, 238 (2013) 67-76.

[33] V. Fristak, M. Pipiska, J. Lesny, F. Soja, W. Friesl-Hanl, A. Packova, Utilization of biochar sorbents for Cd2+, Zn2+, and Cu2+ ions separation from aqueous solutions: comparative study, Environment monitoring and assessment, 187 (2015).

[34] G.M. Walker, H.E. Moursy, C.R. Holland, M.N. Ahmad, Effect of process parameters on the crush strength of granular fertiliser, Powder Technology, 132 (2003) 81-84.

[35] G.M. Walker, T.R.A. Magee, C.R. Holland, M.N. Ahmad, N. Fox, N.A. Moffatt, Compression testing of granular NPK fertilizers, Nutrient Cycling in Agroecosystems, 48 (1997) 231-234.

[36] B.C. Xue, Q. Hao, T. Liu, E.B. Liu, Effect of process parameters and agglomeration mechanisms on NPK compound fertiliser, Powder Technology, 247 (2013) 8.

Chapter 2

2 Introduction to biochar soil amendment properties and granulation

2.1 Introduction

Biochar is a black, carbon rich powder that is currently considered a waste product of pyrolysis. The potential applications of biochar have become an increasing focal point of many works. Biochar has both physical and chemical characteristics that give it the potential to be very useful in both the carbon sequestering and the agricultural areas. Although biochar's ability to be used as a soil amendment has been studied, there has been limited research on the most effective method for applying it to soils. Of the cultivation methods that have been suggested for the addition of biochar to soil, none take into account the processing of the biochar. Packaging, transportation and handling of powders is typically cumbersome and possibly hazardous. Changing the form of biochar powder could not only eliminate processing issues but potentially increase biochar's consumer appeal. Therefore, research into the granulation of biochar is an important stepping stone to assess biochar's potential as a soil amendment.

2.2 Pyrolysis

Biochar is produced through pyrolysis. This process involves raising the temperature of the process in order to induce thermal degradation while using an inert gas to flush oxygen out of the system. The vapors produced are quickly condensed to form the primary product, bio-oil [1]. There are different methods for pyrolysis including the use of a bubbling fluidized bed reactor or fast pyrolysis within a tubular reactor [2, 3]. Both the reactor type and process conditions must be chosen carefully to achieve a primary product with specified properties [4-8]. Pyrolysis also produces gases, which are recycled back into the process, and biochar, a carbon rich powder.

There are many potential biomass feedstocks that can be used for pyrolysis. The feedstock source has one of the largest effects on the chemical structure of biochar. One study found that cornstover-derived biochar contained significantly larger amounts of inorganic compounds compared to corncob-derived biochar [9]. These inorganics are thought to be surface charged species that promote chemisorption, adsorption in which the adsorbed substance is held by chemical bonds. The adsorption of metal ions within the soil onto the surface of biochar can effectively immobilize heavy metals, thus, reducing heavy metal tainting of crops [10]. Feedstock also plays an important role in the physical characteristics of biochar. A comparison of forest residue derived biochar and mill residue derived biochar found that forest residue derived biochar had more potential for water retention due to increased porosity and pore volume [8].

The pyrolysis process conditions impact biochar characteristics. Kloss et al. found that increased process temperature increased the biochar carbon content, aromatic compounds content and surface area [6]. Biochars with increased carbon and aromatic compounds content can be very effective for carbon sequestration. Surface area plays a key role in the retention of water within the soil, with increased surface area having a positive effect on water retention. Bagreev et al. found that increased process temperatures resulted in a larger number of mesopores and micropores within the biochar particles [11]. Increased porosity increases biochar's ability to retain water and is an important biochar characteristic. A comparison of slow and fast pyrolysis processes found that the type of process also played a role on the physical and chemical properties of the biochar produced [12]. The fast pyrolysis process produced smaller and more porous particles compared to the slow pyrolysis process. Biochar produced from the fast pyrolysis process also had decreased aromaticity and an increase in oxygen and nitrogen content.

2.3 Potential Applications of Biochar

Various possible applications of biochar have been suggested including using it as a fuel source, composting additive or heavy metal adsorbent in wastewater [13, 14]. However, the most promising uses for biochar are as a carbon sequestration technique or soil amendment. The physical and chemical properties of biochar make it an ideal candidate for these applications.

2.3.1 Carbon Sequestration

Of the approximately 9 billion tonnes of carbon released into the atmosphere each year, only half is removed by ocean and land sinks [15]. It is estimated that a removal of 40 billion metric tons of carbon dioxide through biochar sequestering could be reached by 2035 [16]. Biochar provides effective carbon sequestration due to its high carbon content and recalcitrant nature [17]. Tests on biochar stability within soils have been conducted. Although a portion degrades quickly, the stability of the remaining biochar is high over a long period of time, up to thousands of years [18].

2.3.2 Soil Amendment

Biochar can be used for soil amendment. Many have studied the physical and chemical characteristics of biochar that would make it useful as a soil amendment [6, 10, 19-23]. The physical characteristics of biochar help increase water retention and microbial growth within the soil while the chemical characteristics help reduce nutrient leaching and heavy metal tainting of crops.

Increased water retention is important for soil amendment in sandy soils where dehydration can inhibit plant growth and yield. Biochar addition to soils provides increased sorption sites due to its large surface area and porosity [6]. In Northern Germany, 50 plots of land were used to compare soil amendments. It was found that biochar not only increased water retention within the soil, but also increased maize yields when added to an organic fertilizer compared to amendment with organic fertilizer alone. Even small amounts of biochar added to a mineral fertilizer significantly increased the efficiency of the soil amendment [19]. Positive effects of biochar on soil conditions and plant growth were attributed to increased soil porosity and increased nutrient uptake.

Microbial activity increases with biochar amendment as the microbes use the nutrients trapped within the biochar structure [20]. The biochar contains adsorbed organic matter and inorganic nutrients providing an excellent habitat for microbe proliferation [21]. The increase in microorganism stimulation results in the increased breakdown of biomass residues which then become available nutrients for plants.

Soils amended with biochar have shown reduced nutrient leaching and heavy metal tainting of crops. In one study, the addition of 20 g of biochar to 1 kg of soil led to a 24% drop in phosphorous leaching. A reduction of by-pass flow and movement of elements with minimal soil matrix interactions was also observed [22]. Angst et al. also found that the addition of biochar to soil significantly decreased the amount of mineral nitrogen leached from the soil [23]. The large surface area of biochar and the large number of surface functional groups on biochar are hypothesized to be the reason for the decrease in mineral leaching [10]. Increasing the retention of nutrients in the soil increases the availability of nutrients to be absorbed by plants. The chemical structure of biochar that adsorbs nutrients also allows heavy metal adsorption, reducing heavy metal tainting of crops. Bian et al. found that the addition of biochar to rice paddies reduced the amount of cadmium in the rice produced [10].

2.4 Granulation

Handling of biochar powder is difficult due to its size. Biochar is a fine powder with a particle size between 1 and 100 microns and can easily become airborne during processing and application to soils. Application to soil in Quebec, Canada, using standard farm machinery resulted in an estimated 30% loss of biochar through entrainment into the air [24]. Entrained biochar can negatively affect human health through respiratory irritation and lung damage [12].

Techniques have been proposed to reduce biochar dust hazards including pelletization, increasing biochar powder moisture and the addition of biochar to aerobically digested slurry [18, 25]. The compaction of biochar powder into pellets increases the ease of handling of biochar and decreases transportation cost through increased packing efficiency. However, the high pressures used during the densification of biomass into pellets causes a loss of porosity and can greatly reduce the effectiveness of biochar in soil [1]. Less dense pellets are more desirable for soil amendment use. The on-site addition of water or slurry to biochar powder to dampen it has the advantage of decreasing dust problems during spreading. On-site liquid addition requires additional manual labour and may not reduce all dust issues [18]. Although beneficial, these applications do not completely eliminate dust hazards and do not consider other possible problems. A potential alternative that could eliminate both processing and cultivation problems is wet granulation of biochar. Granules produced from wet granulation have greatly reduced dustiness, increased packing efficiency and do not require any additional processing or labour before application to soil. Drum granulation does not require high pressures or agitation rates and would therefore produce a less dense biochar granule compared to a biochar pellet.

2.4.1 Wet Granulation

Wet granulation is the process of agglomerating fine powder particles into larger agglomerates or granules using a liquid binding agent. Granulation is commonly used in many industries to reduce dust, improve handling and minimize caking during storage and transportation [26, 27]. There are three main wet granulation processes each differing in the method of powder agitation and distribution of the liquid binder. High shear granulation uses an impeller and chopper to agitate the powder bed while a nozzle sprays the liquid binder onto the top of the powder bed. High shear granulators are commonly used to produce smaller agglomerates in the pharmaceutical and chemical industries. Fluidized bed granulation uses air to fluidize or agitate the powder bed while the liquid binder is sprayed on top or into the bed. The fluidizing air has a dual effect of drying the granules while processing [28]. Fluidized bed granulation is used in both the pharmaceutical and food industries. In drum granulation, an axially mounted drum is used to agitate the powder while a sparger sprays the liquid binder onto the tumbling powder bed surface. Drum granulation is primarily used in the fertilizer industry. Of the three wet granulation processes, drum granulation is the best option for biochar granulation due to the large volumes required for commercial application and the scale up capacity of the process.

2.4.2 Granulation Mechanisms

The common mechanism for the granulation of wettable powders is well documented in literature [29-35]. Granules are formed in three stages: wetting and nucleation, coalescence and consolidation, and attrition and breakage (Figure 2-1). Figure 2-2 shows the first stage of granulation, wetting and nucleation, where the initial contact between the powder bed and a liquid binder droplet occurs. Drops formed by the spray nozzle impact the powder bed and penetrate into the powder forming initial granule nuclei.

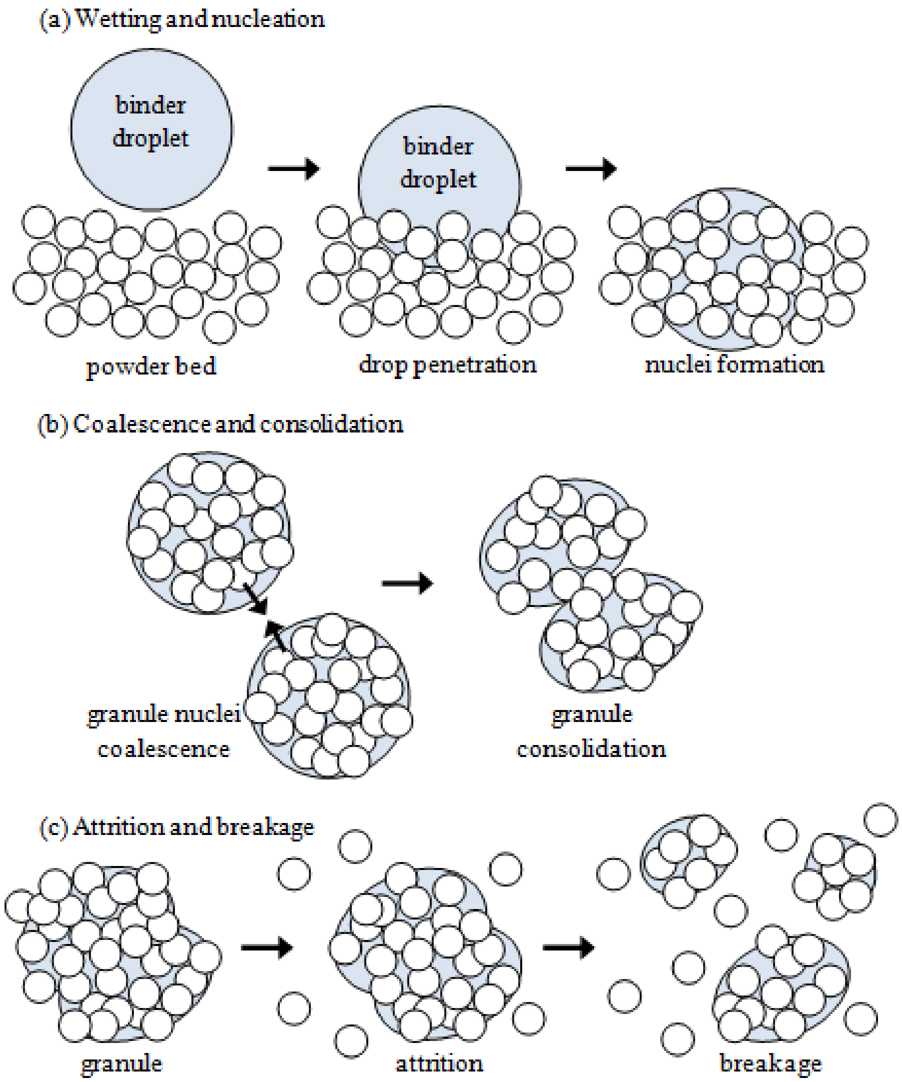


Figure 2-1: Granulation mechanism for wettable powders, adapted from Ennis et al. [31]

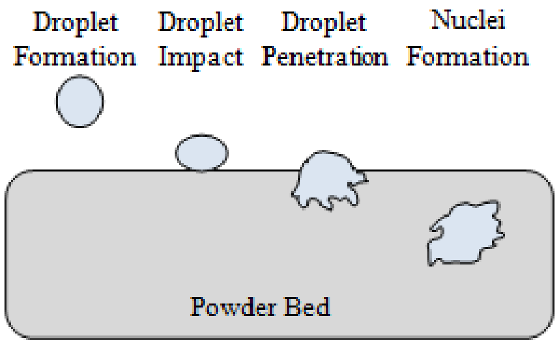


Figure 2-2: Wetting and nucleation of wettable powders adapted from, Hapgood et al. [32]

Growth of the initial nuclei occurs in the second stage, coalescence and consolidation. Agitation of the powder bed causes collisions between nuclei which coalesce into larger granules. Consolidation occurs through the compaction of granules through granule-granule collisions and granule-equipment collisions. Iveson et al. proposed a growth regime map based on two broad classes of growth behavior: steady growth behaviour and induction behaviour [33]. Deformation of the granules is the main indicator of growth behaviour. For steady growth to occur, granules must be highly deformable so a large area of contact forms between granules allowing liquid binder to be moved to the surface of the granules forming a strong bond. Granules with low deformation do not stick together during collision and there is a long induction period of little or no granule growth. Granule coalescence and growth only occur when enough liquid binder is moved onto the surface of the granule to allow for strong enough bonds to form between granules. Powder characteristics and granulation parameters affect which growth behaviour occurs for a particular system. These include particle size, process agitation intensity and liquid binder properties.

The final stage of granulation is attrition and breakage. The attrition of granules occurs when granules collide and do not break, but instead suffer surface wear due to the friction between the granules [34]. Collisions that occur between granules that have grown too large or between granules and the granulator equipment can cause them to break apart. Increased agitation can reduce mean granule size due to an increase in the kinetic energy of the collisions resulting in more attrition and breakage of particles [35].

2.4.3 Hydrophobic Behaviour

In the wetting and nucleation stage, ideal nucleation occurs when one liquid binder drop forms one nucleus. For this happen, the binder spray should occur at a relatively slow rate with small droplets and the droplets should penetrate into the powder bed quickly. The droplet penetration rate depends on the powder-liquid binder interactions [36]. Hydrophilic powders, which are easily wetted by the aqueous liquid binder, generally show fast drop penetration rates while liquid binder droplets may not penetrate into beds of very hydrophobic powders [32].

Many studies have been conducted to examine the drop penetration of hydrophobic powders. Nguyen et al. examined the drop penetration times of distilled water into powders of varying hydrophobicity [17]. The drop penetration time increased with both increasing hydrophobicity and decreasing particle size. Therefore, drop penetration was dependent on the wettability of the powder as well as the powder bed structure including the distribution of hydrophobic particles within the matrix. The drop penetration rate increased as more hydrophilic components were added which increased the number and length of hydrophilic paths available for the liquid to advance. Another study conducted by Whitby et al. examined the drop penetration of alcohol-water solutions on three hydrophobic powders of glass beads, coal and molybdenite [37]. Low surface tensions resulted in penetration of the liquid solution into coarse powder beds compared to high surface tensions which prevent liquid penetration resulting in the liquid droplet sitting on top of the powder bed.

For very hydrophobic powders, liquid binder droplets do not penetrate into the powder bed upon contact, but form a liquid marble instead. The liquid droplet remains at the surface of the powder bed and powder particles are drawn up around the droplet to form a liquid marble or an alternate granule nucleus structure (Figure 2-3) [38, 39].

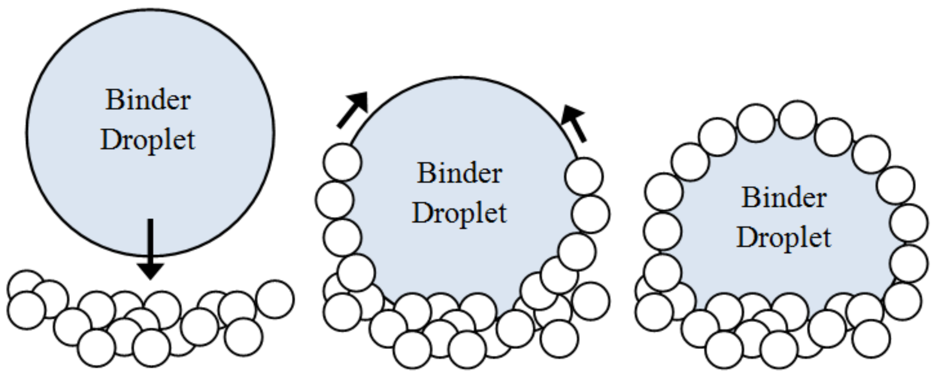


Figure 2-3: Formation of a liquid marble through solids spreading over a binder solution droplet, adapted from Nguyen et al. [40]

Several mechanisms have been proposed to explain the solids spreading around the liquid droplet. The common theory is based on the solid spreading coefficient model developed by Rowe to predict the solids spreading over a liquid [41]. The model is based on the thermodynamic spreading coefficient for a liquid spreading over a solid surface where the spreading coefficient indicated if spreading was thermodynamically favourable and would occur spontaneously [42]. Calculation of the spreading coefficient considers the work of adhesion due to the polar and non-polar intermolecular interactions that occur between the solid and liquid [38]. Other theories include bulk motion within the droplet due to the impaction upon the powder surface, movement from high to low shear regions and induced convection driven flow within the drop due to evaporation [41-44].

Parameters that have been found to affect the formation of liquid marbles are particle size, liquid binder viscosity and surface tension [38]. Larger particles form liquid marbles less often compared to smaller particles possibly due to increased mass and gravitational force acting against the forces pulling the particles around the drop. Liquid binder viscosity was found to also affect the wettability of hydrophobic powders. Hapgood and Khanmohammadi found that higher viscosity polyethylene glycol, PEG, solutions resulted in the formation of less stable liquid marbles compared to lower viscosity PEG solutions [38]. However, the most viscous solution tested, glycerol, did form stable liquid marbles. High surface tensions resulted in liquid marbles that maintained their shape compared to low surface tensions which resulted in collapsed liquid marbles. Although these parameters were found to effect the formation of liquid marbles, there is still a lack of understanding of the mechanisms at play.

Only a few studies have examined granulation of hydrophobic powders. These studies have found that increasing the amount of a hydrophobic powder in powder mixtures resulted in decreased granule sizes [45-47]. Banks examined the granulation of hydrophobic powders in a fluidized bed granulator [45]. The hydrophobicity of the powder mixtures was increased by increasing the salicylic acid content within the mixture. Increasing the hydrophobicity of the powder decreased the mean granule size and produced a narrower size distribution compared to less hydrophobic powder mixtures. The addition of a surfactant, sodium lauryl sulphate, to the liquid binder increased particle size due to increased wettability of the powder. Charles-Williams et al. examined the effect of hydrophobic powder content on both granule size and composition for high shear granulation [48]. They proposed that the hydrophilic component formed a core with the hydrophobic particles attaching as an outer shell. Attrition and breakage of the hydrophilic core granules and subsequent coalescence with other fragments created a more uniform distribution of the hydrophilic and hydrophobic powders throughout the resulting granules. Hapgood et al. granulated a very hydrophobic powder formulation of hydrophobic silica and hydroxypropyl cellulose, HPC, in a high shear mixer [49]. Hollow granules were formed. Larger granules were formed from the coalescence of multiple hollow nuclei connected by a denser layer of particles.

The literature has only reported studies of hydrophobic powders in fluidized bed granulators and high shear granulators [45-49]. There are no published studies of granulation of hydrophobic powders using a drum granulator.

2.4.4 Drum Granulation

For drum granulation, the powder within the drum is agitated through the rotation of the drum while the liquid binder is sprayed onto the tumbling powder bed surface. Operating parameters that can be varied include drum fill volume, drum rotation rate and liquid binder spray distribution and spray rate. The properties of the powder and liquid binder solutions can also affect the granulation and granule properties. All of the research on the effect of the operating parameters, powder and liquid binder solutions has only included wettable or hydrophilic powders.

The drum rotation rate is usually a critical parameter for drum granulation. For wettable powders, granule growth is dependent upon coalescence. Coalescence describes the collision of two granules that results in the formation of one larger granule. Opportunities for coalescence can increase with the drum rotation rate as the increased agitation of the bed increases the frequency and velocity of collisions [29]. The desired bed motion within the drum granulator is cascading flow to ensure the maximum number of granule collisions occur [29]. Low drum rotation rates result in slipping of the granular bed and minimal agitation, while increasing the rotation rate of the drum too much can cause cataracting flow and wall build up. Typically the rotation rate of drum granulators is set at 30 to 50% of the critical speed, N_C, which is defined as:

$$N_c = \sqrt{\frac{g \sin\beta}{2\,\pi^2\, D}} \qquad (2-1)$$

where g is the gravitational constant, β is the angle of the drum and D is the diameter of the drum. Granules also consolidate as they collide with each other and the walls of the granulator. Consolidation reduces granule size and porosity, squeezes out any trapped air within the granules and forces liquid binder to the surface of the granules [30]. A faster drum rotation rate will increase the consolidation rate as the frequency and velocity of collisions increases.

The liquid to powder ratio and the viscosity of the liquid binder both have an effect on the consolidation rate. Ivenson et al. performed drum granulation of glass ballotini and water and glycerol binder solutions and proposed that there were two competing effects during consolidation: interparticle friction and viscous dissipation [51]. Interparticle friction prevents the particles within the granule from sliding across each other inhibiting granule deformation which is required for consolidation to occur. Viscous dissipation restricts movement of the liquid binder through the granule capillaries preventing wetting of the particles and consolidation of the granules. A study found that an increase in volume of low viscosity binder increased the degree of consolidation, whereas, an increase in volume of high viscosity binder content decreased the degree of consolidation [51]. Therefore, increased binder content wets the particle-particle contacts decreasing interparticle friction and decreased binder viscosity reduces the effects of viscous dissipation. However, high viscosity binders are usually required to form strong granules. A balance between volume of binder added and binder viscosity is required to ensure a high rate of consolidation and the production of strong granules.

The size of the feed powder particles also has an effect on the consolidation rate. Smaller feed particles reduce the consolidation rate due to an increase in the specific surface area of the particles [50]. Smaller particles pack closer together increasing particle-particle contacts and interparticle friction within the granule. Closer packing also reduces the size of the pores in between the granule particles. Reduced pore size increases the effects of viscous dissipation and reduces the consolidation rate. Ramachandran et al. performed drum granulation experiments and found that the size distribution of the feed particles also effects consolidation [51]. Broader size distributions result in a larger extent of granulation due to large particles being more likely to coalesce with smaller particles then other larger particles.

Although highly porous granules are optimal for soil amendment applications, granules must still maintain their strength to prevent crushing during packaging, transportation and handling. Granule strength is dependent on granulation time, liquid binder volume and viscosity and granule porosity [52]. Longer granulation times increase consolidation and granule strength [30]. Increased binder volume can increase the strength of granules by forming a larger number of liquid bridges between particles. However, there is a maximum binder volume amount at which granule strength begins to decrease due to over wetting of the granules. Higher binder viscosities form stronger granules by increasing the strength of the bonds formed within the granule [51]. Granule strength and porosity are inversely related. Granules with low porosity are created by increasing consolidation. To obtain granules with properties suitable for soil amendment, a balance between strength and porosity must be considered.

2.4.5 Fertilizer

Fertilizers are produced in granular, slurry and liquid form. The form depends on the chemical components of the fertilizer and the intended application. Some fertilizers can be produced in granular form to be cultivated into personal use gardens and farm soils. The implementation of drum granulation for the production of granular fertilizers is required to reduce dust losses and hazards, improve product appearance and reduce shipping costs through increased bulk density. Diammonium phosphate and NPK fertilizers are both produced using the wet drum granulation process [18].

Key properties for granular fertilizers are the granule size, dissolution rate, flowability and strength. Granule size affects the agronomic response of a fertilizer along with processing and application properties. For example, due to the low solubility of phosphate rock, the particles must be very small to ensure an adequate dissolution rate for plant uptake [53]. Dissolution rate also plays a key role in the agronomic response. Slow release fertilizers have a low dissolution rate to allow for an extended release of chemicals over time compared to liquid fertilizers whose nutrients are available to plants immediately. Flowability is important for granules during processing and application to soils where granules need to flow through equipment. Finally, granule integrity must be maintained to ensure granules are not crushed during transportation or application [53]. Drum granulation parameters must be adjusted to ensure that the product granules meet the required specifications for these fertilizer properties.

Multi-component fertilizers primarily consist of nitrogen, phosphorous and potassium [18]. Nitrogen is vital to plant growth as it is essential for photosynthesis and the production of proteins, chlorophyll and roots [54]. Plants absorb nitrogen in the form of either nitrates or ammonium ions through their roots. Phosphorous enhances the photosynthesis and nitrogen fixation processes and is important in the flowering and fruiting of a plant. Phosphorous is usually available in soil as inorganic phosphate ions such as the hydrogen phosphate ion, $H(PO_4)^{-2}$ [55]. The third most important macronutrient for plant growth is potassium which plays an important role in water retention within leaves and the increase in water up take of roots. Potassium is obtained by plants through the breakdown of minerals such as micas and feldspar.

The ratio of each macronutrient depends on crop requirements and may not always include all three components. Cultivation methods also depend on which macronutrients are required. Unlike nitrogen fertilizers that can be spread on top of soil, phosphorous has a very low solubility and must be incorporated into the soil using farming equipment to ensure good soil-root contact. The need for cultivation of potassium depends on the type of potassium for example, the solubility of potassium sulfate at 20 ^{o}C is 111 g/L versus 209 g/L for potassium nitrate [18].

The manufacturing process for granular fertilizers consists primarily of a drum granulator, screens and a crusher as shown in Figure 2-4. Feed powder enters the drum and liquid binder solution is sprayed onto the surface of the powder. The rotation of the drum along with the flights within the drum agitate the powder thereby promoting the formation of fertilizer granules. The process is made continuous through the slight angle of the drum allowing the powder to move through the length of the drum. Near the end of the drum, no binder addition occurs allowing wet massing of the granules before exiting the drum. The fertilizer is then sent through screens and separated into three size cuts: oversized, optimal size and undersized. Oversized granules are sent to be crushed in the crusher before being added to the undersized cut and recycled back into the system. Depending on the type of fertilizer being produced, the product, optimal sized granules, may go into a cyclone where fines are removed or into a coating or polishing drum to increase consumer appeal.

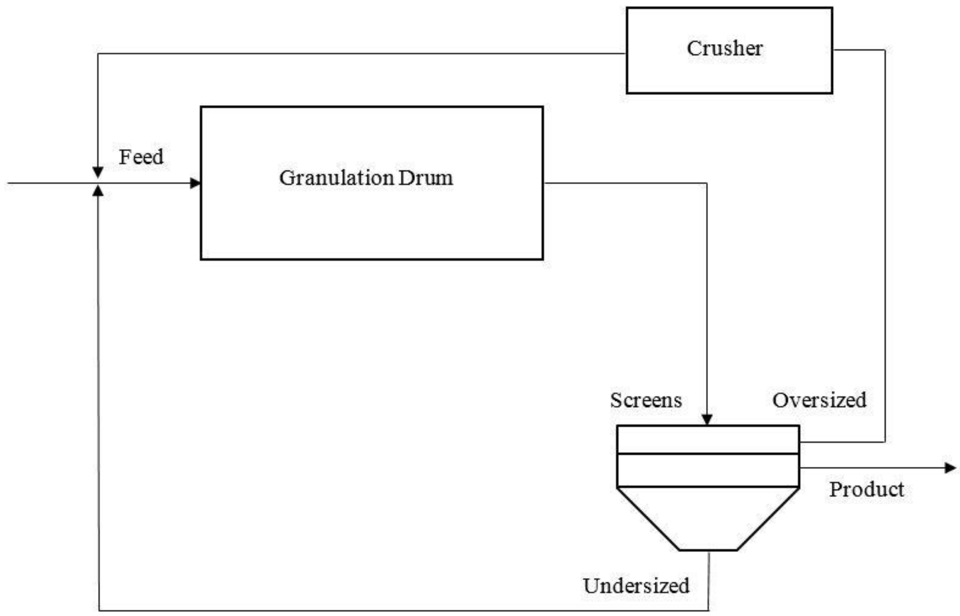


Figure 2-4: Fertilizer manufacturing process schematic.

2.4.5.1 Fertilizer Properties

The production of uniformly sized particles is required in the fertilizer industry. Undersized granules and crushed oversized granules are recycled back into the process increasing operational costs. Granule size is controlled through careful monitoring of the granulation time, liquid binder volume and viscosity and agitation rate. Walker et al. found that granule size increased with higher solid-liquid phase ratios [56]. At higher binder volumes almost all of the fines within the system were removed producing a wide granule size distribution. Increased binder viscosity and higher drum rotation rates also increased coalescence and the mean diameter of the fertilizer granules. Xue et al. performed drum granulation of NPK compound fertilizers and found that increased granulation time, up to a maximum of 3 minutes, increased granule diameter, thereafter, growth was negligible [57].

Flowability is a key fertilizer granule characteristic to ensure ease of handling, packaging and cultivation. A granulation study of NPK fertilizers conducted by Walker et al. found irregular shaped granules were produced from low liquid binder content granulations [52]. Low sphericity granules have reduced flowability compared to spherical granules which can cause problems in processing and consumer use. Flowability can be measured using angle of repose measurements, compaction dynamics and rotating drum measurements [58].

Fertilizer granules must be strong to maintain their shape during storage, processing and transportation. Granule hardness can be measured three ways: crushing strength, resistance to abrasion and impact resistance [59]. Granule crushing strength has been found to be a function of granule size for fertilizers produced in drum granulators [53, 57]. Common fertilizer granule sizes are between 1 and 4 mm [53]. Larger granules have been found to withstand higher crushing forces. However, the break pressure or force per cross sectional area does not change with granules size [59]. Walker et al, measured the crushing strength of NPK fertilizers to be between 4 – 5 MPa [59]. Hygroscopic fertilizers have reduced strength when stored in humid climates which can lead to caking of the fertilizer.

2.5 Conclusions

Biochar has potential as a soil amendment. Biomass feedstock and pyrolysis methods have an effect on the properties of biochar powder and could, therefore, be used to produce biochar for specific needs. However, the fineness of biochar powder makes it difficult for efficient and safe application to soils. Wet drum granulation could be used to modify biochar powder into a form that would reduce dust and associated issues and improve application. Most granulation mechanisms are proposed based on the most common hydrophilic liquid-powder interactions where the binder solutions quickly penetrate into the powder beds forming granule nuclei. Granulation of hydrophobic powders has not been extensively studied and remains poorly understood. Parameters that can affect drum granulation include rotational speed of the drum, binder concentration and binder solution volume. Granular fertilizers are produced using drum granulation. Important granular fertilizer properties are the granule size, dissolution rate, flowability and strength.

2.6 References

[1] R.K. Dumroese, J. Heiskanen, K. Englund, A. Tervahauta, Pelleted biochar: Chemical and physical properties show potential use as a substrate in container nurseries, Biomass and Bioenergy, 35 (2011) 2018-2027.

[2] A. Tumbalam Gooty, D. Li, C. Briens, F. Berruti, Fractional condensation of bio-oil vapors produced from birch bark pyrolysis, Separation and Purification Technology, 124 (2014) 81-88.

[3] T. Qu, W. Guo, L. Shen, J. Xiao, K. Zhao, Experimental Study of Biomass Pyrolysis Based on Three Major Components: Hemicellulose, Cellulose, and Lignin, Industrial & Engineering Chemistry Research, 50 (2011) 10424-10433.

[4] H. Abdullah, H. Wu, Biochar as a Fuel: 1. Properties and Grindability of Biochar from the Pyrolysis of Mallee Wood under Slow-Heating Conditions, Energy & Fuels, 23 (2009) 4174-4181.

[5] K. Kawamoto, K. Ishimaru, Y. Imamura, Reactivity of wood charcoal with ozone, Journal of Wood Science, 51 (2005) 66-72.

[6] S. Kloss, F. Zehetner, A. Dellantonio, R. Hamid, F. Ottner, V. Liedtke, M. Schwanninger, M.H. Gerzabek, G. Soja, Characterization of slow pyrolysis biochars: effects of feedstocks and pyrolysis temperature on biochar properties, J. Environ. Qual., 41 (2012) 990-1000.

[7] Y. Wang, Y. Hu, X. Zhao, S. Wang, G. Xing, Comparisons of Biochar Properties from Wood Material and Crop Residues at Different Temperatures and Residence Times, Energy & Fuels, 27 (2013) 5890-5899.

[8] N. Anderson, G. Jones, D. Dumroese, S. Baker, D. Loeffler, W. Chung, A Comparison of Producer Gas, Biochar, and Activate Carbon from Two Distributed Scale Thermochemical Conversion Systems Used to Process Forest Biomass, Energies, 6 (2013) 164-183.

[9] C.A. Mullen, A.A. Boateng, N.M. Goldberg, I.M. Lima, D.A. Laird, K.B. Hicks, Bio-oil and bio-char production from corn cobs and stover by fast pyrolysis, Biomass and Bioenergy, 34 (2010) 67-74.

[10] R. Bian, D. Chen, X. Liu, L. Cui, L. Li, G. Pan, D. Xie, J. Zheng, X. Zhang, J. Zheng, A. Chang, Biochar soil amendment as a solution to prevent Cd-tainted rice from China: Results from a cross-site field experiment, Ecological Engineering, 58 (2013) 378-383.

[11] A. Bagreev, T. Bandosz, D. Locke, Pore structure and surface chemistry of adsorbents obtained by pyrolysis of sewage sludge-derived fertilizer, Carbon, 39 (2001) 1971-1979.

[12] C.E. Brewer, Biochar characterization and engineering, (2012) 196.

[13] H. Schmidt, 55 uses of biochar, Ithaka Journal (2012).

[14] V. Fristak, M. Pipiska, J. Lesny, F. Soja, W. Friesl-Hanl, A. Packova, Utilization of biochar sorbents for Cd2+, Zn2+, and Cu2+ ions separation from aqueous solutions: comparative study, Environment monitoring and assessment, 187 (2015).

[15] K. Kleiner, The bright prospect of biochar, Nature Reports. (2009) 72-74.

[16] T.M. Lenton, N.E. Vaughan, The radiative forcing potential of different climate geoengineering options, Atmos. Chem. Phys., 9 (2009) 5539-5561.

[17] B.T. Nguyen, R.T. Koide, C. Dell, P. Drohan, H. Skinner, P.R. Adler, A. Nord, Turnover of soil carbon following addition of switchgrass-derived biochar to four soils, Soil Sci. Soc. Am. J., 78 (2014) 531-537.

[18] J. Lehmann, S. Joseph, Biochar for Environmental Management: An Introduction, in: J. Lehmann, S. Joseph (Eds.) Biochar for Environmental Management: Science and Technology, Earthscan, London & Sterling, VA, 2009, pp. 1-9.

[19] B. Glaser, K. Wiedner, S. Seelig, H.-P. Schmidt, H. Gerber, Biochar organic fertilizers from natural resources as substitute for mineral fertilizers, Agronomy for Sustainable Development, 35 (2015) 667-678.

[20] S. Steinbeiss, G. Gleixner, M. Antonietti, Effect of biochar amendment on soil carbon balance and soil microbial activity, Soil Biology and Biochemistry, 41 (2009) 1301-1310.

[21] D. Warnock, J. Lehmann, T. Kuyper, M. Rillig, Mycorrhizal responses to biochar in soil – concepts and mechanisms, Plant and Soil, 300 (2007) 9-20.

[22] D.A. Laird, P. Fleming, D.D. Davis, R. Horton, B. Wang, D.L. Karlen, Impact of biochar amendments on the quality of a typical Midwestern agricultural soil, Geoderma, 158 (2010) 443-449.

[23] T. Angst, C. Patterson, D. Reay, P. Anderson, T. Peshkur, S. Sohi, Biochar Diminishes Nitrous Oxide and Nitrate Leaching from Diverse Nutrient Sources Journal of Environmental Quality, 42 (2013) 672-682.

[24] B. Husk, J. Major, Commercial scale agricultural biochar field trial in Quebec, Canada, over two years: Effects of biochar on soil fertility, biology, crop productivity and quality, BlueLeaf Inc., Quebec, Canada, 2010.

[25] E.W. Bruun, D. Müller-Stöver, P. Ambus, H. Hauggaard-Nielsen, Application of biochar to soil and N2O emissions: potential effects of blending fast-pyrolysis biochar with anaerobically digested slurry, European Journal of Soil Science, 62 (2011) 581-589.

[26] T. Hignett, Fertilizer Manual, Springer Science & Business Media, 2013.

[27] V. Yandapalli, Granulation of Lignocellulosic Powders, Biotechnology, Jawaharlal Nehru Technological University, Athens, Georgia, 2009, pp. 121.

[28] A.D. Salaman, M. Hounslow, J. Seville, Granulation, Elsevier, Amsterdam, The Netherlands, 2007.

[29] J. Litster, B. Ennis, The Science and Engineering of Granulation Processes, Kluwer Academic Publishers, Dordrecht, NLD, 2004.

[30] B. Ennis, B. J., G. I. Tardos, R. Pfeffer, A Microlevel-Based Characterization of Granulation Phenomena, Powder Technology, 65 (1991) 257.

[31] B. Ennis, J. Litster, Particle size enlargement, Perry's Chemical Engineers' Handbook, 7th edn, McGraw-Hill, New York, (1997) 20-56.

[32] K.P. Hapgood, J.D. Litster, S.R. Biggs, T. Howes, Drop Penetration into Porous Powder Beds, Journal of Colloid and Interface Science, 253 (2002) 353-366.

[33] S.M. Iveson, J.D. Litster, Growth regime map for liquid-bound granules, AIChE Journal, 44 (1998) 1510-1518.

[34] P. Rajniak, K. Dhanasekharan, C. Sinka, N. Macphail, R. Chern, Modeling and measurement of granule attrition during pneumatic conveying in a laboratory scale system, Powder Technology, 185 (2008) 202-210.

[35] P.C. Knight, A. Johansen, H.G. Kristensen, T. Schæfer, J.P.K. Seville, An investigation of the effects on agglomeration of changing the speed of a mechanical mixer, Powder Technology, 110 (2000) 204-209.

[36] K.P. Hapgood, J.D. Litster, R. Smith, Nucleation regime map for liquid bound granules, American Institute of Chemical Engineers Journal, 49 (2003) 350-361.

[37] C.P. Whitby, X. Bian, R. Sedev, Rolling, penetration and evaporation of alcohol–water drops on coarse and fine hydrophobic powders, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 436 (2013) 639-646.

[38] K.P. Hapgood, B. Khanmohammadi, Granulation of hydrophobic powders, Powder Technology, 189 (2009) 253-262.

[39] N. Eshtiaghi, J.J.S. Liu, K.P. Hapgood, Formation of hollow granules from liquid marbles: Small scale experiments, Powder Technology, 197 (2010) 184-195.

[40] T. Nguyen, W. Shen, K. Hapgood, Drop penetration time in heterogeneous powder beds, Chemical Engineering Science, 64 (2009) 5210-5221.

[41] R.C. Rowe, Binder–substrate interactions in granulation: a theoretical approach based on surface free energy and polarity, International Journal of Pharmaceutics, 52 (1989) 149–154

[42] D. Zhang, J.H. Flory, S. Panmai, U. Batra, M.J. Kaufman, Wettability of pharmaceutical solids: its measurement and influence on wet granulation, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 206 (2002) 547-554.

[43] D. Leighton, A. Acrivos, Viscous resuspension, Chemical Engineering Science, 41 (1986) 1377-1384.

[44] P. McEleney, G.M. Walker, I.A. Larmour, S.E.J. Bell, Liquid marble formation using hydrophobic powders, Chemical Engineering Journal, 147 (2009) 373-382.

[45] M. Banks, Studies on the fluidized bed granulation process, School of Pharmacy, Leicester Polytechnic Leicester, 1981, pp. 265.

[46] Z. Belohlav, L. Brenková, J. Hanika, P. Durdil, P. Rapek, V. Tomasek, Effect of Drug Active Substance Particles on Wet Granulation Process, Chemical Engineering Research and Design, 85 (2007) 974-980.

[47] K. Jaiyeoba, M. Spring, The granulation of ternary mixtures: the effect of the wettability of powders, Journal of Pharmacy and Pharmacology, 32 (1980) 386-388.

[48] H. Charles-Williams, R. Wengeler, K. Flore, H. Feise, M. Hounslow, A. Salman, Granulation behaviour of increasingly hydrophobic mixtures, 238 (2013) 67-76.

[49] K.P. Hapgood, B. Khanmohammadi, Granulation of hydrophobic powders, Powder Technology, 189 (2009) 253-262.

[50] S.M. Iveson, J.D. Litster, B.J. Ennis, Fundamental studies of granule consolidation Part 1: Effects of binder content and binder viscosity, Powder Technology, 88 (1996) 15-20.

[51] R. Ramachandran, J.M.H. Poon, C.F.W. Sanders, T. Glaser, C.D. Immanuel, F.J. Doyle Iii, J.D. Litster, F. Stepanek, F.-Y. Wang, I.T. Cameron, Experimental studies on distributions of granule size, binder content and porosity in batch drum granulation: Inferences on process modeling requirements and process sensitivities, Powder Technology, 188 (2008) 89-101.

[52] G.M. Walker, H.E.M.N. Moursy, C.R. Holland, M.N. Ahmad, Effect of process parameters on the crush strength of granular fertiliser, Powder Technology, 132 (2003) 81-84.

[53] D. Rutland, J. Polo, Fertilizer dealer handbook: products, storage and handling., IFDC - An International Center for Soil Fertility and Agricultural Development, Muscle Shoals, AL, 2005.

[54] N.C. Brady, R.R. Weil, The nature and properties of soils, 11th ed., Upper Saddle River, NJ, USA, Prentice, 1996.

[55] F. Munshower, Practical handbook of disturbed land revegetation, Lewis Publishers, Minnesota, 1994.

[56] G.M. Walker, C.R. Holland, M.N. Ahmad, J.N. Fox, A.G. Kells, Prediction of Fertilizer Granulation: Effect of Binder Viscosity on Random Coalescence Model, Industrial & Engineering Chemistry Research, 40 (2001) 2128-2133.

[57] B.C. Xue, Q. Hao, T. Liu, E.B. Liu, Effect of process parameters and agglomeration mechanisms on NPK compound fertiliser, Powder Technology, 247 (2013) 8.

[58] G. Lumay, F. Boschini, K. Traina, S. Bontempi, J.C. Remy, R. Cloots, N. Vandewalle, Measuring the flowing properties of powders and grains, Powder Technology, 224 (2012) 19-27.

[59] G.M. Walker, T.R.A. Magee, C.R. Holland, M.N. Ahmad, N. Fox, N.A. Moffatt, Compression testing of granular NPK fertilizers, Nutrient Cycling in Agroecosystems, 48 (1997) 231-234.

Chapter 3

3 An investigation of drum granulation of biochar powder

3.1 Introduction

Biochar, solids produced from the pyrolysis process, can be used agriculturally as a soil amendment. When cultivated into soils, biochar has been shown to reduce nutrient leaching, immobilize heavy metals, and increase water retention and microbial activity [1-5]. As biochar properties can be adjusted, it has also been proposed that biochar can be fine-tuned for specific soil needs. For example, biochar derived from a glucose source stimulated Gram-negative bacteria growth, while yeast derived biochar promoted fungi growth [6].

The major problem with biochar is that it is a fine powder with particle sizes ranging from approximately 1-600 microns and therefore would be easily blown away when used as a soil amendment without any modifications. When biochar particles become airborne, they can negatively impact the health of exposed occupants causing respiratory irritation and lung damage [7]. In addition, very fine powders make packaging difficult and cultivation into soil troublesome. Techniques that have been proposed for application of biochar to soils that minimize dust hazards include surface spreading followed by immediate ploughing into the soil or spraying with water, mixing with liquids and applying using liquid spreading techniques or pelletizing the biochar and applying as for solid fertilizers [7]. Dumrose et al. pelletized biochar after blending with wood flour, polylactic acid and starch [1]. The pellets were combined with Sphagnum peat and the combinations were assessed for potential use in container nurseries. The pellets improved the hydraulic conductivity of the mixture, but expansion at high pellet additions caused potential problems in filling the containers. Recommendations included modifications of pellet composition and porosity to reduce pellet expansion and also improve the carbon to nitrogen ratio of the mixture.

Wet granulation is a process that uses a liquid binder to agglomerate particles into granules. There are three main wet granulation processes: high shear, fluidized bed and drum. Drum granulation would be the best choice for biochar granulation due to its lower capital and operating costs combined with easier scale-up. In drum granulation, powder is loaded into the drum and agitated by rotating the drum while a liquid binder is sprayed onto the powder surface using spargers. The liquid binder wets the particles allowing granule nuclei to form which then develop into larger granules followed by consolidation into the final product.

The objectives of the current research were to demonstrate that biochar could be granulated and then to investigate process parameters that affect biochar granule properties.

3.2 Materials and Methods

3.2.1 Biochar Formation

Biochar was created by the pyrolysis of cornstalk. The cornstalk was treated before pyrolysis by drying at 105 ^{o}C and then grinding to 1-2 mm in size using an IKA Werke model MF10 grinder at 4500 rpm. Pyrolysis was performed in a custom manufactured reactor (University Machine Services, London, Canada) with a diameter of 25 cm and an effective bed height of 60 cm. The reactor temperature was 500 ^{o}C and pressure was 100 kPa. The bed was fixed, but then fluidized at intervals to ensure constant temperature and uniform bed composition. The cornstalk biochar was recovered from the reactor and then ground using the IKA Werke model MF10 grinder. This step only reduced any large clumps of biochar that may have been recovered from the reactor. It was important to eliminate these large clumps at this stage to accurately determine the size enlargement of granulation.

3.2.2 Biochar Characterization

Images of the biochar powder were taken using a Hitachi S-4500 field emission scanning electron microscope. The powder was mounted on a plate using a carbon adhesive and a thin layer of gold was deposited on the sample surface to minimize sample charging. The images allowed the shape and morphology of the biochar powder to be examined. The particle size distribution of the biochar powder was measured using a Malvern Mastersizer 2000.

Flowability of the biochar powder was examined using a Mercury Scientific Revolution Powder Analyzer. A powder sample size of 118 cm^3 was loaded into a drum with a diameter of 11 cm and width of 3.5 cm. The drum was rotated at 0.3 rpm until 128 avalanches had occurred with an avalanche defined as being a rearrangement of at least 0.65 vol% of the sample in the drum. Optical measurements with a resolution of 648 x 488 at 60 frames per second allowed the powder surface to be measured as the sample was rotated. The Mercury Scientific Revolution Powder Analyzer software calculated various flowability indicators. Samples were measured in triplicate.

Drop penetration tests were conducted to examine the interaction between the liquid binder solutions and the biochar powder. The drop penetration measurements were conducted using a procedure similar to the one outlined by Hapgood et al. [8]. The biochar powder was sieved through a 1.4 mm sieve into a petri dish. A spatula removed excess powder to create a loosely packed bed of biochar powder with a level surface. A 25 gauge needle syringe was mounted 1 cm above the powder bed. A liquid binder droplet of 0.0048 mL was gently dropped on the powder bed and a video of the drop penetration was filmed. The procedure was repeated in triplicate. The drop penetration time was determined as the time at which the liquid droplet was no longer visible at the powder bed surface.

Hydroxypropyl methylcellulose (HPMC) (Pharmacoat® 603, Shin-Etsu Chemical Co.) was used as the binder. HPMC is a commonly used binder for granulation of pharmaceutical powders [9]. Binder solutions were prepared by heating distilled water to approximately 85^{o}C and then gradually adding the required amount of HPMC powder. The solutions were stirred until the powder fully dissolved and cooled to about 23 ^{o}C before conducting experimental trials. Viscosity measurements of the binder solutions were conducted using a Brookfield Viscometer with a 00 spindle.

The hygroscopicity of the biochar powder was determined by measuring the change in moisture content of the powder after exposure to air at different humidity levels. The biochar powder was spread into a thin layer on trays and placed in a humidity chamber for 48 hours. The humidity of the air within the chamber was adjusted by varying the flow ratio of dry air and air humidified by bubbling through water in a column. The temperature and the humidity of the air within the humidity chamber were measured using dry and wet bulb temperature sensors. After 48 hours within the humidity chamber, the moisture content of the biochar powder was determined using a Mettler-Toledo HG63 moisture analyzer based on weight loss-on drying at 105 ^{o}C; triplicate samples of approximately 3 g were analyzed.

3.2.3 Granulation

Experimental design allows a series of experimental trials to be planned and conducted in a specific order that maximizes the information gained with a minimum number of trials. StatEase Design Expert 8 statistical software (Stat-Ease, Inc. Minnesota, USA) was used to generate a two-level factorial design of experiments (DoE) to determine the effect of concentration of binder in the liquid solution, volume of liquid binder solution added and drum rotational speed. Based on preliminary trials, all three process parameters were given a low, mid and high. The binder concentration was varied from 3 wt% to 9 wt% with a centre value of 6 wt%, the binder solution volume ranged from 17.9 to 20.5 to 23 ml to correspond to 70, 80 and 90 wt% of binder solution to biochar mass, and the drum rotational speeds were 40, 50 and 60 rpm. An analysis of variance (ANOVA) was conducted with optimal granule size yield, flowability, attrition resistance and crushing strength as the response variables. P-values less than 0.05 were considered significant, indicating at least a 95% confidence level for a specific response variable.

A schematic diagram of the drum granulator is shown in Figure 3-1. The drum had an inner diameter of 7.5 cm, an inner length of 12.0 cm and was made of transparent Plexiglas to allow visual observations. One end of the drum was connected to a motor which allowed for the drum to be rotated. The other end of the drum had an opening to allow a sparger to be inserted. The sparger spanned the length of the drum, had an inner diameter of 3.0 mm, and had four 1.0 mm holes about 3.0 cm apart axially. The sparger was attached to a peristaltic pump to deliver the liquid binder solution. The binder solution was added drop wise onto the powder bed surface with a mean droplet volume of

0.08 ml and at a rate of approximately 8.5 ml/min. The drum granulator and sparger system were custom manufactured by University Machine Services (London, Canada).

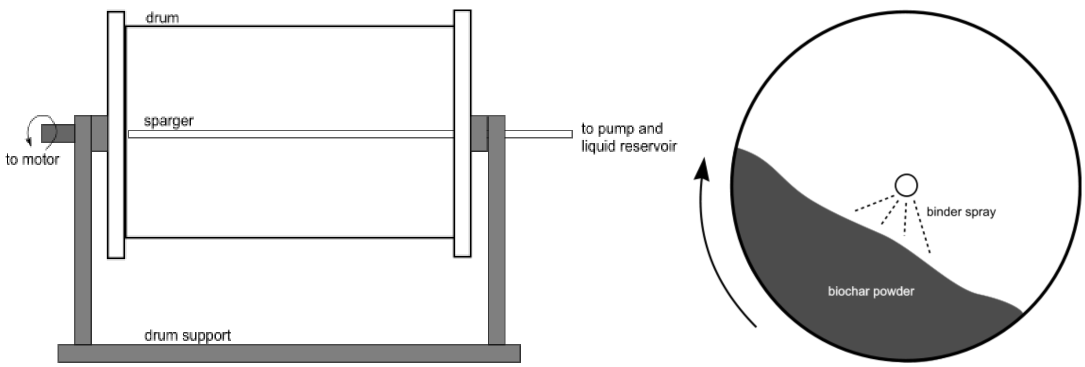


Figure 3-1: Schematic diagram of the drum granulator.

For the granulation trials, 25 g of the biochar powder was added to the granulation drum. The drum was rotated at the required speed for the specified trial. Liquid binder solution was added drop wise onto the cascading powder surface until the specified volume for a given trial was reached. Liquid binder addition was then stopped. The drum was rotated for two more minutes to allow wet massing before the granulation was stopped. Granules were removed, spread onto trays and dried at 24 ^{o}C and a relative humidity of 3 - 5 % for more than 24 hours. The dried granules were then analyzed for various properties.

3.2.4 Granule Characterization

As the biochar granules would be applied to soils similarly to fertilizers, granule and fertilizer properties were compared. Based upon common fertilizer granule size specifications**,** the optimal biochar granule size range was defined as granules whose diameters were between 1 and 4 mm [10]. Granules under 1 mm in diameter were classified as undersized and granules larger than 4 mm as oversized. The mass percentage of granules from each trial within these three groupings was determined through sieving with 1 and 4 mm sieves. The size distribution of the granules was measured through sieving using standard sieve sizes between 0.6 – 6.3 mm (0.60, 0.85, 1.00, 1.18, 1.40, 2.00, 2.36, 2.80, 3.35, 4.00 and 6.30 mm).

Images of the biochar granules were taken using a Hitachi S-4500 field emission scanning electron microscope. The granules were mounted on a plate using a carbon adhesive and coated with a layer of gold before examination. The images allowed the shape, surface morphology and sizes of the biochar granules to be examined.

Flowability was again examined using a Mercury Scientific Revolution Powder Analyzer using the procedure outlined for the powder flowability measurements. For the granules, however, a sample size of 25 cm^3 was loaded into a smaller drum with a diameter of 5.0 cm and width of 3.5 cm. Only granules within the 1 – 4 mm size range were tested.

Granules within the optimal size range of 1 - 4 mm were tested for strength as evaluated through attrition resistance measurements and crushing strength. Many attrition tests have been developed, some of which are summarized by Utsumi et al. [11], and generally involve agitation of the solids, with or without additional solids to provide enhanced agitation, and a comparison of size changes through sieving. For the attrition resistance measurements of the biochar granules, a test procedure was developed based on literature descriptions including tests designed for fertilizer granules [12]. A 25 cm^3 sample combined with 20, 5 mm diameter steel beads were placed in a drum with a diameter of 11 cm and width of 3.5 cm. The drum was rotated at 30 rpm for 128 rotations. The granules were then sieved with a 1 mm sieve and reweighed. The resistance to attrition was defined as:

$$\text{attrition resistance} = \frac{\text{granule mass after test}}{\text{granule mass before test}} \times 100\% \qquad (3-1)$$

Crushing strength measurements were conducted on individual granules. It was therefore difficult to obtain values representative of a specified trial. Only estimates were possible, using measurements repeated in triplicate. Using an Instron 8874, granules were compressed at a speed of 0.5 mm/s between platens with 26 mm x 26 mm dimensions. The force was plotted with respect to time and the maximum force measured before breakage was recorded for each tested granule.

Plots were created to show the effect each process parameter had on the granule properties. Centre points were included in each plot to identify possible curvature and deduce variability in the data.

3.3 Results and Discussion

3.3.1 Biochar Powder

Figure 3-2 shows the SEM images of the biochar powder. There were both small and large particulates (Figure 3-2a). The small particles appeared to be pieces broken off from larger particles. The large particulates were either fibrous particles (Figure 3-2b) or agglomerates of the smaller particles (Figure 3-2c). Both the fibrous particles and the agglomerates were porous, a key feature of biochar for soil amendment [13, 14]. Lehmann et al. found a similar porous biochar powder structure for cornstover derived biochar [15].

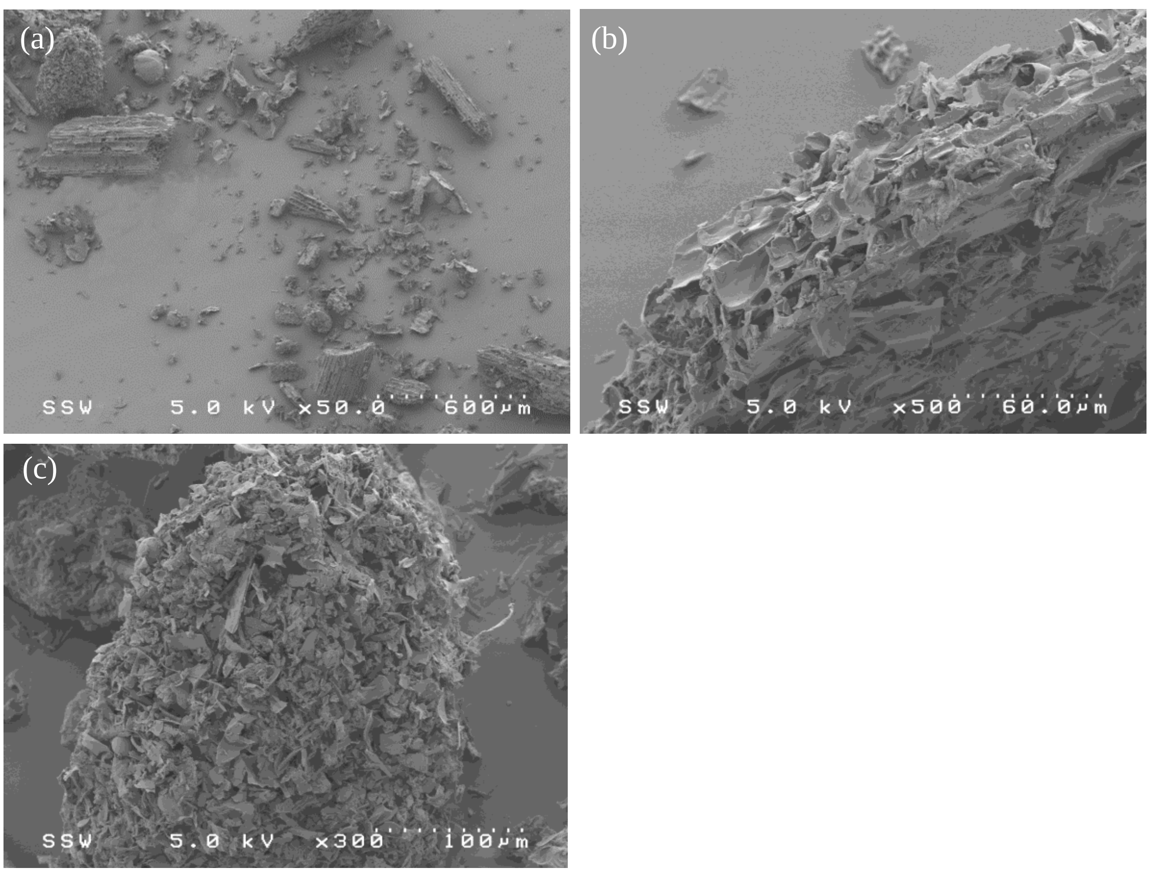


Figure 3-2: SEM images of the biochar powder.

The particle size distribution of the biochar powder from the Malvern Mastersizer 2000 analysis is given in Figure 3-3. The distribution was bimodal with peaks near 110 μm and 515 μm. These results confirm the size variations observed in the SEM images (Figure 3).

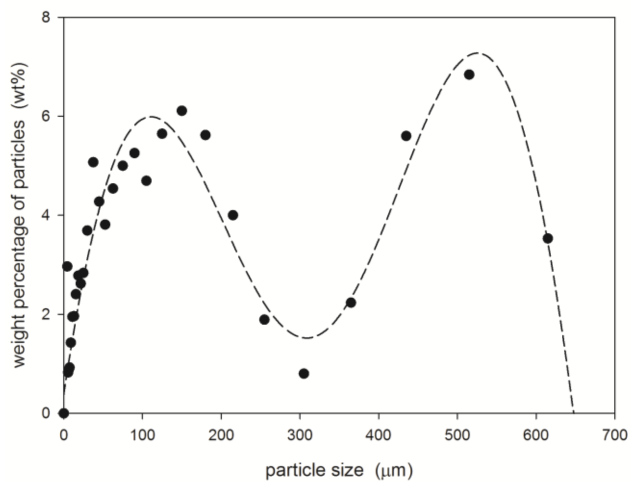


Figure 3-3: Particle size distribution of the biochar powder.

Flowability along with size and shape measurements of the biochar powder are summarized in Table 3-1. These results are presented with measurements of sand, a free-flowing powder, and corn starch, a very poor flowing and cohesive powder, for comparison. The irregular shape of the biochar particles would inhibit flowability while sizes larger than 10 μm would minimize relative contributions of van der Waal's forces that promote cohesive behaviour. In summary, parameters indicated that although the biochar may not always flow very freely and uniformly, it does flow and should tumble relatively easily within a drum granulator. Visual observations of the biochar powder within the drum confirmed continuous movement during rotation similar to cascading flow that is recommended for drum granulation [16].

Table 3-1: Comparison of biochar size, shape and flowability measurements.

Measurement	Biochar Powder	Sand	Corn Starch
Avalanche Time (s)	3.2	1.9	5.0
Standard Deviation of Avalanche Time (s)	2.1	0.6	6.4
Mean Particle Size (µm)	158	260	15
Particle Circularity	0.35	0.80	0.72

Hygroscopicity measurements indicated that the biochar is non-hygroscopic. Even after 48 hours of exposure to air at a humidity level of 80% the moisture content of the powder reached only 5 wt%. Drop penetration measurements further showed that the biochar was hydrophobic; drop penetration times ranged from 1.25 to 3.25 min using liquid droplets of 3 to 9 wt% HPMC solutions. Figure 3-4 shows images of drop penetration of the 6 wt% HPMC liquid binder solution into the cornstalk biochar powder. Within the first 15 to 60 s of the droplet contacting the powder bed surface, particles were drawn up and around the droplet forming a shell. This initial behaviour was similar to that of other hydrophobic powders [17]. Liquid droplets on very hydrophobic powders do not penetrate into a powder bed, but draw particles around the droplet and form a hollow granule or “liquid marble” structure [18]. The droplets of HPMC solutions on the biochar powder bed initially formed liquid marble structures. The liquid marbles then collapsed, allowing the liquid to penetrate into the surrounding powder to form a granule nuclei of particles linked through liquid bridges.

Time (min)		
Contact	0.5	1
		

Figure 3-4: Drop penetration of 6 wt% HPMC liquid binder into bed of cornstalk biochar powder.

Biochar powder interactions with liquids have implications for granulation. Based on both the drop penetration behaviour and visual observations during granulation, a granulation mechanism was hypothesized, Figure 3-5. As the liquid binder solution was dropped onto the cascading biochar powder bed surface, the impacting liquid droplets did not penetrate quickly. The droplets first remained near the surface and rolled down the inclined powder bed accumulating particles on the droplet surface. The liquid marble structure started to penetrate into the powder bed surface where it collapsed. Granule growth then occurred primarily through collisions and coalescence of the granule nuclei formed from collapsed liquid marble structures.

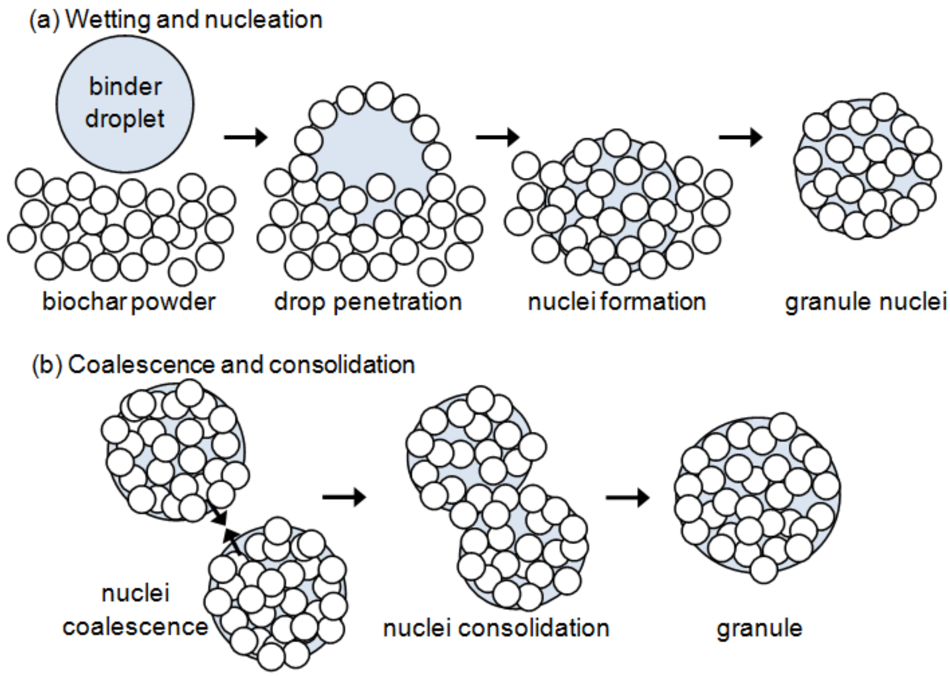


Figure 3-5: Proposed granulation mechanism for cornstalk biochar and HPMC binder solution.

3.3.2 Biochar Granules

Figure 3-6 shows a scanning electron micrograph image of a biochar granule. The granules were approximately spherical and incorporated the biochar particles into their structure. Individual biochar particles were visible at the surface of the granules.

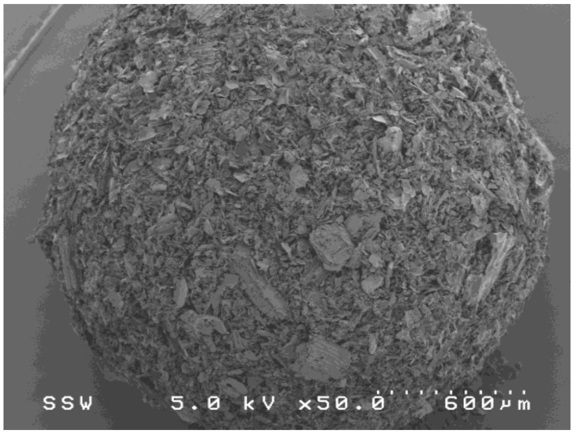


Figure 3-6: SEM image of the biochar granule.

Examples of the size distributions of the biochar granules are given in Figure 3-7. The sizes ranged from very small fines (less than 150 µm) indicating no granulation to granules almost as large as 5 mm in diameter. The optimal biochar granule size range was identified as 1 to 4 mm, based upon common fertilizer granule sizes. The amount of optimal granules within this size range varied from 14.8 to 43.0 wt%. ANOVA showed that the significant parameters affecting this granule size range were the rotation speed of the drum and the interaction between the concentration of binder and volume of total binder solution added during the granulation. The interaction plots are provided in Figure 3-8. As the rotational speed of the drum increased, the amount of optimal granules also increased (p-value of 0.0434) (Figure 3-8a). The increased agitation of the powder bed from the rotation provided better distribution of the liquid binder throughout the bed and more opportunities for coalescence resulting in granule growth to within the optimal 1 to 4 mm diameter range. The higher rotation speed also increased the impact force of collisions leading to high probabilities that collisions would result in successful coalescence to form larger granules.

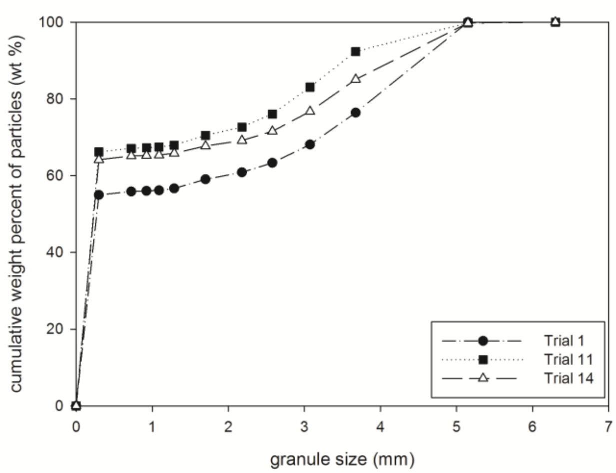


Figure 3-7: Biochar granule size distribution for Trials 1, 11 and 14.

Figure 3-8b shows that the addition of more liquid binder solution resulted in a larger amount of optimal granules and this effect was more significant for the low binder concentration compared to the high binder concentration solutions. The liquid binder was required to form the granule nuclei and then the liquid bridges between the particles within granules. Larger volumes of the liquid binder solution allowed formation of more nuclei and liquid bridges, increasing the granule size to within the optimal range. The interactive effect with binder concentration is complex, including viscous dissipation and hydrophobic behaviour. Increasing the binder concentration from a low of 3wt% to a high of 9 wt% correspondingly increased the viscosity of the binder solution from 0.009 Pas to 0.046 Pas. For coalescence, granules must deform with collisions. Iveson et al. showed that granule deformation was affected by inter-particle friction and viscous dissipation and therefore the effects of liquid content and viscosity are interactive [19]. Increasing the amount of liquid added to the granulation lubricated particle-particle contacts to decrease interparticle friction allowing deformation with collisions. The deformation increased the area of contact between the colliding granules thereby increasing the likelihood of successful coalescence [20]. Increasing the viscosity of the liquid by adding more HPMC, however, increased the resistance to deformation as viscous dissipation inhibited the required movement of liquid within the pores of the granules. At low binder concentrations, the viscous dissipation forces were minimal such that the increase in binder volume promoted granule deformation increasing the coalescence to larger granules. At high binder concentrations, the viscous dissipation forces were significant and inhibited deformation even at high binder volumes thereby reducing granule coalescence such that the yield of granules within the 1 to 4 mm size range remained relatively low.

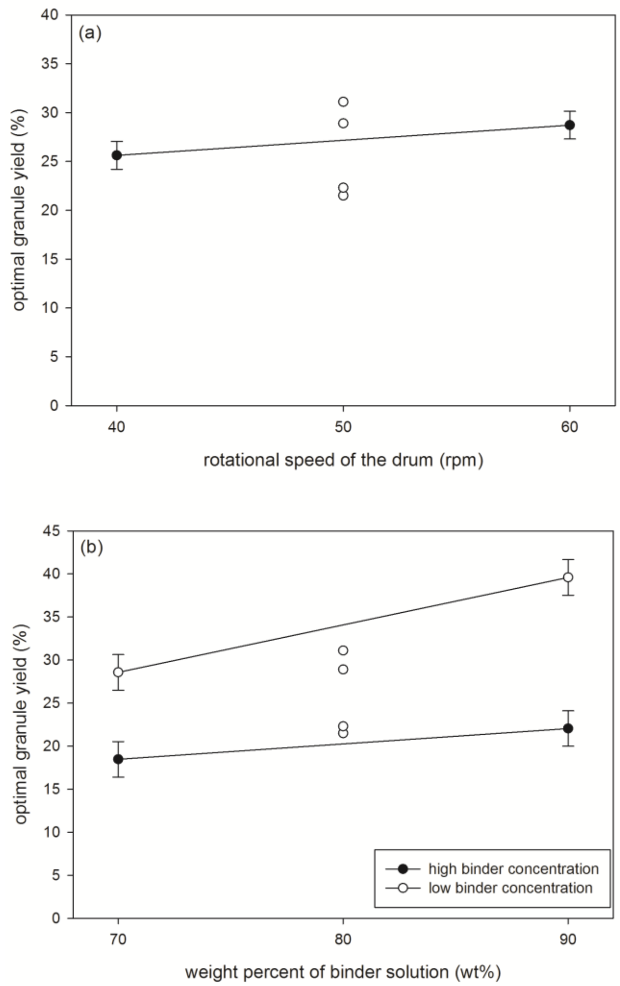


Figure 3-8: Granulation parameters that affect the yield of optimal size biochar granules.

The drop penetration times ranged from 1.25 to 3.25 minutes as the binder concentration was increased from 3 to 9 wt% HPMC. Liquid binder droplets with high HPMC concentrations therefore took longer to penetrate into the cascading powder bed and collapse compared to droplets with lower HPMC concentrations. The longer times would have resulted in a delay in the formation of granule nuclei available to coalesce and grow through collisions, contributing to the low yield of granules within the 1 to 4 mm optimal size range observed for the trials conducted with high binder concentrations.

The granules must flow well to allow easy distribution from storage and machinery to the fields for soil amendment. Granule flowability was assessed through the avalanche time and its standard deviation using the Mercury Scientific Revolution Powder Analyzer. Both values were very low for all trials, varying between only 2.50 and 2.87 for the avalanche time and 2.00 and 2.37s for the standard deviation of avalanche time, indicating that the biochar granules were free flowing. This was expected due to the size and almost spherical shape of the granules. None of the tested granulation parameters significantly affected the measured flowability parameters of the biochar granules.

Granules must have sufficient strength to remain intact during handling and distribution. Attrition of the granules would create fine particles that could then become airborne when the granules are applied to soils. As shown in Figure 3-9, the granule resistance to attrition was high and was affected by the rotational speed of the granulator drum as well as the concentration of the liquid binder or liquid binder viscosity. Granule strength primarily depends on granule porosity. Consolidation occurs through granule collisions with other granules and the walls of the granulator and it reduces the porosity thereby increasing the granule strength. The agitation from the drum rotation provided stronger forces and more opportunities for granule collisions thereby increasing consolidation and granule strength. Granule behaviour during a collision is controlled by inter-particle friction, viscous dissipation and capillary forces. As granules consolidate, inter-particle friction and viscous resistance increase as the number of inter-particle contacts increase. Increasing the viscosity of the binder solution reduces the rate of consolidation. However, a viscous binder increases the capillary forces that help bind the particles together and promote consolidation.

Therefore, although the rate of consolidation can be lower, the extent of consolidation can be higher with a viscous binder [16]. As the attrition resistance of the granules was high under all conditions, the viscosity of the liquid binder solution allowed capillary forces to bind particles together into strong granules. With the low viscosity binder, the resistance to consolidation through viscous dissipation was minimized and therefore the effect of increasing the drum rotational speed was relatively larger than with the high viscosity binder.

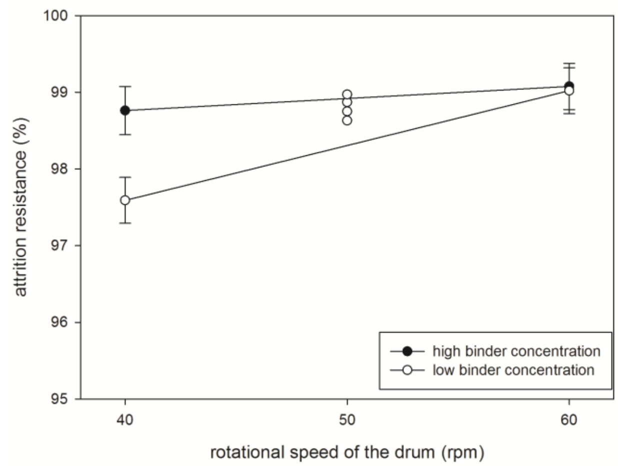


Figure 3-9: Granulation parameters that affect the granule resistance to attrition.

Granules can be crushed during handling and storage. As shown in Figure 3-10, the granule crushing strength increased with binder concentration or liquid binder solution viscosity (p-value of < 0.0001). The higher viscosity binder solutions increased capillary forces to strengthen bonds between particles within a granule resulting in stronger granules. The crushing strength of the biochar granules ranged from about 0.15 to 0.50 MPa. This was comparable to the crushing strength of organic fertilizer granules of limestone powder and anaerobic digestion liquor produced by Mangwandi et al., but much lower than the 4 – 5 MPa crushing strength of NPK fertilizers measured by Walker et al. [21, 22]. As the accepted limit for crushing strength of fertilizer granules is 2 MPa, an alternative binder must be investigated for further development and future agricultural application of biochar granules [23].

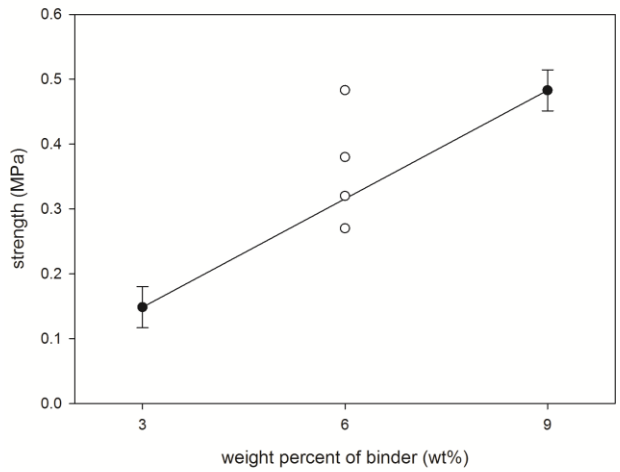


Figure 3-10: The effect of binder concentration on granule strength.

The attrition resistance was found to be significantly affected by both the drum rotational speed and the concentration of the liquid binder while the crushing strength was only significantly affected by the concentration of the liquid binder. The attrition resistance and crushing strength are related granule strength indicators. It was, therefore, expected that both would have been similarly affected by operational parameters. The difference was attributed to the samples used for the measurements: large, 25 cm^3 samples that would have included many granules and therefore were approximately representative of a trial were used for the attrition measurements while non-representative samples of only three granules were possible for the crushing strength measurements.

3.4 Conclusions

Drum granulation of biochar, created from the pyrolysis of cornstalk, was investigated as a method for modifying the biochar to a form that could easily be applied to soils. The cornstalk biochar was irregular in shape, very porous, had a bimodal size distribution and was relatively free flowing. A Design of Experiments examined the effect of binder concentration, total volume of binder solution and drum rotational speed on the size, flowability and strength of the resulting granules. The granules were approximately spherical with a significant yield between a size range of 1 to 4 mm, free flowing and relatively strong as measured through resistance to attrition and crushing. All three tested parameters affected granule size. Increasing the drum rotational speed increased the granule collisions while adding more binder solution volume decreased inter-particle friction forces promoting deformation and coalescence to larger granules. Low binder concentrations minimized the resistance to deformation from viscous dissipation. Consolidation to form strong granules was promoted through collisions with increasing drum rotational speed and through increasing binder solution viscosity. Although a higher viscosity reduced the rate, the extent of consolidation was higher due to stronger liquid capillary forces. The results clearly demonstrated that cornstalk biochar granules could be made through drum granulation to a size range of 1 to 4 mm similar to fertilizer granules. Further research is required to identify an appropriate binder to form a granule with a higher crushing strength closer to minimum fertilizer requirements to ensure that the granules remain intact during storage, handling and then distribution onto soils.

3.5 References

[1] R.K. Dumroese, J. Heiskanen, K. Englund, A. Tervahauta, Pelleted biochar: Chemical and physical properties show potential use as a substrate in container nurseries, Biomass and Bioenergy, 35 (2011) 2018-2027.

[2] R. Kookana, X. Yu, G. Ying, Black is the new green: The blue shades of biochar, 19th World Congress of Soil Science, Brisbane, 1-6 August 2010, International Union of Soil Sciences, Brisbane, 2010, pp. 1-4.

[3] D.A. Laird, P. Fleming, D.D. Davis, R. Horton, B. Wang, D.L. Karlen, Impact of biochar amendments on the quality of a typical Midwestern agricultural soil, Geoderma, 158 (2010) 443-449.

[4] R. Bian, D. Chen, X. Liu, L. Cui, L. Li, G. Pan, D. Xie, J. Zheng, X. Zhang, J. Zheng, A. Chang, Biochar soil amendment as a solution to prevent Cd-tainted rice from China: Results from a cross-site field experiment, Ecological Engineering, 58 (2013) 378-383.

[5] L. Van Zwieten, S. Kimber, S. Morris, K.Y. Chan, A. Downie, J. Rust, S. Joseph, A. Cowie, Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility, Plant and Soil, 327 (2010) 235-246.

[6] S. Steinbeiss, G. Gleixner, M. Antonietti, Effect of biochar amendment on soil carbon balance and soil microbial activity, Soil Biology and Biochemistry, 41 (2009) 1301-1310.

[7] C.E. Brewer, Biochar characterization and engineering, (2012) 196.

[8] K.P. Hapgood, J.D. Litster, S.R. Biggs, T. Howes, Drop penetration into porous powder beds, Journal of Colloid and Interface Science, 253 (2002) 353-366.

[9] R. Rowe, P. Sheskey, S. Owen, Hypromellose, Handbook of Pharmaceutical Excipients, Pharmaceutical Press, London, UK, 2006, pp. 346-348.

[10] D. Rutland, J. Polo, Fertilizer dealer handbook: products, storage and handling., IFDC - An International Center for Soil Fertility and Agricultural Development, Muscle Shoals, AL, 2005.

[11] R. Utsumi, T. Hirano, H. Mori, J. Tsubaki, T. Maeda, An attrition test with a sieve shaker for evaluating granule strength, Powder Technology, 122 (2002) 199-204.

[12] V. Gowariker, V. Krishnamurthy, S. Gowariker, M. Dhanorkar, K. Paranjape, The Fertilizer Encyclopedia, John Wiley and Sons Inc., Hoboken, New Jersey, 2009.

[13] X. Zhang, H. Wang, L. He, K. Lu, A. Sarmah, J. Li, N. Bolan, J. Pei, H. Huang, Using biochar for remediation of soils contaminated with heavy metals and organic pollutants, Environmental Science and Pollution Research, 20 (2013) 8472-8483.

[14] R. Bian, S. Joseph, L. Cui, G. Pan, L. Li, X. Liu, A. Zhang, H. Rutlidge, S. Wong, C. Chia, C. Marjo, B. Gong, P. Munroe, S. Donne, A three-year experiment confirms continuous immobilization of cadmium and lead in contaminated paddy field with biochar amendment, Journal of Hazardous Materials, 272 (2014) 121-128.

[15] J. Lehmann, M. Rillig, J. Thies, C. Masiello, W. Hockaday, D. Crowley, Biochar effects on soil biota - a review, Soil Biology & Biochemistry, 43 (2011) 1812-1836.

[16] J. Litster, B. Ennis, The Science and Engineering of Granulation Processes, Kluwer Academic Publishers, Dordrecht, NLD, 2004.

[17] N. Eshtiaghi, J.J.S. Liu, K.P. Hapgood, Formation of hollow granules from liquid marbles: Small scale experiments, Powder Technology, 197 (2010) 184-195.

[18] N. Eshtiaghi, K.P. Hapgood, A quantitative framework for the formation of liquid marbles and hollow granules from hydrophobic powders, Powder Technology, 223 (2012) 65-76.

[19] S.M. Iveson, J.D. Litster, B.J. Ennis, Fundamental studies of granule consolidation Part 1: Effects of binder content and binder viscosity, Powder Technology, 88 (1996) 15-20.

[20] H.G. Kristensen, P. Holm, T. Schaefer, Mechanical properties of moist agglomerates in relation to granulation mechanisms part I. Deformability of moist, densified agglomerates, Powder Technology, 44 (1985) 227-237.

[21] C. Mangwandi, L. JiangTao, A.B. Albadarin, S.J. Allen, G.M. Walker, Alternative method for producing organic fertiliser from anaerobic digestion liquor and limestone powder: high Shear wet granulation, Powder Technology, 233 (2013), pp. 245-254

[22] G.M. Walker, T.R.A. Magee, C.R. Holland, M.N. Ahmad, N. Fox, N.A. Moffatt, Compression testing of granular NPK fertilizers, Nutrient Cycling in Agroecosystems, 48 (1997) 231-234.

[23] P. Kiwietniak, Strength of fertilizer granules and methods for testing it, Mechanizacja Rolnictwa, 34 (1985).

Chapter 4

4 A comparison of wet drum granulation of three different biochar powders

4.1 Introduction

Biochar can be used as a soil amendment and also provides a form of carbon sequestration. When applied to soils, biochar has been shown to reduce the leaching of nutrients and heavy metals [1-6]. Biochar can also increase the amount of water retained within the soil and promote the microbial activity level of the soil. The long residence time of biochar is one of the major characteristics that makes it attractive for carbon sequestration [7, 8].

Pyrolysis, the thermal degradation of biomass, produces biofuel, gases and biochar. The biochar produced from this process is a fine powder with particle sizes ranging from 1-100 microns. Fine powders can easily become airborne during packaging and application to soils. The biochar powder that would be entrained in the air would not only lead to a loss of product, but would also cause health problems such as respiratory irritation and lung damage [9]. There have been application techniques proposed to reduce dust hazards. These techniques include on-site addition of water to dampen the powder, creating a liquid slurry solution or applying as a solid fertilizer after pelletization of the biochar [10, 11]. Although promising, these applications may not completely eliminate dust hazards and may also have additional steps or complications with their applications [2].

A possible solution for minimizing dust hazards is size enlargement. Wet granulation is a well-known process used for size enlargement of powders which not only eliminates dust hazards, but also improves powder characteristics such as flowability, dispersibility and handling [12]. In the wet granulation process, a liquid binder is used to create granules through the agglomeration of powder particles. The three main wet granulation processes are high shear, fluidized bed and drum granulation [13]. The most cost effective wet granulation process is drum granulation due to lower capital and operating costs. Drum granulation also has the advantage of relatively easy scale-up that would allow large volumes of biochar to be processed. Drum granulation uses a drum loaded with powder. Agitation is achieved by the rotation of the drum and the liquid binder addition occurs through spargers placed above the powder bed. The increased size of biochar granules made through wet granulation compared to individual biochar particles would minimize entrainment into the air and improve handling and application to soils.

Hydrophobic interactions between biochar powders and aqueous liquids have been reported [14, 15]. When liquid droplets contact a hydrophobic powder, they do not immediately penetrate into the powder bed. Instead the droplet rests at the surface of the powder bed and can draw powder particles up around itself to form a liquid marble structure [15]. This structure, if stable, can develop into granules through layering of particles at the surface. The liquid marble could also collapse allowing the liquid to penetrate into the powder to form a granule nucleus.

Pyrolysis conditions are usually adjusted to increase the yield of the primary product, biofuel. Common pyrolysis feedstocks include agricultural residues, residual wood and grasses. The composition of biochar powder produced from pyrolysis varies with both feedstock and process conditions [16-19]. Liu et al. compared pyrolysis process temperatures and found higher temperatures removed polar surface functional groups and increased the formation of more aromatic structures [22]. Mullen et al. found that cornstover-derived biochar contained significantly larger amounts of inorganic components compared to corncob-derived biochar [23]. Another study compared biochar produced from mill and forest residues and found that even these similar feedstocks were broken down differently resulting in a range of biochar characteristics [20].

The feedstock and the pyrolysis process used to produce biochar can result in biochar powder with a range of properties that could affect its wet granulation into biochar granules. The objective of the current research was to investigate the effect of biochar from different feedstocks on wet drum granulation. Specifically, the biochar granule properties of size and strength were measured for biochar from cornstalk, birchbark, and miscanthus feedstocks under a range of operating conditions for wet drum granulation using hydroxypropyl methylcellulose (HPMC) as the liquid binder. As the feedstock can easily change, the effect of this change on granulation is important to study to ensure that granulation operating parameters are adjusted to produce biochar granules with specified properties.

4.2 Materials and Methods

4.2.1 Biochar Formation

Three feedstock were chosen for the biochar: cornstalk, birchbark and miscanthus. The feedstock were treated by drying at 105 ˚C and grinding to 1-2 mm in size using an IKA Werke model MF10 Ginder at 4500 rpm. The feedstocks were then pyrolyzed separately in a custom manufactured fixed bed reactor (University Machine Services, London, Canada) with a 25 cm diameter and an effective bed height of approximately 60 cm. The temperature and pressure of the reactor were set to 500 ˚C and 100 kPa. The fixed bed was fluidized at intervals to ensure constant temperature and uniform bed composition. Following pyrolysis, the biochars were recovered from the reactor.

4.2.2 Biochar Characterization

A Hitachi S-4500 field emission scanning electron microscope was used to take images of samples of each biochar powder. The images allowed the size, shape and morphology of the biochar powder to be examined. A Malvern Mastersizer 2000 was used to measure the biochar powder particle size distribution.

A Mercury Scientific Revolution Powder Analyzer was used to measure the flowability of the biochar powders. A sample size of 118 cm^3 was loaded into a drum (diameter of 11 cm and length of 3.5 cm) and rotated at 0.3 rpm until 128 avalanches had occurred with an avalanche defined as a rearrangement of at least 0.65 vol% of the sample in the drum. During revolution testing, optical measurements with a resolution of 648 x 488 at 60 frames per second allowed the powder surface to be examined. Measurements were made in triplicate. The main indicators of flowability were the avalanche time and its standard deviation and the dynamic angle of repose.

The carbon, hydrogen, nitrogen and oxygen content of the biochar powders was determined using a FlashEA 2000 CHN-O Analyzer. Measurements were conducted in triplicate to ensure the reproducibility of the results.

Drop penetration tests were performed to investigate the interactions between the liquid binder solutions and the biochar powders. The drop penetration measurements were conducted using a similar procedure as outlined by Hapgood et al. [26] A loosely packed powder bed was formed by sieving the biochar powder through a 1.7 mm sieve into a petri dish and using a spatula to remove any excess powder. A 25 gauge needle syringe was mounted 1 cm above the petri dish. Liquid binder droplets of 0.0048 mL were carefully dropped onto the powder bed surface and the drop penetration time was determined as the time at which the liquid droplet was no longer visible at the powder bed surface.

The liquid binders were aqueous solutions of hydroxypropyl methylcellulose, HPMC (Pharmacoat® 603, Shin-Etsu Chemical Co.). HPMC is a commonly used binder for granulation of pharmaceutical powders [27]. Distilled water was heated to 85 ˚C and then HPMC was added and stirred until fully dissolved. The liquid was cooled to room temperature (23 ˚C) before use. Viscosity measurements of the binder solutions were conducted using a Brookfield Viscometer with a 00 spindle.

4.2.3 Granulation

A two-level factorial design of experiment (DoE) was created using StatEase Design Expert 8 statistical software (Stat-Ease, Inc. Minnesota, USA) to examine the effect of concentration of binder in the liquid solution, mass of liquid binder solution added and drum rotational speed. Based on previous work, the binder concentration was varied from 3 wt% to 9 wt% with a center value of 6 wt%, the binder solution added was a 70, 80 and 90 wt% ratio of binder to biochar powder, and the drum rotational speeds were 40, 50 and 60 rpm [14]. An analysis of variance (ANOVA) was conducted with granule size and strength, as evaluated using attrition resistance and crushing strength, as the response variables. P-values less than 0.05 were considered significant, indicating at least a 95% confidence level for a specific response variable.

A schematic diagram of the drum granulator can be seen previously in Figure 3-1 [14]. The drum was transparent Plexiglas with a diameter of 7.5 cm and a width of 12.0 cm. The drum was mounted axially with a motor connected to one end to allow for the rotation of the drum. An opening at the other end allowed for a sparger to be inserted into the drum. The sparger had four 1.0 mm holes spaced evenly across its length. A peristaltic pump allowed the binder solution to be delivered drop wise through the sparger onto the powder surface with a mean droplet volume of 0.08 ml and at a rate of approximately 8.5 ml/min. The drum granulator and sparger system were custom manufactured by University Machine Services (London, Canada).

For the granulation trials, biochar powder was added to the granulation drum to a 30 vol% fill level. The drum was rotated at the required speed for the specified trial. Liquid binder solution was added dropwise onto the powder until the required liquid binder solution volume was added for the specified trial. The binder addition was then stopped and the drum was rotated for two more minutes for wet massing. The granules were removed and spread onto trays to dry at 24 ˚C and a relative humidity of 3-5 % for more than 24 hours. The dried granules were then analyzed for various properties.

4.2.4 Granule Characterization

The size distribution of the granules was measured through sieving using standard sieve sizes between 0.6 – 6.3 mm (0.60, 0.85, 1.00, 1.18, 1.40, 2.00, 2.36, 2.80, 3.35, 4.00 and 6.30 mm). The optimal granule size range was defined between 1 and 4 mm to correspond to common fertilizer granule sizes [28]. Granules not within this size range were classified as undersized (smaller than 1 mm in diameter) and oversized (larger than 4 mm in diameter). The mass percentage of granules from each trial within the three size groupings was determined using sieving with 1mm and 4 mm sieves. Only granules within the optimal 1-4 mm size range were used for further characterization.

Images of the biochar granules were taken to examine shape and surface morphology. The granules were mounted on a plate using a carbon adhesive, coated with gold and then images were taken with a Hitachi S-4500 field emission scanning electron microscope.

Further images of the biochar granules were examined with Image Pro software to estimate the circularity of the granules.

Strength was evaluated through attrition resistance and crushing strength measurements. A procedure for attrition resistance measurements was developed based on literature descriptions including tests designed for fertilizers [29]. A 25 cm^3 sample of granules was combined with 20, 5 mm diameter steel beads and loaded into a drum with a diameter of 11.0 cm and a width of 3.5 cm. The drum was rotated at 30 rpm for 128 rotations. The sample was then sieved through a 1 mm sieve and reweighed. The resistance to attrition was defined by equation 4-1:

$$\text{attrition resistance} = \frac{\text{granule mass after test}}{\text{granule mass before test}} \times 100\% \qquad (4-1)$$

Crushing strength measurements were conducted on individual granules, in triplicate, using an Instron 8874. The granules were compressed at a speed of 0.5 mm/s between platens with dimensions of 26 mm x 26 mm. The maximum vertical force of compression before granule breakage was measured and converted into MPa using the cross-sectional area of the granules as a basis.

Plots were created to show the effect each process parameter had on the granule properties and included centre points to identify possible curvature and variability in the data.

4.3 Results

4.3.1 Biochar Characterization

A comparison of the SEM images of the three biochars revealed differences between the powders. Figure 4-1a shows that cornstalk biochar powder had large fibrous particles, many particle fragments and agglomerates of smaller particles and fragments. Birchbark biochar had a range of particle sizes from large fibres to small fragments (Figure 4-1b). Miscanthus biochar powder had primarily large fibres (Figure 4-1c). All three biochar powder particles were very porous which had been determined previously in other studies [30-33].

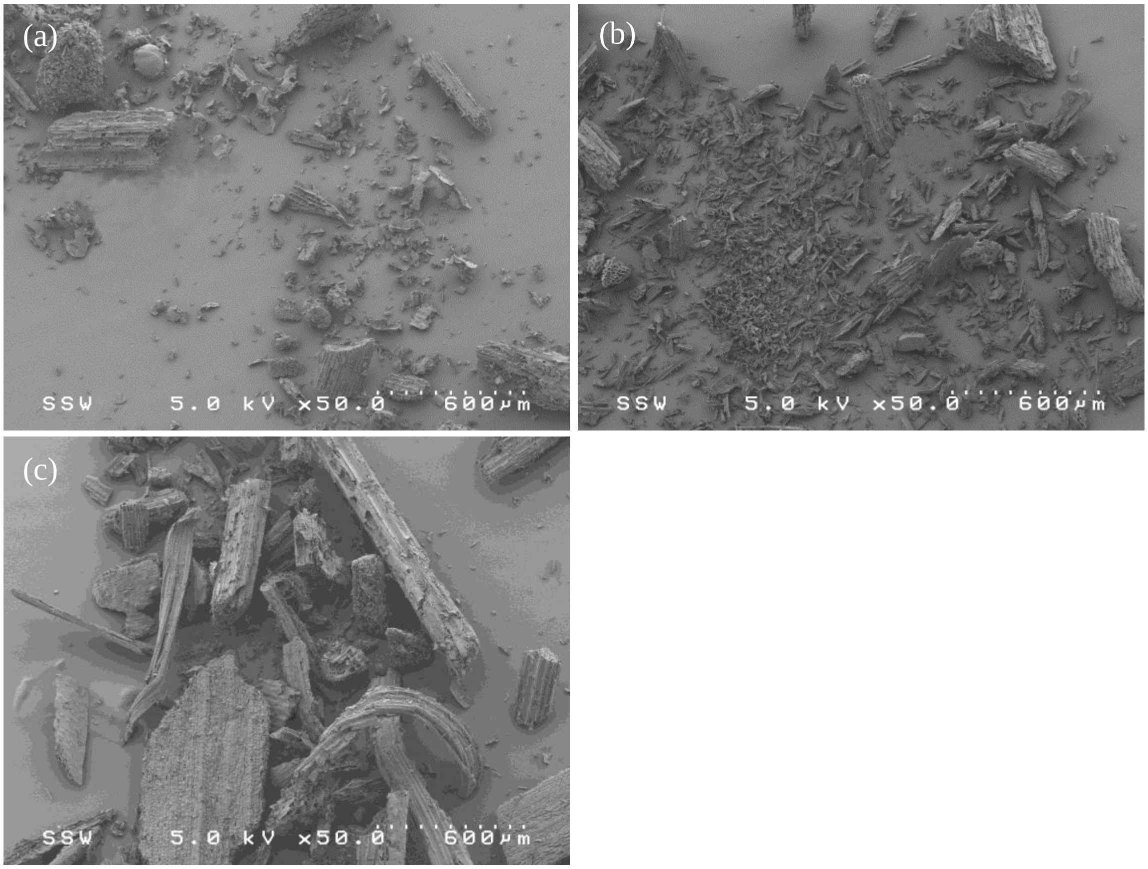


Figure 4-1 SEM images of a) cornstalk, b) biochar and c) miscanthus biochar powders

The particle size distributions of the biochar powders were measured using the Malvern Mastersizer 2000. The measurements supported the observations from the SEM images (Figure 4-2). Cornstalk biochar powder showed a biomodal size distribution with peaks near 110 µm and 515 µm reflecting its wide range in size and type of particle. The size distribution of birchbark biochar showed a peak near 250 µm while the miscanthus particles were larger with a peak near 350 µm.

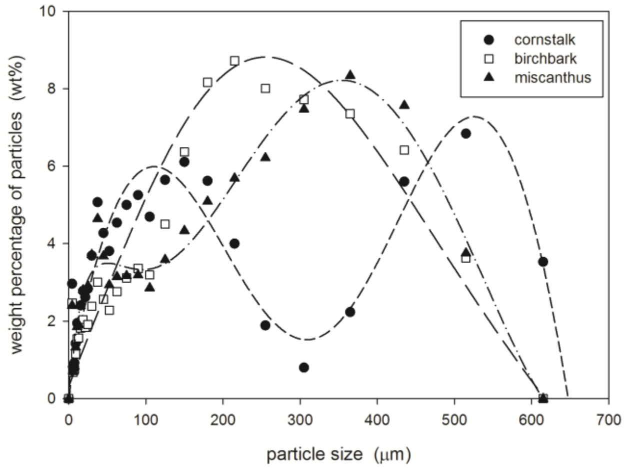


Figure 4-2: Particle size distribution of the biochar powders

Table 4-1 shows the elemental analysis of the biochar powders. As expected, the carbon content was high. However, the ratios of the elements varied with feedstock. Differences indicated variability in the chemical composition of the biochars and possibly the surface functional groups present on the biochars particle surfaces. Different surface functional groups could interact differently with the binder solution during granulation effecting the overall granulation process [1,22].

Table 4-1: Elemental analysis of the cornstalk, birchbark and miscanthus biochar powders.

Biochar Powder	Carbon	Hydrogen	Nitrogen	Oxygen
Cornstalk	73.5%	2.5%	1.3%	7.0%
Birchbark	57.8%	3.4%	0.2%	20.0%
Miscanthus	83.8%	2.6%	0.5%	5.0%

Table 4-2 summarizes the flowability along with the size and shape of each biochar powder. Excellent and uniform flow is usually indicated by a low avalanche time and its standard deviation as well as a low dynamic angle of repose. Parameters for sand and corn starch were included for comparison; sand is a free flowing powder while corn starch is cohesive and does not flow easily and uniformly. Although the biochar powders had irregular shapes, their relatively large particle sizes would minimize the relative contributions of cohesive van der Waal's forces. Therefore, the flowability parameters indicated that the three biochar powders would flow and tumble relatively easily within the rotating granulator drum. Visual observations of the powder movement within the transparent granulator drum confirmed continuous powder flow similar to cascading flow that is that is recommended for drum granulation [34].

Table 4-2: Flowability, size and shape measurements of the biochar powders, sand and cornstarch.

Measurement	Cornstalk	Birchbark	Miscanthus	Sand	Cornstarch
Avalanche Time (s)	3.2	3.4	2.4	1.9	5.0
Standard Deviation of Avalanche Time (s)	2.1	1.8	2	0.6	6.4
Dynamic Angle (degrees)	11.9	9.3	8.3	9.1	63.0
Mean Particle Size (µm)	158	183	173	260	15
Particle Circularity (-)	0.35	0.42	0.41	0.80	0.72

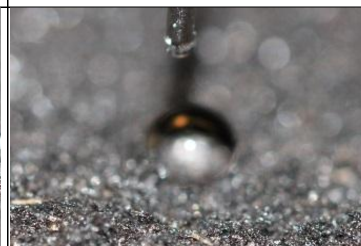
Drop penetration measurements reflect the interaction of the liquid binder droplets impacting the powder bed surface. This interaction directly affects granulation. Table 4-3 summarizes the drop penetration times of the liquid binders into the biochar powders. Both the cornstalk and birchbark biochars had increased drop penetration times with increased weight percent of HPMC in the binder solutions or increased liquid binder solution viscosity. The binder droplets did not completely penetrate the powder bed of the miscanthus biochar indicating a very hydrophobic powder.

Table 4-3: Drop penetration times of HPMC binder into biochar powders

Liquid Binder Solution		Drop Penetration Time (minutes)		
wt% HPMC	Viscosity (Pas)	Cornstalk	Birchbark	Miscanthus
3	0.0046	1.25 ± 0.2	23 ± 6	-
6	0.0156	2.50 ± 0.2	30 ± 7	-
9	0.0456	3.25 ± 0.2	-	-

Table 4-4 shows images of drop penetration of the 6 wt% HPMC liquid binder solution into the biochar powders. After contacting the cornstalk biochar, the binder droplet immediately drew powder particles around itself. Once fully covered, the droplet sank into the powder bed maintaining its size and shape. Birchbark biochar was drawn around the liquid binder droplet after contact. However, once approximately three quarters of the droplet was covered in birchbark biochar particles, the droplet diameter started to decrease slightly. This change in size then caused the droplet to become completely covered in powder particles and the droplet subsequently penetrated into the powder bed. Liquid binder droplets drew miscanthus biochar particles slowly around themselves. The droplet did not fully penetrate into the powder bed.

Table 4-4: Drop penetration of 6 wt% HPMC liquid binder into bed of the biochar powders.

Time (min)	Biochar Powder		
	Cornstalk	Birchbark	Miscanthus
Contact			
0.5			
5			
10			
20			
30			

4.3.2 Granule Characterization

Scanning electron micrograph images provided confirmation of granule size and also allowed visualization of the granule shape and surface morphology. As shown in Figure 4-3, the granules were agglomerates of biochar particles. The surface morphology appeared to be more uniform and the overall shape more spherical for the cornstalk and miscanthus biochar granules compared to the birchbark biochar granules. More photos of the granules were taken and the circularity of the granules within the 1 to 4 mm size range was obtained using Image Pro software. The measurements supported the observations; the cornstalk and miscanthus biochar granules had high circularities of 0.78 and 0.81 and respectively, while the circularity of the birchbark biochar granules was lower at 0.72.

The size distributions of the granules were measured through sieving. The size distributions are compared for three trials in Figure 4-4. The birchbark biochar granules were much larger than the cornstalk and miscanthus biochar granules. The cornstalk biochar granules were slightly larger than the miscanthus biochar granules.

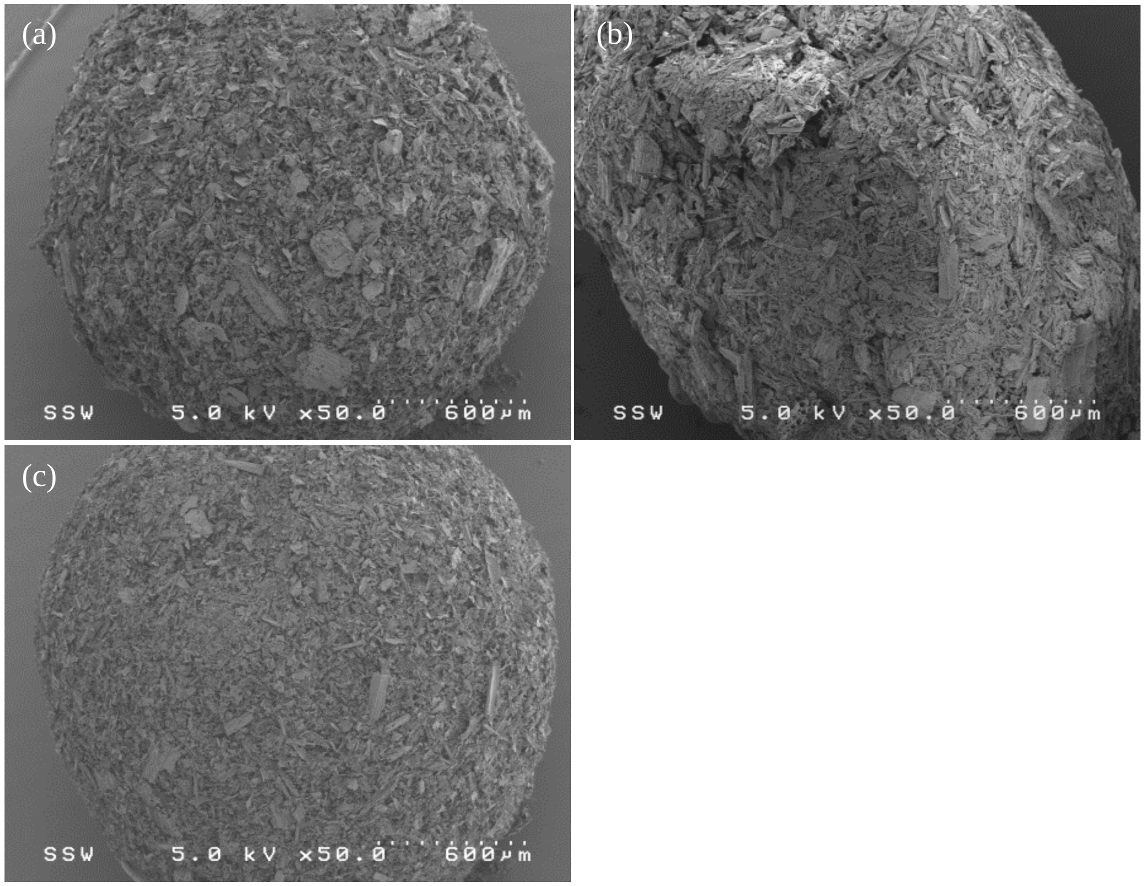


Figure 4-3: SEM images of granules from a) cornstalk, b) birchbark and c) miscanthus biochar powders.

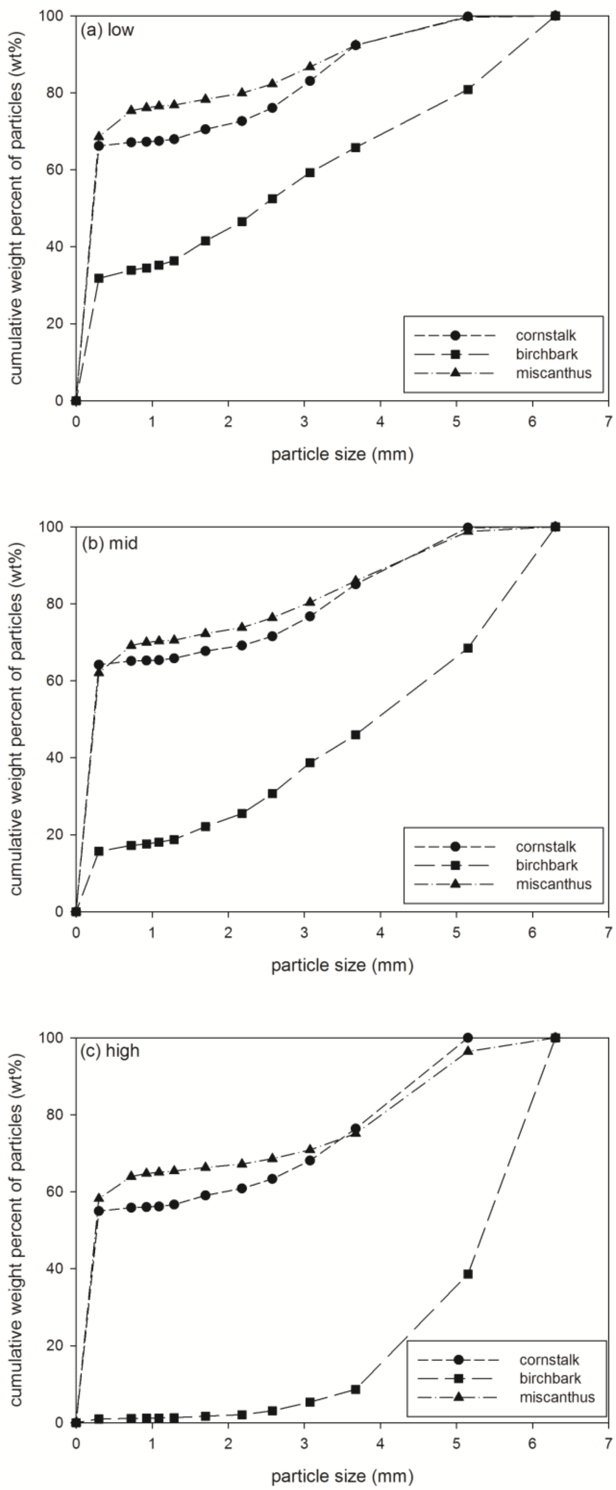


Figure 4-4: The granule size distributions for cornstalk, birchbark and miscanthus granules produced at a) low, b) mid and c) high granulation parameters.

The optimal granule size range was defined as 1-4 mm based on common solid fertilizer sizes [28]. Sieving allowed the yield of granules within this size range to be determined. The optimal granule yield ranged from 5.5 to 43.0 wt%, depending on the trial and the type of biochar. The yield of optimal size granules was much lower for the miscanthus compared to the other biochars. Figure 4-5 shows that the optimal granule yield was significantly affected by drum rotational speed (p-values of 0.0434, 0.0452, and 0.0450 for cornstalk, birchbark, and miscanthus biochar, respectively). Higher rotational speeds increased the optimal granule yield for the cornstalk and miscanthus biochar, 25.5 to 29.5 wt% and 15.3 to 17.5 wt% respectively. However, the opposite trend was observed for the birchbark biochar, 29 to 22 wt%.

The amount of liquid binder solution added and the concentration of HPMC in the solution were also shown to affect the optimal granule yield. Figure 4-6 shows that increasing the amount of liquid binder solution increased the optimal granule yields for cornstalk and miscanthus biochar by 7 wt% and 4.5 wt% respectively (p-values of 0.0001 and < 0.0001, respectively). Again, the opposite trend was observed for the birchbark biochar with a 15.5 wt% decrease (p-value of 0.0001) (Figure 4-6b).

Increasing the HPMC concentration in the binder solution decreased the optimal granule yield for all biochars, (Figure 4-7). The decrease was significant for the cornstalk and miscanthus biochar (p-value < 0.0001 for both biochars), but not significant for the birchbark biochar (p-value of 0.0576).

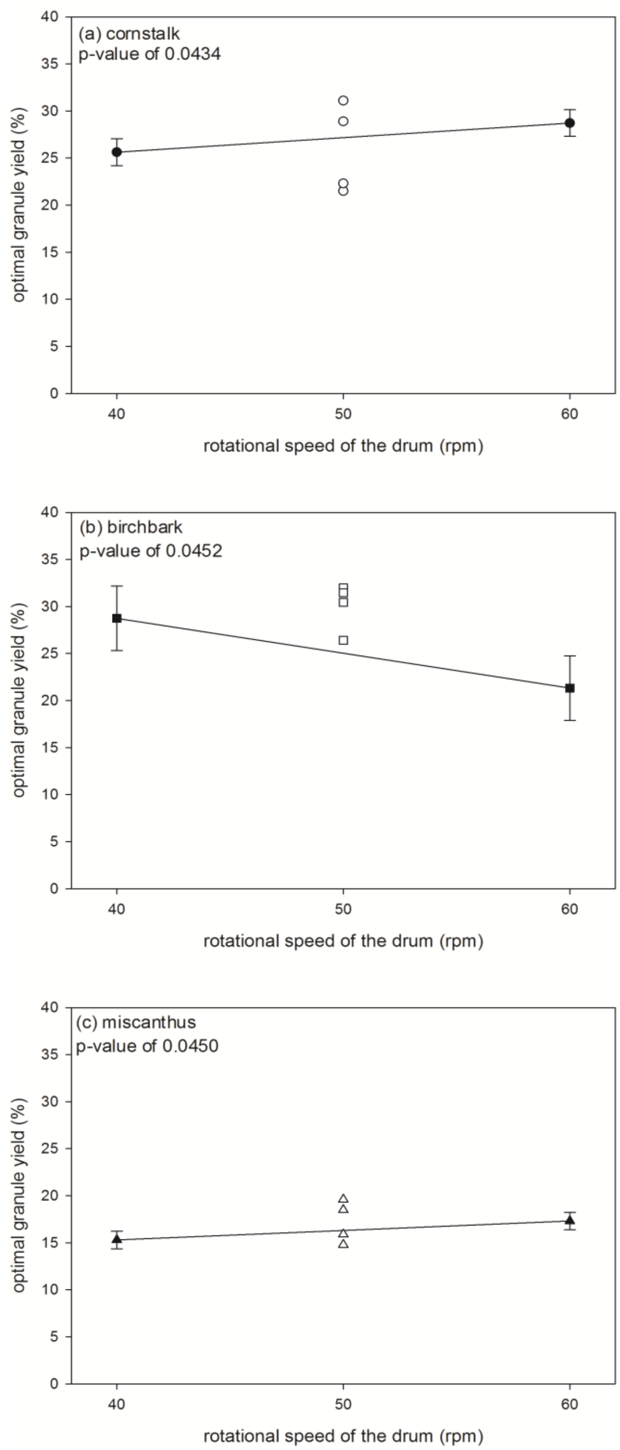


Figure 4-5: The effect of rotational speed of the granulation drum on the yield of optimal size granules produced from a) cornstalk, b) birchbark and c) miscanthus biochar. Solid points represent the low and high process parameter values while open points represent the centre points in the data.

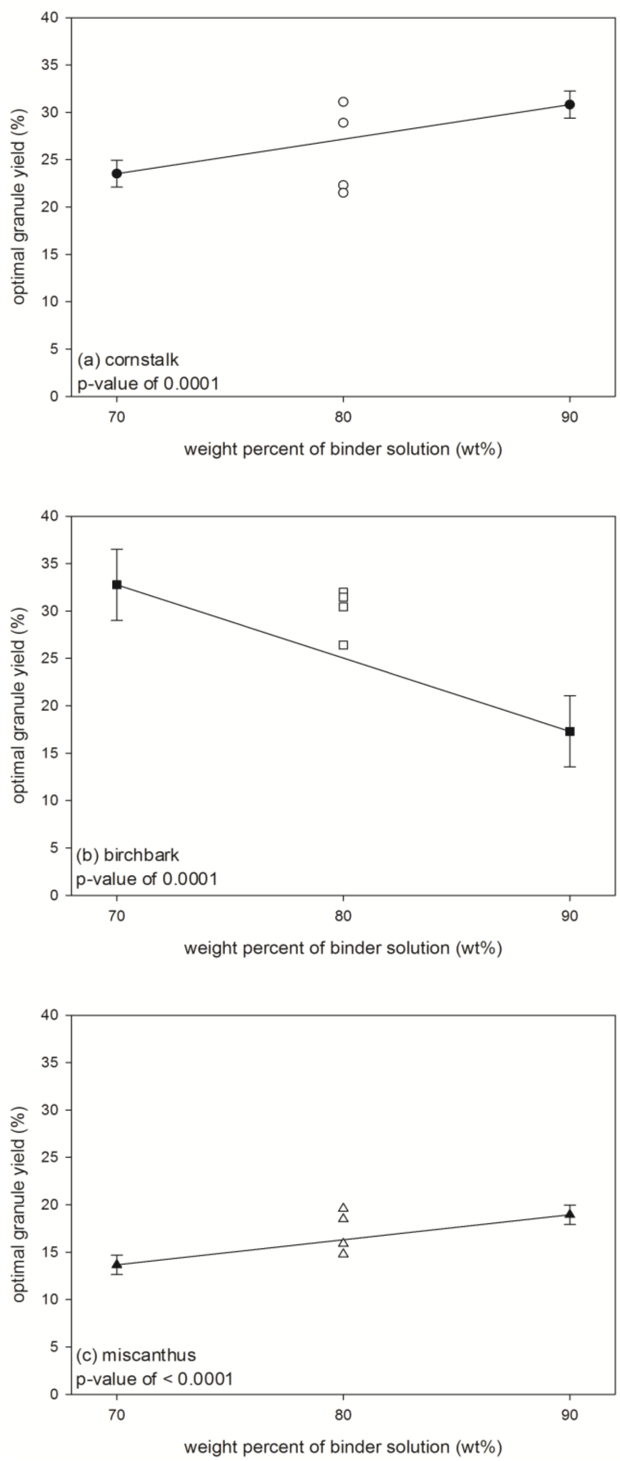


Figure 4-6: The effect of amount of binder solution on the yield of optimal size granules produced from a) cornstalk, b) birchbark and c) miscanthus biochar. Solid points represent the low and high process parameter values while open points represent the centre points in the data.

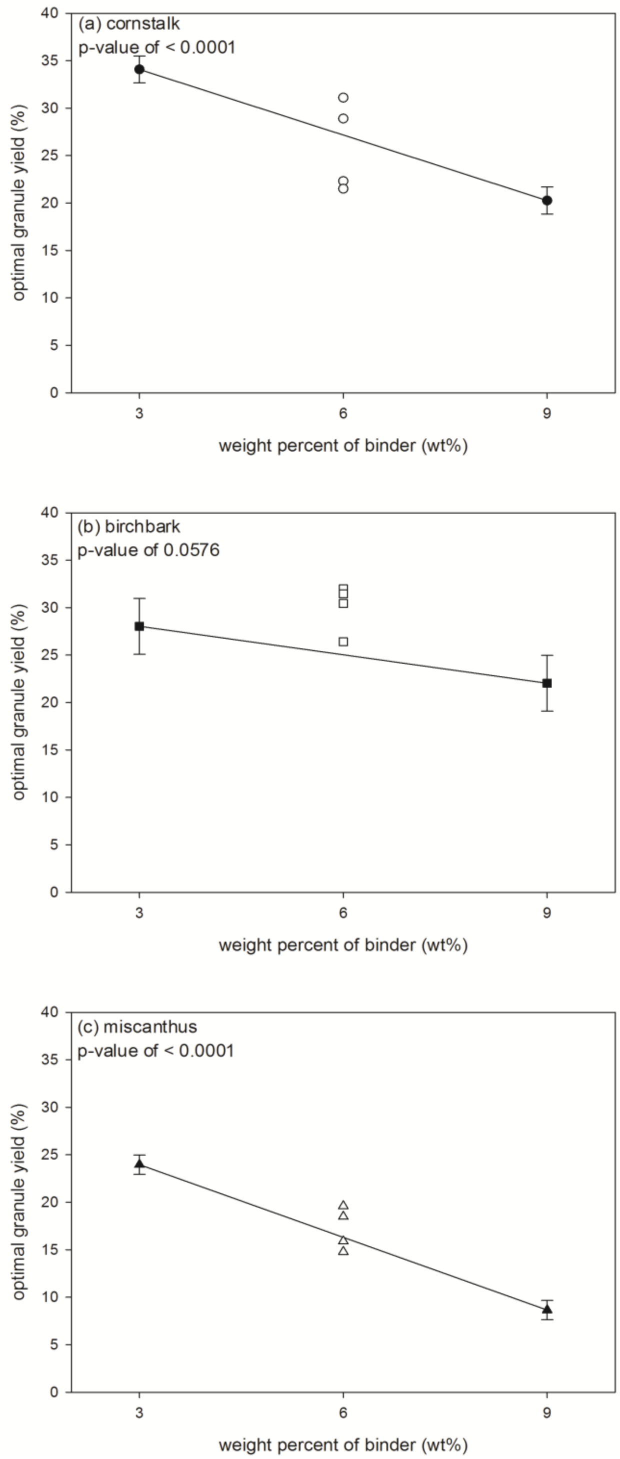


Figure 4-7: The effect of binder concentration on the yield of optimal size granules produced from a) cornstalk, b) birchbark and c) miscanthus biochar. Solid points represent the low and high process parameter values while open points represent the centre points in the data.

Strong granules are required to ensure that the granules remain intact during packaging, shipping and application to soils. Granule strength was evaluated based on resistance to attrition and crushing strength. Figures 4-8 and 4-9 show that the drum rotational speed and the HPMC concentration in the binder solution affected attrition resistance. Increasing the drum rotational speed increased attrition resistance for the cornstalk and miscanthus biochar granules, but decreased attrition resistance for birchbark biochar. The effect, however, was only significant for the cornstalk biochar granules (p-value of 0.0004).

As shown in Figure 4-9, the effect of HPMC in the binder solution on the attrition resistance was positive and significant for granules made from cornstalk and birchbark biochar (p-values of 0.0056 and 0.0001 respectively). Increasing binder concentration had less of an effect on the attrition resistance for the cornstalk granules compared to the birchbark granules, 98.2 to 98.9 % and 96.2 to 98.7% respectively. Increasing HPMC in the binder solution had a slight negative, but not significant, effect on the attrition resistance of miscanthus biochar granules.

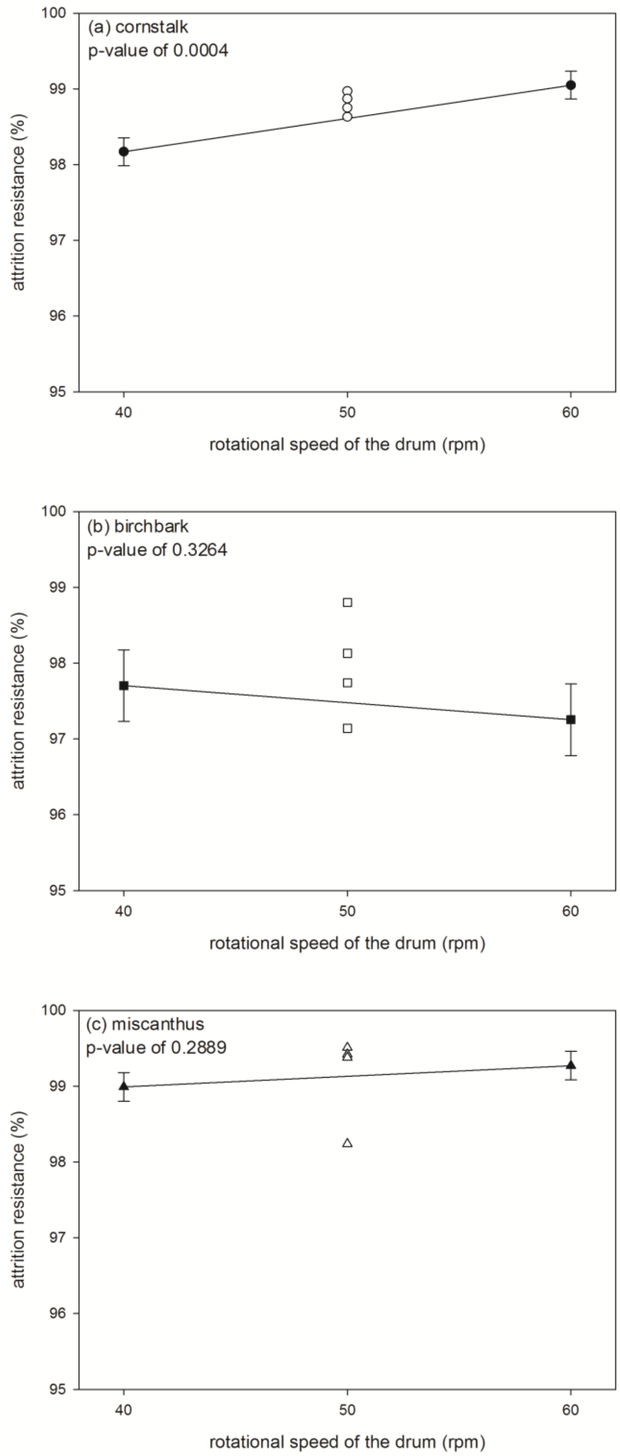


Figure 4-8: The effect of rotational speed of the drum on the attrition resistance of a) cornstalk, b) birchbark and c) miscanthus biochar granules. Solid points represent the low and high process parameter values while open points represent the centre points in the data.

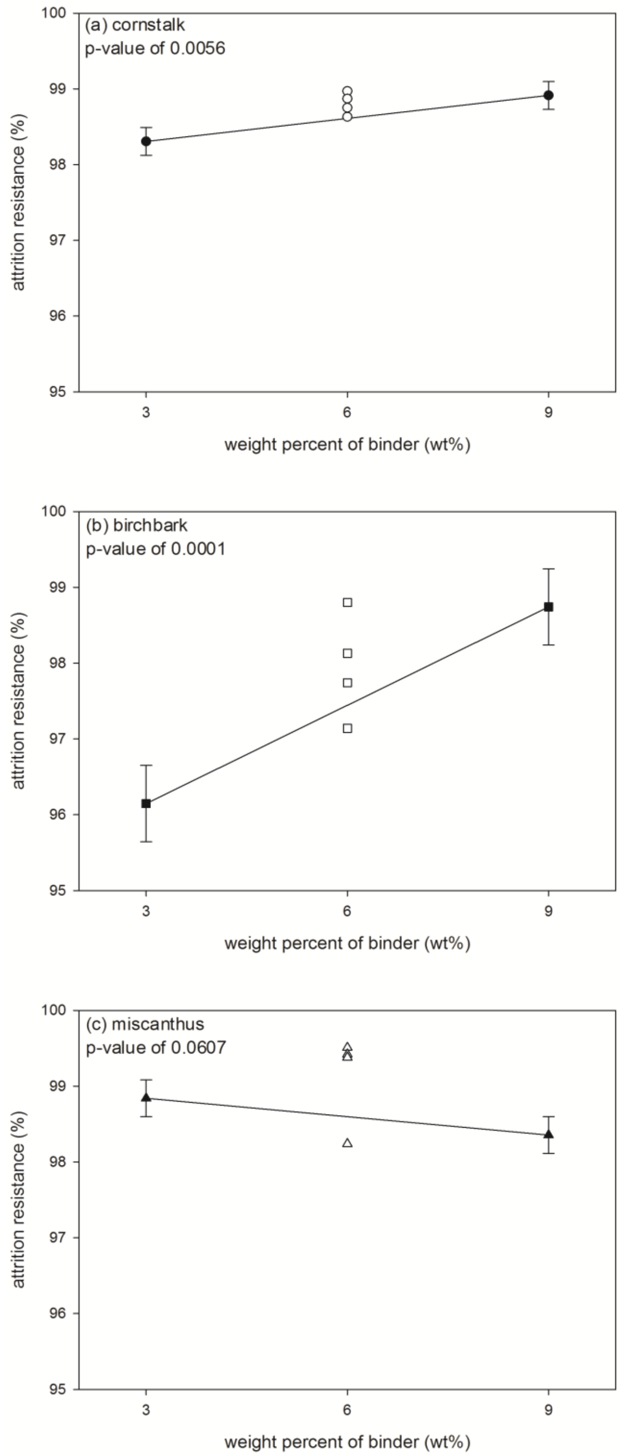


Figure 4-9: The effect of binder concentration on the attrition resistance of a) cornstalk, b) birchbark and c) miscanthus biochar granules. Solid points represent the low and high process parameter values while open points represent the centre points in the data.

The volume of binder solution added was also a significant parameter (p-value of 0.0080) for the birchbark biochar granules, but not for the other granules, Figure 4-10. As the binder volume increased, there was a significant increase in crushing strength for the birchbark biochar granules. Increasing binder volume had almost no effect on the crushing strength of cornstalk and a negative effect on the miscanthus biochar granules. Of the three tested parameters, only the percentage of HPMC in the binder solution or binder concentration significantly affected crushing strength of all three biochar powders, Figure 4-11 (p-values of < 0.0001).

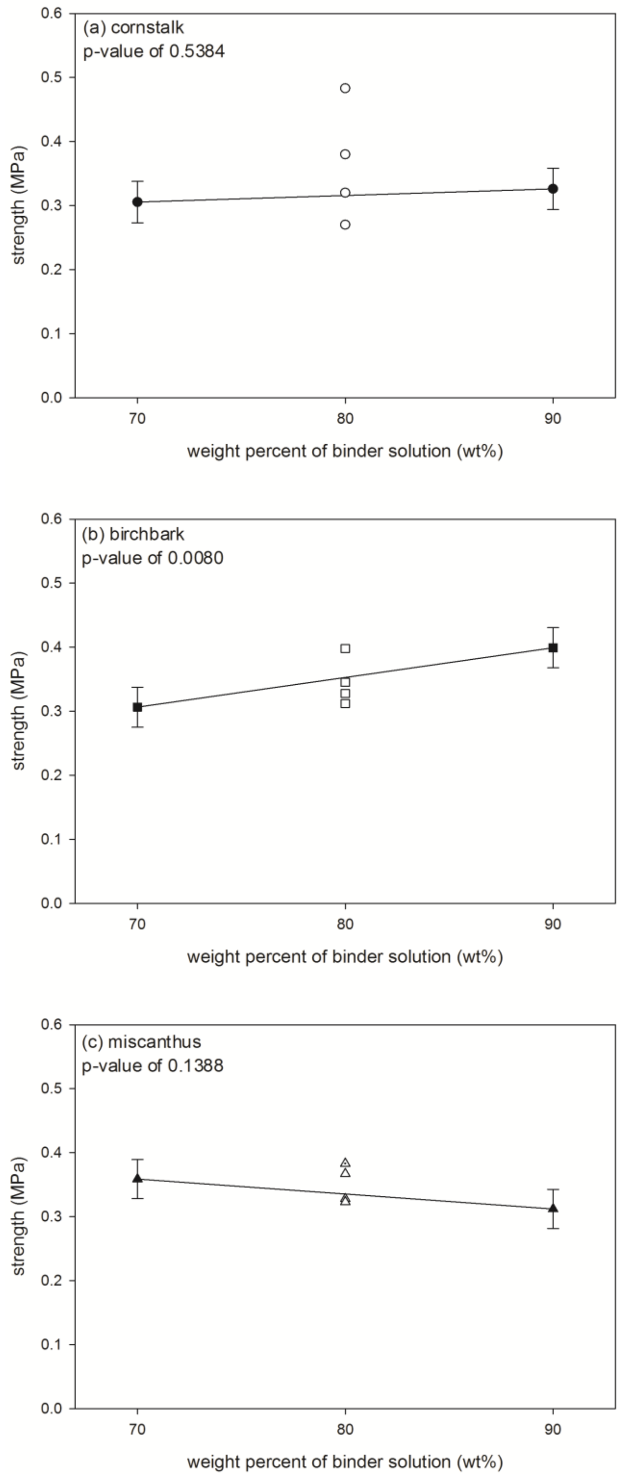


Figure 4-10: The effect of the amount of binder solution on the crushing strength of a) cornstalk, b) birchbark and c) miscanthus biochar granules. Solid points represent the low and high process parameter values while open points represent the centre points in the data.

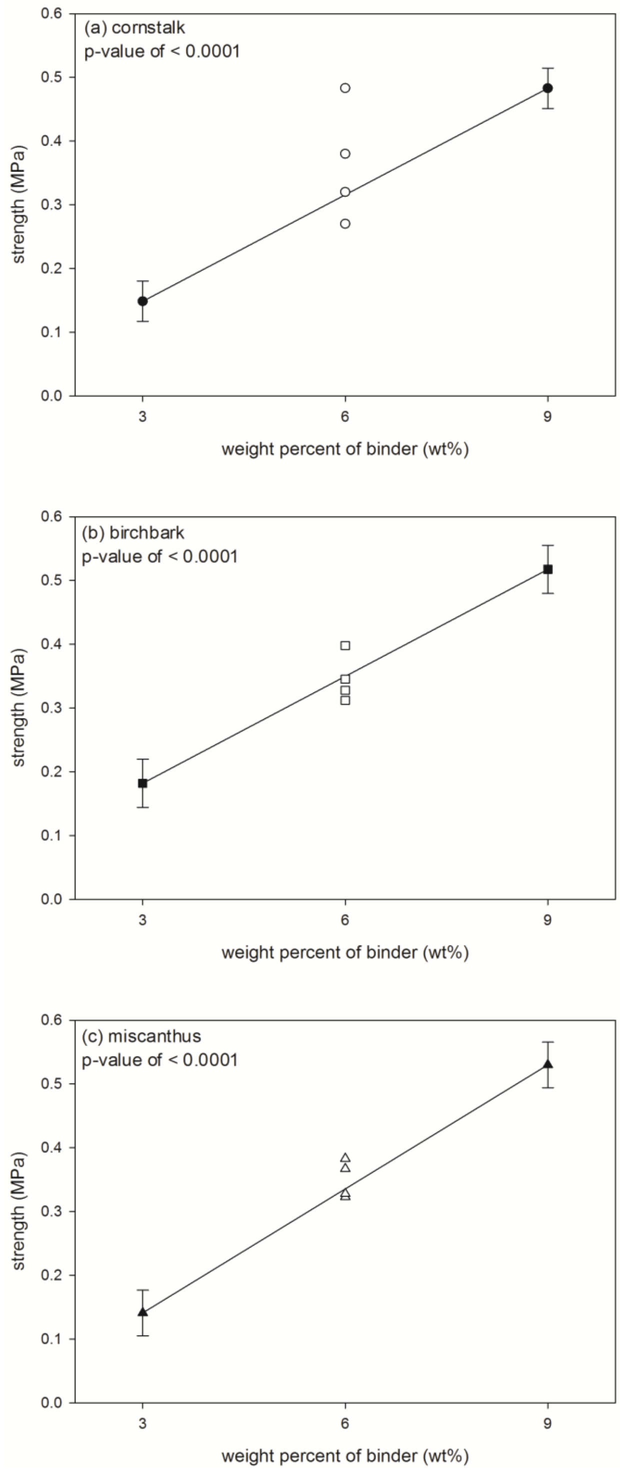


Figure 4-11: The effect of binder concentration on the crushing strength of a) cornstalk, b) birchbark and c) miscanthus biochar granules. Solid points represent the low and high process parameter values while open points represent the centre points in the data.

4.4 Discussion

The largest difference in the measured biochar properties was in hydrophobicity as shown through drop penetration behaviour. The liquid binder droplets did not immediately penetrate into the biochar powder indicating hydrophobic interactions. Liquid binder droplets penetrated into the cornstalk biochar after a few minutes, into the birchbark biochar after longer times, and did not completely penetrate into the miscanthus biochar powder beds. Cornstalk biochar was therefore classified as slightly hydrophobic, birchbark biochar as moderately hydrophobic and miscanthus biochar as very hydrophobic. In addition to the drop penetration times, the formation of a liquid marble varied with the biochar. The cornstalk biochar particles completely covered the liquid binder droplet before penetration into the bed. The birchbark particles did not immediately completely cover the liquid binder droplet; complete coverage and formation of a liquid marble did not occur until the droplet decreased in size. Miscanthus biochar particles were not completely drawn up around the liquid binder droplets.

Studies have been conducted examining the penetration behavior of liquid droplets into static beds of powders of varying hydrophobicity [15, 26, 35-37]. There has, however, been very limited research linking this to actual granulation behaviour and the effect of hydrophobicity on granulation mechanisms and granule properties [35, 38, 39]. Furthermore, these studies have focused on only wet high shear granulation, fluidized bed granulation or wet twin-screw granulation. There appears to be no literature describing wet drum granulation of hydrophobic powders. Lister and Ennis stated that drum granulators are unsuitable for granulating hydrophobic powders as the applied stress is too low to promote liquid distribution [34]. In a high shear or twin screw granulator, the high applied stress from the impeller or screw blades would force the liquid to be distributed throughout the powder similar to a hydrophilic system [34]. Considering the goal of producing biochar granules for soil amendment, drum granulation is attractive due to easy scale up to manufacture large amounts of granules.

The effect of operation parameters on the granule properties combined with varying hydrophobic behaviour and visual observations indicated that the granulation mechanisms were different for each of the tested biochar powders. It is hypothesized that cornstalk biochar powder exhibited some hydrophobic behaviour, but the primary granulation mechanisms were similar to hydrophilic powders seen previously in Figure 3-4. The liquid binder droplets remained near the surface of the powder bed, rolling down the inclined and cascading powder surface drawing up particles around the droplet. This structure then collapsed, allowing the liquid to penetrate into the surrounding powder to form a more common granule nuclei structure. The granule nuclei then grew through coalescence.

Increasing the rotational speed of the drum and the amount of binder solution increased the cornstalk biochar granule size to increase the optimal granule yield (Figures 4-5a and 4-6a) while increasing the weight percent of binder had the opposite effect (Figure 4-7a). Liquid binder is required to form granule nuclei and to reduce interparticle friction to allow deformation upon collision which is required for successful coalescence. More liquid binder leads to a large number of nuclei to form granules and more granules with critical liquid levels required for easy deformation and successful coalescence into larger granules [40]. The higher drum rotation speed then also contributes to coalescence through increasing the impact force of collisions.

Increasing the binder concentration from 3 – 9 wt% increased the viscosity of the binder solution from 0.009 – 0.046 Pas. Granules must deform during collisions for successful coalescence. Increasing the viscosity of the liquid binder solution increased the resistance to deformation as viscous dissipation inhibited the movement of the liquid through the granule voids. The probability of successful coalescence following the collision of two granules then decreases with increased liquid viscosities. As a result, the granule growth into the optimal range decreased as the HPMC binder concentration increased from 3 – 9 wt% (Figure 4-7).

For the cornstalk biochar, the granule strength improved with drum rotational speed and HPMC concentration in the liquid binder solution. Consolidation occurs through granule collisions with other granules and the walls of the granulator. It reduces the voids of the granules thereby increasing granule strength. Increasing the drum rotational speed increases the rate and extent of consolidation thereby strengthening the granules. A viscous liquid binder solution increases the capillary forces that bind particles together and promote consolidation and granule strength [40]. Granules were therefore stronger using liquid binder solutions with high HPMC concentrations.

The birchbark biochar showed moderately hydrophobic behaviour. It is hypothesized that the liquid binder droplets initially rolled down the powder bed surface drawing up particles around the droplet, Figure 4-12. These liquid marble structures were relatively stable and continued to accumulate particles around the droplet as they tumbled within the rotating powder bed. Collisions between two liquid marbles formed one large liquid marble structure. At a critical particle layer thickness around the droplet and/or liquid marble size, the structures collapsed to form large granule nuclei. Granule growth then continued through collisions of the nuclei.

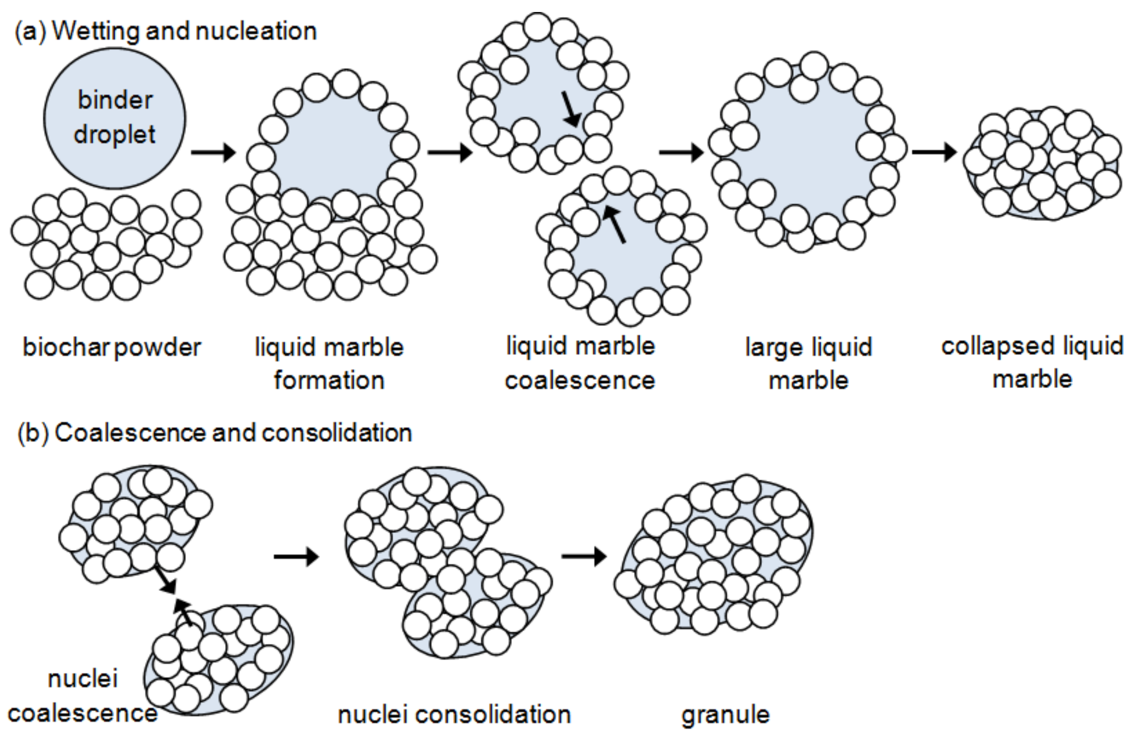


Figure 4-12: Proposed granulation mechanism for birchbark biochar and HPMC binder solution.

The birchbark biochar granules were larger than the granules formed from the other two biochars. Increasing the drum rotational speed and the binder volume decreased the optimal granule yield as many granules grew beyond the 4 mm diameter size. The larger granule size was attributed to the larger granule nuclei. It is well documented that granule nuclei size affects final granule size [34, 41]

The drum rotation speed did not have a significant effect on granule strength. Initially, liquid marbles were formed and there was a delay in the formation of granule nuclei. Due to this delay, the consolidation phase was reduced. Consolidation promotes granule strength by reducing voids within the granules. The drum rotation speed would normally affect the rate and extent of consolidation. However, as this phase was shortened, the influence of the drum rotation speed on consolidation, and in turn on granule strength, was reduced and not significant [34].

For the birchbark biochar, the granule strength increased with HPMC concentration in the liquid binder solution similar to the cornstalk biochar. Due to the longer consolidation time that the cornstalk granules had the effect of binder concentration on the attrition resistance was minimized compared to the birchbark granules.

The miscanthus biochar showed very hydrophobic behaviour. The liquid droplets drew up particles and continued to accumulate particles to form an outside layer and stable liquid marble structures. Collisions between two liquid marbles did not frequently form one large structure. Granule growth and formation were therefore primarily from particle layering around liquid marbles, Figure 4-13. Granules formed from miscanthus biochar were small (Figure 4-4) and optimal yields varied between 5.5 – 30.5 wt%. The rotational speed of the drum and the volume of binder significantly and positively affected optimal granule yield (Figures 4-5c and 4-6c) while increasing the binder concentration significantly decreased the yield (Figure 4-7c).

Granules formed from the very hydrophobic miscanthus biochar were expected to be small. Charles-William et al. showed that granule size decreased as hydrophobicity increased [38]. Each liquid binder droplet formed a liquid marble that developed into a granule through layering of solids at its surface. Increasing the rotation speed of the drum promoted the solids layering thereby growing the granule size to within the optimal range. However, the drum rotation speed had less of an affected on the growth through solids layering for the miscanthus biochar compared to growth through coalescence for the other biochar powders as there was only a 2.2 wt% increase in the optimal granule yield compared to a 4 wt% and 7 wt% difference for the cornstalk and birchbark biochar granules. Adding more binder solution provided more droplets to become liquid marbles and then granules. The liquid binder solution viscosity increased with binder concentration (Table 4-2). The liquid-powder interaction became even more hydrophobic; visual observations of the drop penetration experiments showed that it became more difficult for the particles to be drawn up and around the droplet to form a liquid marble. As a result, the probability of a liquid marble developing into a granule was reduced with increased binder concentration thereby decreasing the optimal granule yield.

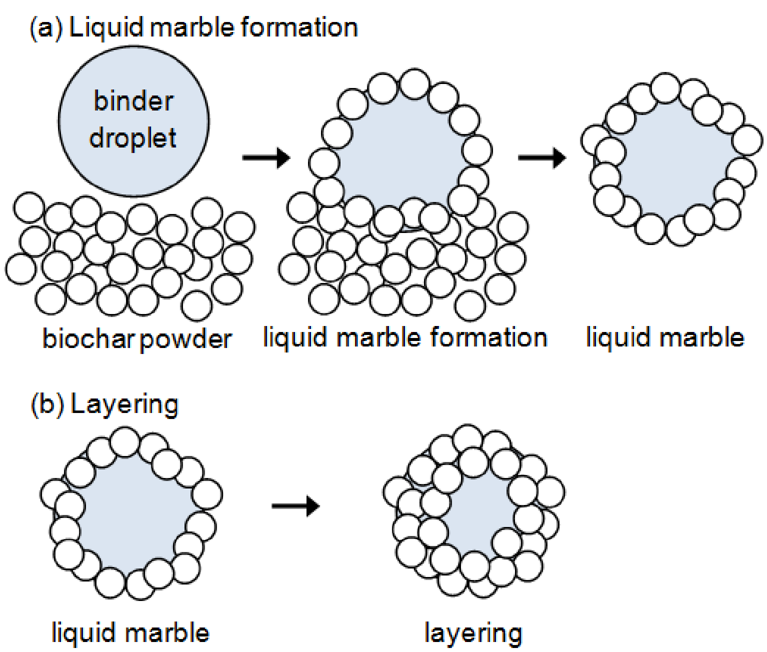


Figure 4-13: Proposed granulation mechanism for miscanthus biochar and HPMC binder solution.

Only the crushing strength of the miscanthus biochar granules was significantly affected by the weight percentage of binder. The crushing strength increased from about 0.15 – 0.55 MPa as the concentration of HPMC in the liquid binder solution increased from 3 – 9 wt% (Figure 4-11). This trend was similar for all three types of biochar granules; the capillary forces that bind the particles together to form strong granules increased as the viscosity of the liquid binder solution increased. The crushing strength of the biochar granules from all three feedstocks ranged from approximately 0.15 to 0.55 MPa and was lower than the accepted 2 MPa limit for fertilizer granules [42]. An alternative binder must be investigated to ensure the strength of the granules is high enough to remain intact during processing and application to soil.

The proposed granulation mechanisms varied from penetration to form nuclei followed by coalescence for the cornstalk biochar to a sequence of liquid marble formation with delayed penetration and minimal coalescence for the birchbark biochar to layering around liquid marbles for the miscanthus biochar. The variation in granule properties with operating parameters supported these mechanisms. The visual observations of the granule shape and surface morphology (Figure 4-3) also support the proposed granulation mechanisms. The cornstalk biochar granules were approximately spherical with a uniform surface. The liquid binder droplets penetrated into the powder bed relatively quickly to form nuclei. These nuclei had many opportunities for coalescence and then consolidation to form compact, spherical shapes. The delayed formation of nuclei for the birchbark biochar limited the extent of consolidation. As a result, the granules were more irregular in shape. The miscanthus granules were also spherical. The liquid binder droplets formed spheres due to surface tension and then granules formed through layering of the biochar particles around the spherical droplets.

4.5 Conclusions

Cornstalk, birchbark and miscanthus biochar powders were drum granulated with HPMC liquid binder solutions to examine the effect of biochar on granulation. The interactions between the liquid binder solutions and the biochar varied from slightly hydrophobic for the cornstalk biochar to moderately hydrophobic for the birchbark biochar to very hydrophobic for the miscanthus biochar. The cornstalk biochar granules were formed primarily through coalescence and consolidation. The birchbark biochar granules formed from large collapsed liquid marbles followed by some coalescence and a short consolidation phase. The miscanthus biochar granules formed from layering around a liquid marble. The effect of the operational parameters of drum rotational speed, concentration of binder and the amount of liquid binder solution on the granule properties varied due to the different proposed granulation mechanisms. The results confirmed that biochar can be wet drum granulated to form biochar granules similar to solid fertilizers. However, as the type of biochar can significantly impact the granulation, preliminary tests are required to select appropriate operational parameters to produce granules with specified properties.

4.6 References

[1] R. Bian, D. Chen, X. Liu, L. Cui, L. Li, G. Pan, D. Xie, J. Zheng, X. Zhang, J. Zheng, A. Chang, Biochar soil amendment as a solution to prevent Cd-tainted rice from China: Results from a cross-site field experiment, Ecological Engineering, 58 (2013) 378-383.

[2] R.K. Dumroese, J. Heiskanen, K. Englund, A. Tervahauta, Pelleted biochar: Chemical and physical properties show potential use as a substrate in container nurseries, Biomass and Bioenergy, 35 (2011) 2018-2027.

[3] R. Kookana, X.-Y. Yu, G.-G. Ying, Black is the new green: The blue shades of biochar, 19th World Congress of Soil Science, Brisbane, 1-6 August 2010, International Union of Soil Sciences, Brisbane, 2010, pp. 1-4.

[4] D.A. Laird, P. Fleming, D.D. Davis, R. Horton, B. Wang, D.L. Karlen, Impact of biochar amendments on the quality of a typical Midwestern agricultural soil, Geoderma, 158 (2010) 443-449.

[5] L. Van Zwieten, S. Kimber, S. Morris, K.Y. Chan, A. Downie, J. Rust, S. Joseph, A. Cowie, Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility, Plant and Soil, 327 (2010) 235-246.

[6] X. Zhang, H. Wang, L. He, K. Lu, A. Sarmah, J. Li, N. Bolan, J. Pei, H. Huang, Using biochar for remediation of soils contaminated with heavy metals and organic pollutants, Environmental Science and Pollution Research, 20 (2013) 8472-8483.

[7] B.T. Nguyen, R.T. Koide, C. Dell, P. Drohan, H. Skinner, P.R. Adler, A. Nord, Turnover of soil carbon following addition of switchgrass-derived biochar to four soils, Soil Sci. Soc. Am. J., 78 (2014) 531-537.

[8] J. Lehmann, S. Joseph, Biochar for Environmental Management: An Introduction, in: J. Lehmann, S. Joseph (Eds.) Biochar for Environmental Management: Science and Technology, Earthscan, London & Sterling, VA, 2009, pp. 1-9.

[9] C.E. Brewer, Biochar characterization and engineering, (2012) pp. 196.

[10] T.K. Oh, Y. Shinogi, S.-J. Lee, B. Choi, Utilization of biochar impregnated with anaerobically digested slurry as slow-release fertilizer, Journal of Plant Nutrition and Soil Science, 177 (2014) 97-103.

[11] E.W. Bruun, D. Müller-Stöver, P. Ambus, H. Hauggaard-Nielsen, Application of biochar to soil and N2O emissions: potential effects of blending fast-pyrolysis biochar with anaerobically digested slurry, European Journal of Soil Science, 62 (2011) 581-589.

[12] P.A.L. Wauters, R. van de Water, J.D. Litster, G.M.H. Meesters, B. Scarlett, Growth and compaction behaviour of copper concentrate granules in a rotating drum, Powder Technology, 124 (2002) 230-237.

[13] P.J. Cullen, N. Abatzaglou, C. Rielly, R. Romanach, Pharmaceutical Blending and Mixing, John Wiley & Sons, United Kingdom, 2015.

[14] B. Bowden-Green, L. Briens, An investigation of drum granulation of biochar powder, Powder Technology, 288 (2016) 249-254

[15] N. Eshtiaghi, J.J.S. Liu, K.P. Hapgood, Formation of hollow granules from liquid marbles: Small scale experiments, Powder Technology, 197 (2010) 184-195.

[16] H. Abdullah, H. Wu, Biochar as a Fuel: 1. Properties and Grindability of Biochar from the Pyrolysis of Mallee Wood under Slow-Heating Conditions, Energy & Fuels, 23 (2009) 4174-4181.

[17] K. Kawamoto, K. Ishimaru, Y. Imamura, Reactivity of wood charcoal with ozone, Journal of Wood Science, 51 (2005) 66-72.

[18] S. Kloss, F. Zehetner, A. Dellantonio, R. Hamid, F. Ottner, V. Liedtke, M. Schwanninger, M.H. Gerzabek, G. Soja, Characterization of slow pyrolysis biochars: effects of feedstocks and pyrolysis temperature on biochar properties, J. Environ. Qual., 41 (2012) 990-1000.

[19] Y. Wang, Y. Hu, X. Zhao, S. Wang, G. Xing, Comparisons of Biochar Properties from Wood Material and Crop Residues at Different Temperatures and Residence Times, Energy & Fuels, 27 (2013) 5890-5899.

[20] N. Anderson, G. Jones, D. Dumroese, S. Baker, D. Loeffler, W. Chung, A Comparison of Producer Gas, Biochar, and Activate Carbon from Two Distributed Scale Thermochemical Conversion Systems Used to Process Forest Biomass, Energies, 6 (2013) 164-183.

[21] L. Hale, M. Luth, D. Crowley, Biochar characteristics relate to its utility as an alternative soil inoculum carrier to peat and vermiculite, Soil Biology and Biochemistry, 81 (2015) 228-235.

[22] X. Liu, Y. Zhang, Z. Li, R. Feng, Y. Zhang, Characterization of corncob-derived biochar and pyrolysis kinetics in comparison with corn stalk and sawdust, Bioresource Technology, 170 (2014) 76-82.

[23] C.A. Mullen, A.A. Boateng, N.M. Goldberg, I.M. Lima, D.A. Laird, K.B. Hicks, Bio-oil and bio-char production from corn cobs and stover by fast pyrolysis, Biomass and Bioenergy, 34 (2010) 67-74.

[24] S. Steinbeiss, G. Gleixner, M. Antonietti, Effect of biochar amendment on soil carbon balance and soil microbial activity, Soil Biology and Biochemistry, 41 (2009) 1301-1310.

[25] X. Xu, X. Cao, L. Zhao, Comparison of rice husk- and dairy manure-derived biochars for simultaneously removing heavy metals from aqueous solutions: Role of mineral components in biochars, Chemosphere, 92 (2013) 955-961.

[26] K.P. Hapgood, J.D. Litster, S.R. Biggs, T. Howes, Drop Penetration into Porous Powder Beds, Journal of Colloid and Interface Science, 253 (2002) 353-366.

[27] R. Rowe, P. Sheskey, S. Owen, Hypromellose, Handbook of Pharmaceutical Excipients, Pharmaceutical Press, London, UK, 2006, pp. 346-348.

[28] D. Rutland, J. Polo, Fertilizer dealer handbook: products, storage and handling., IFDC - An International Center for Soil Fertility and Agricultural Development, Muscle Shoals, AL, 2005.

[29] V. Gowariker, V. Krishnamurthy, S. Gowariker, M. Dhanorkar, K. Paranjape, The Fertilizer Encyclopedia, John Wiley and Sons Inc., Hoboken, New Jersey, 2009.

[30] J. Lehmann, M. Rillig, J. Thies, C. Masiello, W. Hockaday, D. Crowley, Biochar effects on soil biota - a review, Soil Biology & Biochemistry, 43 (2011) 1812-1836.

[31] D. Mohan, H. Kumar, A. Sarswat, M. Alexandre-Franco, C. Pittman, Cadmium and lead remediation using magnetic oak wood and oak bark fast pyrolysis bio-chars, Chemical Engineering Journal, 236 (2014) 513-528.

[32] L. Sun, S. Wan, W. Luo, Biochars prepared from anaerobic digestion residue, palm bark and eucalyptus for adsorption of cationic methylene blue dye: characterization, equilibrium, and kinetic studies, Bioresource Technology, 140 (2013) 406-413.

[33] W. Kwapinski, C. Byrne, E. Kryachko, P. Wolfram, C. Adley, J. Leahy, E. Novotny, M. Hayes, Biochar from biomass and waste, Waste Biomass Valor, 1 (2010) 177-189.

[34] J. Litster, B. Ennis, The Science and Engineering of Granulation Processes, Kluwer Academic Publishers, Dordrecht, NLD, (2004) 65-67.

[35] T. Nguyen, W. Shen, K. Hapgood, Drop penetration time in heterogeneous powder beds, Chemical Engineering Science, 64 (2009) 5210-5221.

[36] N. Eshtiaghi, K.P. Hapgood, A quantitative framework for the formation of liquid marbles and hollow granules from hydrophobic powders, Powder Technology, 223 (2012) 65-76.

[37] D.E. Walton, C.J. Mumford, The Morphology of Spray-Dried Particles: The Effect of Process Variables upon the Morphology of Spray-Dried Particles, Chemical Engineering Research and Design, 77 (1999) 442-460.

[38] H. Charles-Williams, R. Wengeler, K. Flora, H. Feise, M. Hounslow, A. Salman, Granulation behaviour of increasingly hydrophobic mixtures, Powder Technology, 238 (2013) 64-76.

[39] S. Yu, G. Reynolds, Z. Huang, M. Matas, A. Salman, Granulation of increasingly hydrophobic formulations using a twin screw granulator, International Journal of Pharmaceutics, 475 (2014) 82-96.

[40] S.M. Iveson, J.D. Litster, B.J. Ennis, Fundamental studies of granule consolidation Part 1: Effects of binder content and binder viscosity, Powder Technology, 88 (1996) 15-20.

[41] T. Gluba, The effect of wetting liquid droplet size on the growth of agglomerates during wet drum granulation, Powder Technology, 130 (2003) 219-224.

[42] P. Kiwietniak, Strength of fertilizer granules and methods for testing it, Mechanizacja Rolnictwa, 34 (1985).

Chapter 5

5 A comparison of binder solutions for the purpose of drum granulation of biochar powder

5.1 Introduction

Biochar is a black, carbon rich powder produced from pyrolysis of biomass. Biochar can increase microbial growth and water retention within the soil due to its high porosity [1, 2]. Research also indicates that the porosity and cation exchange capacity of biochar help reduce nutrient leaching and prevent heavy metal absorption by crops [3-5]

One of the main problems with using biochar as a soil amendment is dust. This causes difficulty in handling, transporting and dispersing the biochar. During application to soils, biochar powder can easily become airborne causing a loss of product and negative health effects [6]. Possible dust control and cultivation techniques that have been examined include the on-site addition of water to biochar, creating a mixture of biochar and aerobically digested slurry or pelletizing the biochar [7-9].

A solution that minimizes dust and, therefore, handling and soil application challenges is size enlargement. Size enlargement through wet granulation occurs when a liquid binder solution is used to agglomerate particles into granules. For wet drum granulation, powder is added to a horizontal drum and a sparger system sprays a liquid binder onto the powder. Agitation occurs through rotation of the drum, incorporating the liquid binder into the powder to begin granule formation and growth.

Research has confirmed that biochar can be wet granulated using a drum granulator and hydroxylpropyl methylcellulose (HPMC), as a binder [10]. HPMC is commonly used as a binder in pharmaceutical applications. However, HPMC would not be suitable for large scale production of biochar granules for soil amendment as the biochar granules produced would not have adequate crushing strength [10]. An HPMC binder solution would also lack any additional nutrients that could be beneficial to plant growth such as nitrogen, potassium or phosphorous. For the biochar granules to be an effective soil amendment they should break apart once within the soil increasing the surface area of the biochar. A polymer binder such as HPMC may not easily degrade within the soil inhibiting biochar from being as effective within the soil. A more ideal liquid binder solution is required for the drum granulation of biochar powder into a soil amendment.

Molasses has been used as a soil amendment. Molasses can supply plants with potassium as well as small amounts of nitrogen, magnesium, phosphate and calcium [11]. Molasses has also been shown to improve the aeration of clay soils and to help reduce nematode reproduction and root galling, the abnormal enlargement of the root of a plant due to a parasitic organism [12, 13]. Rodriguez-Kabana and King found that a urea and molasses mixture had a dual effect of suppressing nematode reproduction and increasing microbial activity within the soil [14].

Molasses has also been used as a binding agent [15, 16]. Ghasemi et al. successfully granulated compost fertilizer using sugar beet molasses in a drum granulator and found that increased rotational rate increased the percentage of granules within the optimal size range [16]. Pendyal et al. conducted a study comparing the characteristics of granular activated carbon produced using four different binders (coal tar, sugarcane molasses, sugar beet molasses and corn syrup) [17]. The results showed that both molasses binders produced granules with the highest surface area which is an important soil amendment characteristic. However, the molasses binder also produced the weakest granules. Molasses has the potential to be a suitable binder for the granulation of biochar.

Multi-component fertilizers primarily consist of nitrogen, potassium and phosphorous [18]. The ratio of the nutrients depends on crop requirements. Nitrogen is vital to plant growth as it is essential for photosynthesis and it is the main component of chlorophyll. Plants absorb nitrogen in the form of either nitrates or ammonium ions through their roots. Heeb et al. monitored plant growth between three different types of nitrogen sources: nitrate, ammonium and organic nitrogen [19]. Ammonium was found to be equivalent to nitrate, based on plant growth, and it was believed that plants save energy by taking up ammonium versus nitrates. Sherrington et al. successfully granulated a mixture of glass beads and sand using an ammonium nitrate binder solution in a drum granulator [20]. The study found that increased volume of liquid binder increased granule size for sand trials and the addition of glass beads caused layering of the sand onto the beads. Ammonium nitrate could be a successful binder for the granulation of biochar granules.

Differences in binder solutions can impact wet granulation and the properties of the final granules. The objectives of the current research were to compare wet drum granulation of birchbark biochar using different binder solutions and to investigate process parameters that effect the biochar granule properties. Binders can complement biochar properties to form biochar granules that provide many benefits for plant growth.

5.2 Materials and Methods

5.2.1 Biochar Formation

Biochar was created by the pyrolysis of birchbark. Before pyrolysis, the birchbark was dried at 105 ^{o}C and then ground to 1-2 mm in size using an IKA Werke model MF10 Grinder at 4500 rpm. Pyrolysis was performed in a custom manufactured reactor (University Machine Services, London, Canada) with a diameter of 25 cm and an effective bed height of about 60 cm. The reactor temperature was 500 ^{o}C and pressure was 100 kPa. The bed was fixed, but then fluidized at intervals to ensure constant temperature and uniform bed composition. The birchbark biochar was then recovered from the reactor.

5.2.2 Biochar Characterization

A Hitachi S-4500 field emission scanning electron microscope was used to take images of the biochar powder. Using a carbon adhesive, the powder was mounted on a plate and a thin layer of gold was deposited on the sample surface to minimize charging. The particle size distribution of the biochar powder was measured using a Malvern Mastersizer 2000.

A Mercury Scientific Revolution Powder Analyzer was used to measure the flowability of the biochar powder. A powder sample size of 118 cm^3 was loaded into a drum with a diameter of 11 cm and width of 3.5 cm. The drum was rotated at 0.3 rpm until 128 avalanches had occurred with an avalanche defined as being a rearrangement of at least 0.65 vol% of the sample in the drum. Optical measurements with a resolution of 648 x 488 at 60 frames per second allowed the powder surface to be measured as the sample was rotated. Flowability indicators of the avalanche time and its standard deviation were obtained from the Powder Revolution analysis. Samples were measured in triplicate.

The interaction between the liquid binder solutions and the biochar powder was examined using drop penetration tests. The drop penetration measurements were conducted using a similar procedure as outlined by Hapgood et al. [21] The biochar powder was sieved through a 1 mm sieve into a petri dish, producing a loosely packed bed of biochar to mimic the powder bed during tumbling. Excess powder was removed. A 25 gauge needle syringe was mounted 1 cm above the powder bed. A liquid binder droplet of 0.0048 mL was gently dropped onto the powder bed and the drop penetration time was determined as the time at which the liquid droplet was no longer visible at the powder bed surface. The procedure was repeated in triplicate.

5.2.3 Granulation

Experimental design allows a series of experimental trials to be planned and conducted in a specific order that maximizes the information gained with a minimum number of trials. StatEase Design Expert 8 statistical software (Stat-Ease, Inc. Minnesota, USA) was used to generate a two-level factorial design of experiments (DOE) with duplicates and centre points to determine the effect of drum rotational speed, concentration of binder in the liquid solution and volume of liquid binder solution added. An analysis of variance (ANOVA) was conducted with optimal granule size yield, flowability, attrition resistance and crushing strength as the response variables. P-values less than 0.05 were considered significant, indicating at least a 95% confidence level for a specific response variable.

The rotational speeds were 40, 50 and 60 rpm, selected based on previous experiments [10]. Preliminary trials were conducted to determine appropriate ranges for the binder concentration and the volume of each liquid binder solution. Table 5-1 lists the parameters used in the DOE.

Table 5-1: Parameters used in the DoE.

Binder Level	Rotational Speed (rpm)	Binder Concentration (wt%)			Binder Solution Volume (wt%)		
		HPMC	Molasses	Ammonium Nitrate	HPMC	Molasses	Ammonium Nitrate
Low	40	3	20	20	70	32	45
Mid	50	6	30	30	80	43	55
High	60	9	40	40	90	54	65

Three binders were chosen for the granulation: hydroxypropylmethyl cellulose (HPMC) (Pharmacoat® 603, Shin-Etsu Chemical Co.), molasses (Crosby's 100% Natural) and ammonium nitrate (Granular Ammonium Nitrate ACS, Alfa Aesar).

The binder solutions were carefully prepared and stirred until the binder was fully dissolved into the distilled water. Viscosity measurements of the binder solutions were conducted using a Brookfield Viscometer with a 00 spindle.

The drum was custom manufactured by University Machine Services (London, Canada) and had an inner diameter of 7.5 cm, an inner length of 12.0 cm and was made of transparent Plexiglas to allow visual observations, Figure 3-1. One end of the drum was connected to a motor which allowed for the drum to be rotated. The other end of the drum had an opening to allow a sparger to be inserted. The sparger spanned the length of the drum, had an inner diameter of 3.0 mm and had four 1.0 mm holes about 3.0 cm apart axially. The sparger was attached to a peristaltic pump to deliver the liquid binder solution. The binder solution was added drop wise onto the powder bed surface with a mean droplet volume of 0.08 ml and at a rate of about 8.5 ml/min.

For the granulation trials, 25 g of the biochar powder was added to the granulation drum. The drum was rotated at the required speed for the specified trial. Liquid binder solution was added dropwise onto the tumbling bed surface at a rate of 8.5 ml/min until the required liquid binder solution volume was added for the specified trial. Liquid binder addition was then stopped. The drum was rotated for two more minutes to allow wet massing. The granulation was stopped. Granules were removed, spread onto trays and dried at 24 ^{o}C and a relative humidity of 3-5 % for more than 24 hours. The dried granules were then analyzed for various properties.

5.2.4 Granule Characterization

Granule size distributions were conducted using 11 sieve between 0.6 – 6.3 mm (0.60, 0.85, 1.00, 1.18, 1.40, 2.00, 2.36, 2.80, 3.35, 4.00 and 6.30 mm). Based upon common fertilizer granule size specifications**,** the optimal biochar granule size range was defined between 1 and 4 mm [22]. Granules under 1 mm in diameter were classified as undersized and granules larger than 4 mm as oversized. The mass percentage of granules from each trial within these three groupings was determined through sieving with 1mm and 4 mm sieves.

Images of the biochar granules were taken using a Hitachi S-4500 field emission scanning electron microscope. The granules were mounted on a plate using a carbon adhesive and coated with a layer of gold before examination. The images allowed the shape, surface morphology and size of the biochar granules to be examined.

Granules within the optimal size range of 1 - 4 mm were tested for strength as evaluated through attrition resistance measurements and crushing strength. A 25 cm^3 sample combined with 20, 5 mm diameter steel beads were placed in a drum with a diameter of 11 cm and width of 3.5 cm. The drum was rotated at 30 rpm for 128 rotations. The granules were then sieved with a 1 mm sieve and reweighed. The resistance to attrition was defined in equation 5-1.

$$\text{attrition resistance} = \frac{\text{granule mass after test}}{\text{granule mass before test}} \times 100\% \qquad (5-1)$$

Crushing strength measurements were conducted on individual granules. It was therefore difficult to obtain values representative of a specified trial. Only estimates were possible, using measurements repeated in triplicate. Using an Instron 8874, granules were compressed at a speed of 0.5 mm/s between platens with dimensions of 26 mm x 26 mm.

The force was plotted with respect to time and the maximum force measured before breakage was recorded for each tested granule.

The effect each process parameter had on the granule properties was plotted and included centre points to identify possible curvature and deduce variability in the data.

5.3 Results

5.3.1 Biochar Characterization

Figure 5-1 shows the SEM images of the birchbark biochar powder. Both small and large particulates were present (Figure 5-1a). The smaller particulate matter appeared to be fragments from the larger particles (Figure 5-1b). The particles were fibrous and very porous.

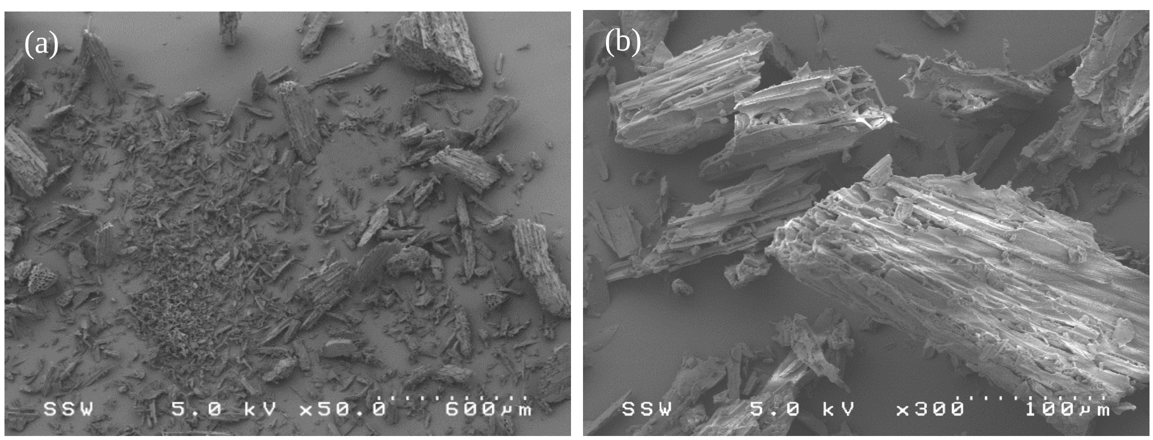


Figure 5-1: SEM images of the birchbark biochar powder at a) 50X magnification and b) 300X magnification.

Figure 5-2 shows the particle size distribution of the birchbark biochar. The birchbark biochar had a wide size distribution with a peak at 250 μm.

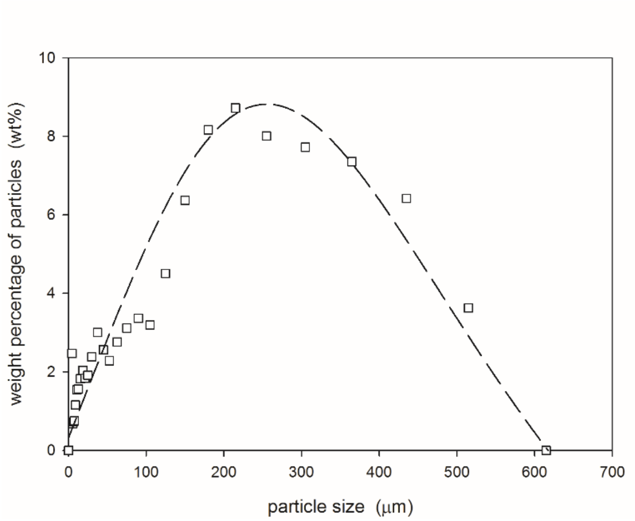


Figure 5-2: Particle size distribution of the birchbark biochar powder.

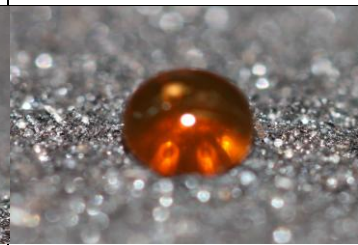
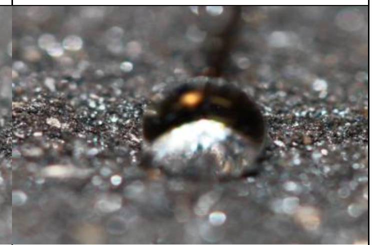
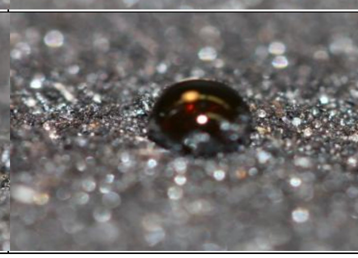
Drop penetration measurements were conducted to estimate liquid-powder interactions that could affect granulation. Table 5-2 summarizes the viscosities of the binder solutions and the drop penetration times for HPMC, molasses, and ammonium nitrate binder solutions into the birchbark biochar powder. The drop penetration times increased for all three liquid binder solutions with increasing binder concentration or liquid viscosity. However, the relationship between viscosity and drop penetration times were not consistent between binder solutions as lower viscosity binders did not have the lowest drop penetration times and vice versa.

Table 5-2: Viscosity and drop penetration times of HPMC, molasses and ammonium nitrate liquid solutions into birchbark biochar powder.

Binder Level	Viscosity (Pa·s)			Drop penetration time (min)		
	HPMC	Molasses	Ammonium Nitrate	HPMC	Molasses	Ammonium Nitrate
Low	0.0046	0.0017	0.0011	23 ± 6	47 ± 5	74
Mid	0.0156	0.0023	0.0012	30 ± 7	50 ± 8	-
High	0.0456	0.0035	0.0013	-	56 ± 18	-

Table 5-3 shows images of drop penetration of the binder solutions at mid-level values into the birchbark biochar powder. After contacting the birchbark biochar, the HPMC binder solution slowly drew up powder particles around itself. Once approximately three quarters of the droplet was covered in birchbark biochar particles, the droplet diameter started to decrease slightly and it then sank into the powder bed. Only a small amount of biochar powder was drawn up the molasses and ammonium nitrate solution droplets. After 20 minutes the molasses and ammonium nitrate binder droplet diameter started to decrease causing the powder particles to cover more of the droplet surface. The molasses binder solution droplet diameter continued to shrink until the powder particles completely covered the droplet and the structure sank into the bed becoming flush with the powder surface. The ammonium nitrate solution droplet never fully penetrated into the powder bed.

Table 5-3: Drop penetration of mid-level binder concentration solutions into a bed of birchbark biochar powder.

Time (min)	Binder Solution		
	HPMC	Molasses	Ammonium Nitrate
Contact			
5			
20			
30			

5.3.2 Granule Characterization

Granule shape was observed using scanning electron micrograph images. Figure 5-3 shows that the granules were approximately spherical.

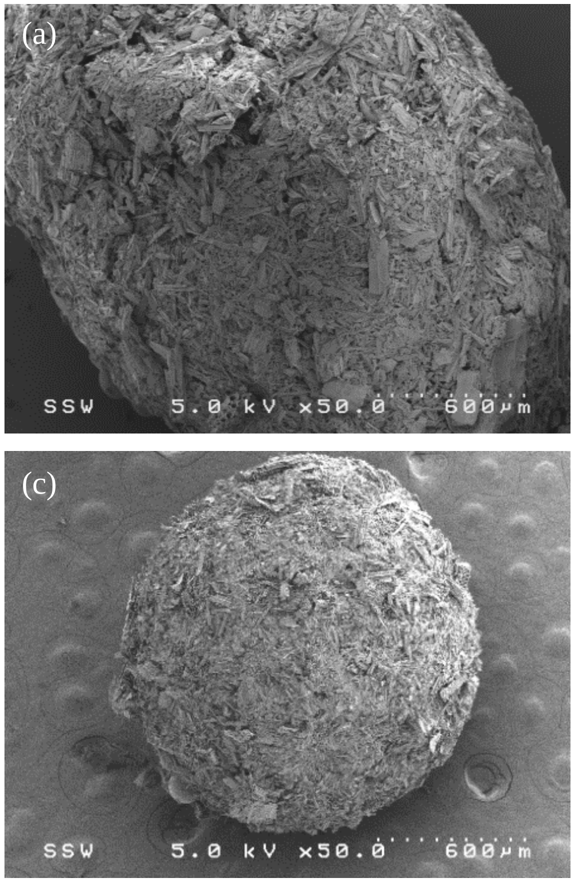


Figure 5-3: SEM images of the biochar granules at the low level drum rotational speed, binder solution volume and binder concentration for granulation with binders of a) HPMC, b) molasses and c) ammonium nitrate.

Granule size was measured through sieving. Figure 5-4 shows the granule size distributions for trials at the low, mid and high granulation parameters. Overall, granules formed using HPMC as the binder were larger than those formed using molasses or ammonium nitrate binders. At the low level granulation parameters, the highest weight percent of fines was present, Figure 5-4a. Increasing the granulation parameter values decreased the amount of fines and increased the granule sizes.

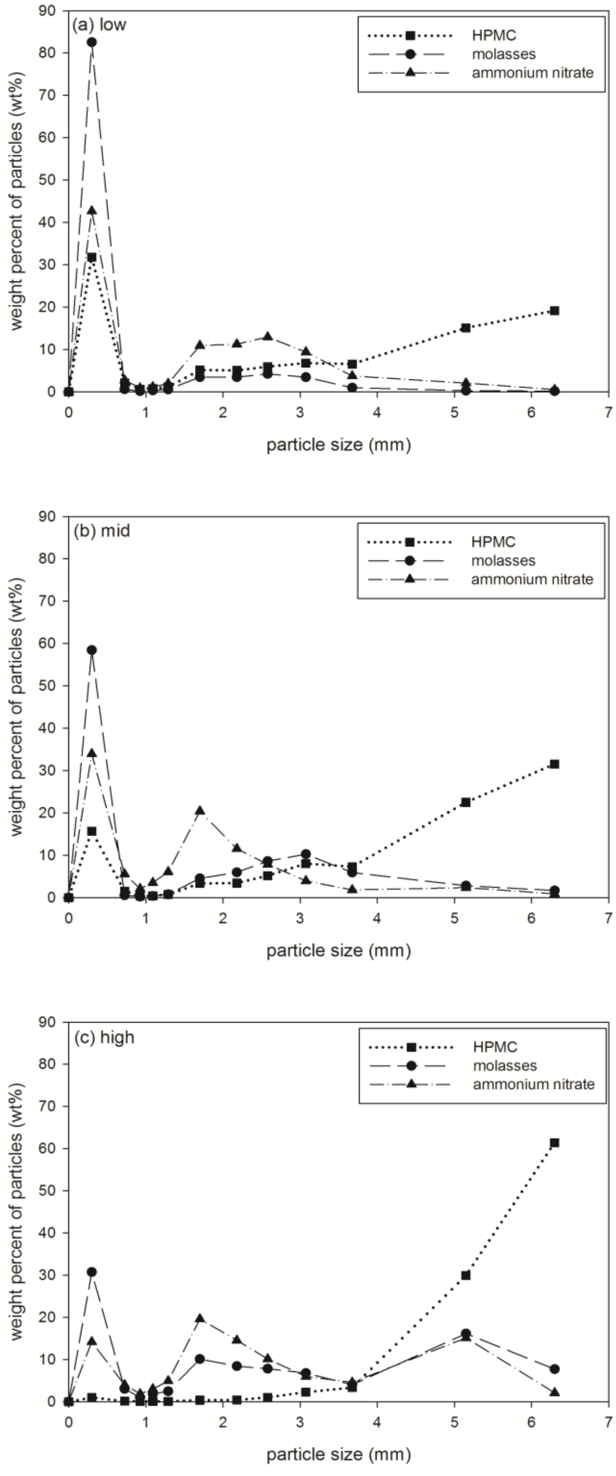


Figure 5-4: Granule size distributions for granulations using HPMC, molasses, and ammonium nitrate solutions at a) low, b) mid and c) high granulation parameters.

The optimal size range of the granules was considered to be 1 to 4 mm, based on common solid fertilizer sizes [22]. The granules produced with HPMC binder solutions yielded the lowest amount of optimal granules (9 – 38 wt%). Granules from molasses binders gave 23 – 48 wt% optimal granule yield while granules from ammonium nitrate binders produced the highest yield, 35 – 63 wt% optimal granule yield.

The optimal granule yield was affected by all three operational parameters: drum rotational speed, concentration of binder and weight percent of binder solution (Figure 5-5). Only the weight percent of binder solution had a significant effect for all three types of binders. The effect, however, varied from negative for the HPMC binder to positive for the molasses and ammonium nitrate binders (p-values of 0.0001, 0.0269 and 0.0416 respectively) (Figure 5-5b). The concentration of binder was only significant for the molasses binder and even then only slightly increased the granule yield from 33 – 37 wt% (p-value of < 0.0001). The drum rotational speed only significantly affected the optimal granule yield for the HPMC binder, decreasing from 29 – 21 wt% (p-value of 0.0229).

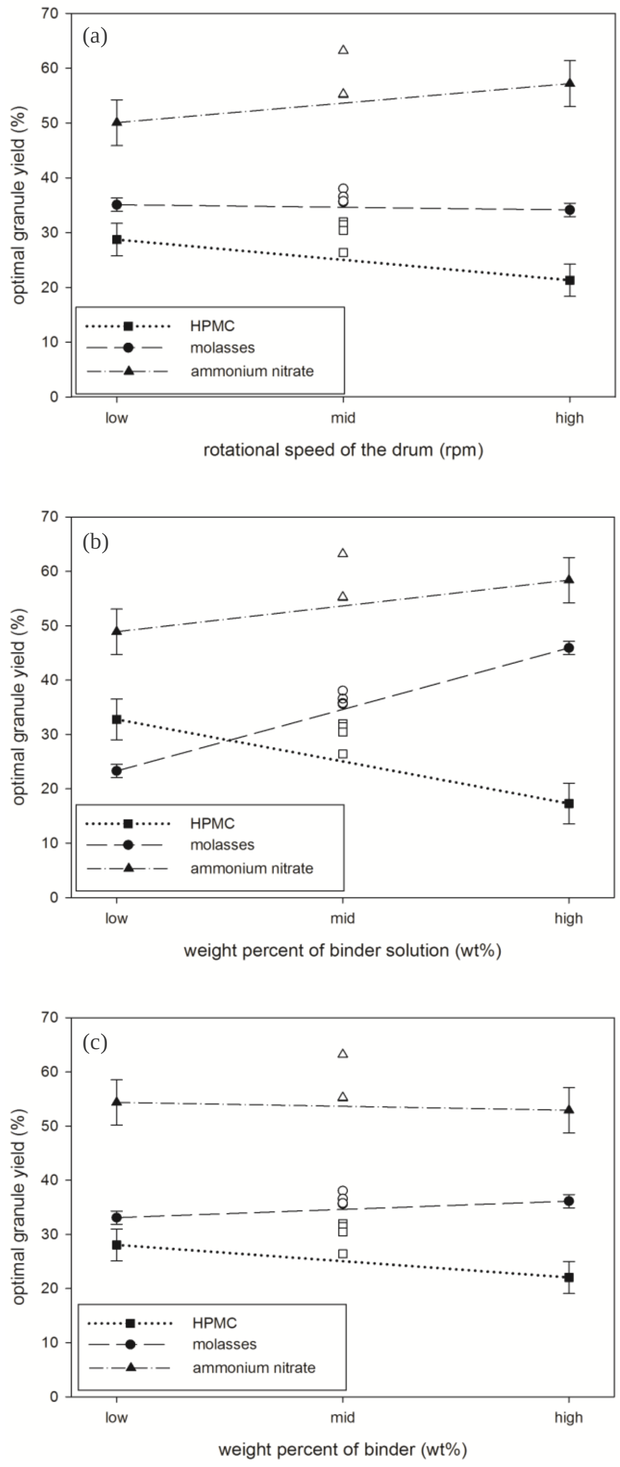


Figure 5-5: The effect of (a) drum rotational speed, (b) amount of binder solution and (c) binder concentration on the optimal granule yield for granules produced using HPMC, molasses and ammonium nitrate binders. Solid points represent the low and high process parameter values while open points represent the centre points in the data.

The granule strength was evaluated by measuring the attrition resistance and the crushing strength. Only the amount of binder solution and binder concentration affected the attrition resistance of the granules (Figure 5-6). The amount of binder solution only significantly affected the attrition resistance of granules produced using molasses as a binder; increasing the amount of binder solution decreased the attrition resistance of the granules (p-value of < 0.0001). Binder concentration had a significant positive effect on the attrition resistance for all three binder solutions (p-values of < 0.0001, 0.0005 and 0.0215 for granules made with HPMC, molasses and ammonium nitrate).

Figure 5-7 shows the effect of the process parameters on the crushing strength of the granules. The rotational speed of the drum only significantly affected the crushing strength of granules produced using molasses (p-value of 0.0060). The amount of binder solution only significantly affected the crushing strength of granules produced using HPMC (p-value of 0.0080). Binder concentration only significantly affected granules produced using the HPMC and molasses binders (p-values of < 0.0001 and 0.0010 respectively).

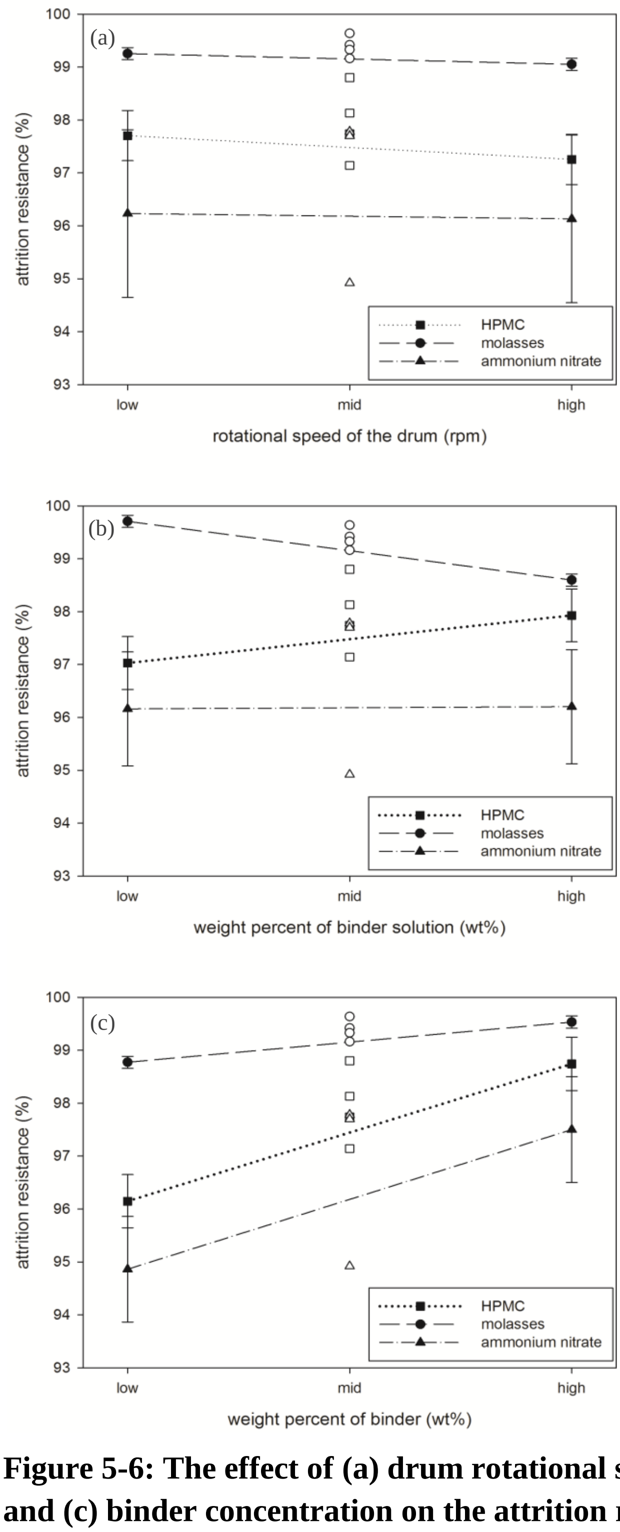


Figure 5-6: The effect of (a) drum rotational speed, (b) amount of binder solution and (c) binder concentration on the attrition resistance for granules produced using HPMC, molasses and ammonium nitrate binders. Solid points represent the low and high process parameter values while open points represent the centre points in the data.

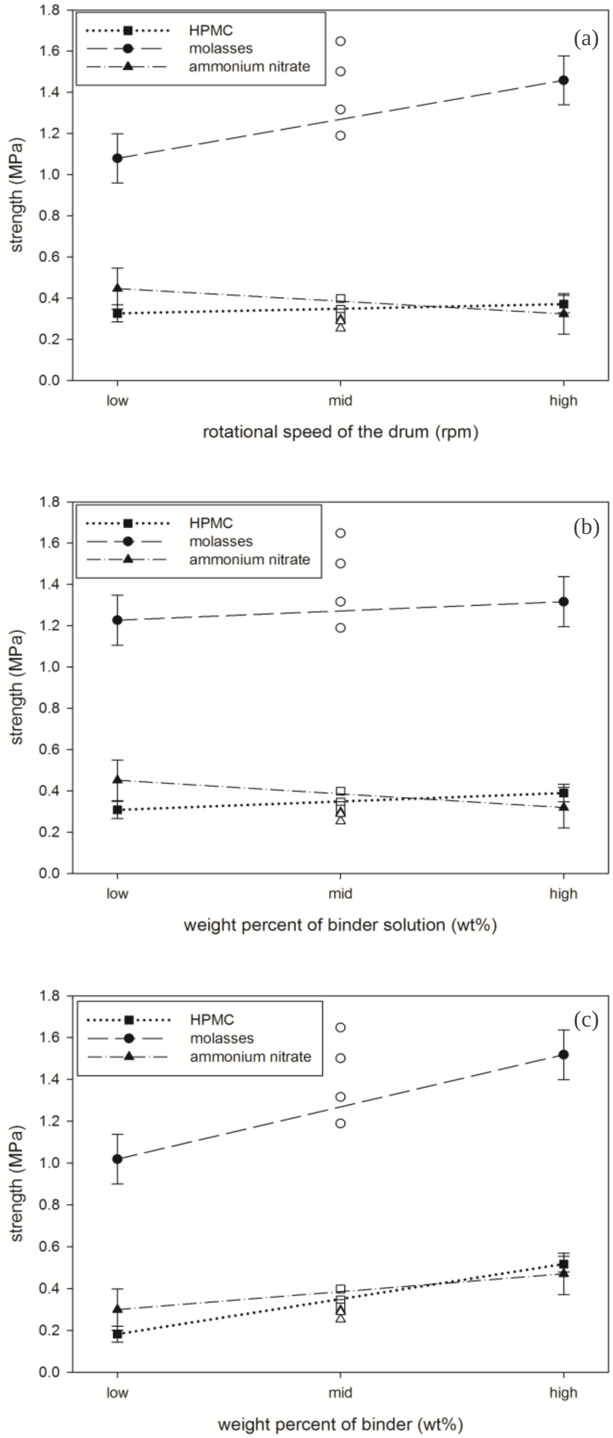


Figure 5-7: The effect of (a) drum rotational speed, (b) amount of binder solution and (c) binder concentration on the attrition resistance for granules produced using HPMC, molasses and ammonium nitrate binders. Solid points represent the low and high process parameter values while open points represent the centre points in the data.

5.4 Discussion

The drop penetration measurements indicated that the three tested liquid binder solutions interacted differently with the birchbark biochar (Table 5-2). The HPMC binder solution had the lowest drop penetration times followed by the molasses solutions and then the ammonium nitrate solutions. As expected from other measurements and models that have been developed to describe liquid penetration into a powder bed, as the binder concentration or its solution viscosity increased, the drop penetration time increased [10, 23-25]. However, a comparison between binder solutions indicated that more factors must also affect the drop penetration behaviour; a 20 wt% ammonium nitrate solution had a viscosity of 0.0011 Pa·s and a drop penetration time of 74 minutes while a higher 0.0046 Pa·s viscosity solution of 3 wt% HPMC had a shorter drop penetration time of 23 minutes.

The difference in the drop penetration behaviour of the tested binder solutions indicated varying granulation mechanisms. The proposed mechanisms are based upon the drop penetration behaviour, observations of the granulations through the transparent granulator drum and the measured granule properties. None of the liquid binder droplets immediately penetrated into the tumbling bed of birchbark biochar powder. The biochar particles were drawn around the droplets to form liquid marble structures. As a liquid marble tumbled with the powder bed, the structure grew through layering of the particles at the surface of the droplet. For liquid marbles formed from HPMC binder solutions, collisions between the liquid marbles formed larger liquid marble structures, Figure 4-12. As the particle layer thickness continued to grow, these large liquid marbles collapsed to form granule nuclei that continued to grow through collisions. Liquid marbles formed from molasses and ammonium nitrate binder solutions did not easily form larger marbles through collisions. Instead, granules developed primarily through layering of the biochar particles at the droplet surface, Figure 4-13.

The granulation mechanism affected the sizes of the biochar granules. Granules formed from HPMC binder solutions were larger than those formed from molasses and ammonium nitrate solutions (Figure 5-4). The formation of the larger liquid marble structures followed by the collapse and further growth through collisions allowed the granules formed with HPMC binder solutions to grow very large. Granule growth primarily through layering of liquid marbles with the molasses and ammonium nitrate solutions was much slower and limited resulting in smaller granules.

The amount of binder solution was the only operational parameter that significantly affected the optimal yield of granules formed from all binder solutions (Figure 5-5b). The effect was opposite for granules formed from the HPMC binder solutions compared to those formed from the molasses and ammonium nitrate binder solutions. This was attributed to the different proposed granulation mechanisms. Adding more HPMC binder solution formed more liquid marbles increasing opportunities for collisions into larger structures resulting in more granules growing beyond 4 mm in diameter. Adding more molasses or ammonium nitrate binder solution would also have allowed the formation of more liquid marbles. However, these liquid marbles only developed into granules through layering of the biochar particles and growth past 4 mm in diameter was limited. Therefore, the formation of more liquid marbles resulted in the development of more granules that grew to within the optimal size range.

The optimal granule yield was only significantly affected by drum rotational speed for granules made using HPMC as a binder. Increasing the drum rotational speed decreased the yield. As the drum rotational speed increased, both the number of opportunities for nuclei collisions and the kinetic energy of the collisions increased [26]. Collisions allowed coalescence of nuclei to form granules that grew beyond 4 mm diameter. Granules formed using molasses or ammonium nitrate as the binder primarily grew through layering instead of collisions and coalescence, and varying the drum rotational speed did not have a significant impact upon their optimal granule yield.

Attrition resistance reflects the granule strength. Only the weight percent of binder significantly affected attrition resistance for the three tested binders. The attrition resistance increased as the weight percent of binder increased. Adding more binder to the solutions increased their viscosities which then promoted stronger bonds between particles increasing the granule strength.

Figure 5-7 shows that granules produced from the molasses binder solution were stronger than the granules produced from HPMC and ammonium nitrate binder solutions. A possible explanation for this is differences in the chemical makeup of the binder solutions and, therefore, the bonds formed. Of the three binder solutions, only the granules produced using molasses had a crushing strength close to the accepted crushing strength limit of 2 MPa for granular fertilizers [27].

Increasing the weight percent of binder also positively affected the measured crushing strength of the granules. The effect, however, was only determined to be significant for the HPMC and molasses binders. Both attrition resistance and crushing strength indicate granule strength and, therefore, should be similarly affected by operational parameters. Differences were attributed to the sample size used for the measurements. The attrition resistance measurements used large samples that approximately represented the granules of a trial while, for the crushing strength measurements, only non-representative samples of three granules were tested.

The amount of binder solution and the drum rotational speed did not significantly affect the granule strength. The changes were small with a decrease in attrition resistance from 99.7 – 98.6 % with increased binder solution for granules made using molasses and changes of about 0.4 MPa in crushing strength with increased rotation speed for granules made using the HPMC or ammonium nitrate binders.

5.5 Conclusions

A comparison of three binder solutions on the wet drum granulation of birchbark biochar was conducted to evaluate the effect of binder on granulation and granule properties. A Design of Experiments examined the effect of drum rotational speed, binder concentration and total volume of binder solution on the size and strength of the resulting granules. All three binder solutions produced a significant amount of granules between a size range of 1 to 4 mm that were relatively strong as measured through resistance to attrition and crushing strength tests.

Measurements and observations indicated differences in granulation mechanisms between the binder solutions. The HPMC binder solution initially formed liquid marbles that grew through collisions with other liquid marbles forming large granule nuclei. Granules were formed from molasses and ammonium nitrate solutions primarily through layering. The range of effects of the operational parameters on the granule sizes and strength was attributed to these different granulation mechanisms.

The research demonstrated that birchbark biochar could be wet drum granulated using HPMC, molasses or ammonium nitrate as a binder. The granules produced had a significant yield in the 1 to 4 mm size range, a high resistance to attrition and relatively high granule crushing strength. The binder can be adjusted to complement the biochar and provide additional nutrients to the soil. However, the binder interaction with the biochar must be examined to select appropriate process parameters to ensure the production of biochar granules with specified properties.

5.6 References

[1] S. Kloss, F. Zehetner, A. Dellantonio, R. Hamid, F. Ottner, V. Liedtke, M. Schwanninger, M.H. Gerzabek, G. Soja, Characterization of slow pyrolysis biochars: effects of feedstocks and pyrolysis temperature on biochar properties, J. Environ. Qual., 41 (2012) 990-1000.

[2] B. Glaser, K. Wiedner, S. Seelig, H.-P. Schmidt, H. Gerber, Biochar organic fertilizers from natural resources as substitute for mineral fertilizers, Agronomy for Sustainable Development, 35 (2015) 667-678.

[3] D.A. Laird, P. Fleming, D.D. Davis, R. Horton, B. Wang, D.L. Karlen, Impact of biochar amendments on the quality of a typical Midwestern agricultural soil, Geoderma, 158 (2010) 443-449.

[4] Bian, D. Chen, X. Liu, L. Cui, L. Li, G. Pan, D. Xie, J. Zheng, X. Zhang, J. Zheng, A. Chang, Biochar soil amendment as a solution to prevent Cd-tainted rice from China: Results from a cross-site field experiment, Ecological Engineering, 58 (2013) 378-383.

[5] S. Steinbeiss, G. Gleixner, M. Antonietti, Effect of biochar amendment on soil carbon balance and soil microbial activity, Soil Biology and Biochemistry, 41 (2009) 1301-1310.

[6] B. Husk, J. Major, Commercial scale agricultural biochar field trial in Quebec, Canada, over two years: Effects of biochar on soil fertility, biology, crop productivity and quality, BlueLeaf Inc., Quebec, Canada, 2010.

[7] R.K. Dumroese, J. Heiskanen, K. Englund, A. Tervahauta, Pelleted biochar: Chemical and physical properties show potential use as a substrate in container nurseries, Biomass and Bioenergy, 35 (2011) 2018-2027.

[8] E.W. Bruun, D. Müller-Stöver, P. Ambus, H. Hauggaard-Nielsen, Application of biochar to soil and N2O emissions: potential effects of blending fast-pyrolysis biochar with anaerobically digested slurry, European Journal of Soil Science, 62 (2011) 581-589.

[9] J. Lehmann, S. Joseph (Eds.) Biochar for Environmental Management: Science and Technology, Earthscan, London & Sterling, VA, 2009, pp. 1-9.

[10] B. Bowden-Green, L. Briens, An investigation of drum granulation of biochar powder, Powder Technology, 288 (2016) 249-254.

[11] T. Cleasby, Use of molasses on the land: a report of four experiments being carried out by the Tongaat Sugar Company Ltd., South African Sugar Technology AssociationSouth Africa, 1959, pp. 95-102.

[12] S. Schenck, Molasses soil amendment for crop improvement and nematode management, Hawaii Agriculture Research Center, 3 (2001) 1-7.

[13] L.L. Vawdrey, G.R. Stirling, Control of root-knot nematode (Meloidogyne javanica) on tomato with molasses and other organic amendments, Australasian Plant Pathology, 26 (1997) 179-187.

[14] R. Rodriguez-Kabana, P. King, Use of Mixtures of urea and blackstrap molasses for control of root-knot nematodes in soil, Nematropica, 10 (1980) 38-44.

[15] F. Mohamed, N. El-Hussiny, M. Shalabi, Granulation of coke breeze fine for using in the sintering process, Science of Sintering, 42 (2010) 193-202.

[16] Y. Ghasemi, M. Kianmehr, A. Mirzabe, B. Abooali, The effect of rotational speed of the drum on physical properties of granulated compost fertilizer, Physiochemical Problems of Mineral Processing, 49 (2013) 743-755.

[17] B. Pendyal, M.M. Johns, W.E. Marshall, M. Ahmedna, R.M. Rao, The effect of binders and agricultural by-products on physical and chemical properties of granular activated carbons, Bioresource Technology, 68 (1999) 247-254.

[18] T. Hignett, Fertilizer Manual, Springer Science & Business Media, 2013.

[19] A. Heeb, B. Lundegårdh, T. Ericsson, G.P. Savage, Effects of nitrate-, ammonium-, and organic-nitrogen-based fertilizers on growth and yield of tomatoes, Journal of Plant Nutrition and Soil Science, 168 (2005) 123-129.

[20] P.J. Sherrington, Liquid phase relationships in fertilizer granulation by a layering process, The Canadian Journal of Chemical Engineering, 47 (1969) 308-316.

[21] K.P. Hapgood, J.D. Litster, S.R. Biggs, T. Howes, Drop Penetration into Porous Powder Beds, Journal of Colloid and Interface Science, 253 (2002) 353-366.

[22] D. Rutland, J. Polo, Fertilizer dealer handbook: products, storage and handling., IFDC - An International Center for Soil Fertility and Agricultural Development, Muscle Shoals, AL, 2005.

[23] S. Middleman, Modeling axisymmetric flows: dynamics of films, jets, and drops, Academic Press 1995.

[24] T. Nguyen, W. Shen, K. Hapgood, Drop penetration time in heterogeneous powder beds, Chemical Engineering Science, 64 (2009) 5210-5221.

[25] N. Eshtiaghi, J.J.S. Liu, K.P. Hapgood, Formation of hollow granules from liquid marbles: Small scale experiments, Powder Technology, 197 (2010) 184-195.

[26] J. Litster, B. Ennis, The Science and Engineering of Granulation Processes, Kluwer Academic Publishers, Dordrecht, NLD, (2004) 65-67.

[27] P. Kiwietniak, Strength of fertilizer granules and methods for testing it, Mechanizacja Rolnictwa, 34 (1985).

Chapter 6

6 General Discussion and Conclusions

Biochar has properties that make it suitable as a soil amendment. For example, its high porosity and chemical composition allows biochar to increase water retention and microbial growth while decreasing nutrient leaching and heavy metal tainting within soils. Biochar, however, is a fine powder that can easily become air-borne during cultivation into soils causing loss of product and health concerns. A solution to the dust hazards is the size enlargement of biochar powder particles to biochar granules using wet drum granulation. The modification of biochar into granules results in an increased weight and size compared to biochar particles thereby reducing dust hazards and minimizing handling challenges. No research has previously been conducted on wet drum granulation of biochar. For successful granulation of biochar, the effects of granulation parameters on granule properties must be studied. Along with granulation parameters, the variability in biochar properties due to feedstock and pyrolysis conditions may have an effect on granulation and granule properties. Therefore, the overall objectives of this research were to investigate the wet drum granulation of biochar and the factors that affect the product granule properties.

Tests were conducted to evaluate the biochar powder properties which included flowability testing, SEM imaging and drop penetration tests. The granulation of biochar was conducted in a lab scale drum granulator that used a sparger for liquid binder solution addition. A factorial DoE was set up to determine the effect of rotational speed of the drum, binder concentration and volume of binder solution on granule properties. An ANOVA was conducted with granule flowability, optimal granule size yield, granule attrition resistance and granule crushing strength as the response variables.

The biochar powder was found to be free flowing, porous and somewhat irregular in shape. Drop penetration tests indicated that the biochar powder was hydrophobic. The biochar powder was successfully granulated into biochar granules with a significant fraction of granules within the 1 to 4 mm optimal size range. Granule property testing found that the granules were generally free flowing, had a high resistance to attrition and were relatively strong with a maximum strength of 0.5 MPa although not as strong as recommended for commercial granular fertilizers.

Biochars from three different feedstocks (cornstalk, birchbark and miscanthus) were tested along with three binders of HPMC, molasses and ammonium nitrate. The biochar-binder solution interactions varied from slightly to very hydrophobic which impacted the granulation mechanism. In turn, the effects of the tested operational parameters of drum rotational speed, binder concentration and amount of binder solution varied. The research showed that biochar could be granulated using wet drum granulation. The process parameters required adjustment for each biochar–binder solution combination to ensure the production of granules with specified properties. The experimental results showed the need for careful selection and preliminary testing of biochar feedstocks and binder solutions to ensure that the granules produced have the required granule properties to be an effective soil amendment.

Currently the primary goal of the pyrolysis of agricultural residues is to produce bio-oil as an alternative fuel or fuel supplement. Biochar is considered a secondary product. Modification of biochar to a form that could be used as a soil amendment would increase the value of biochar and the overall potential of pyrolysis. The research conducted indicated that the wet drum granulation process could be used to produce granules which can be successfully cultivated into soil with limited dust problems. The research further indicated that the drum granulation process can be optimized to produce a significant amount of granules in the optimal size range with sufficient strength to remain intact during transportation and cultivation.

6.1 Future Work

There are many possible directions for future work from this research: (i) the hydrophobic interaction between the biochar and the binder solutions remains poorly understood. As this interaction affects granulation, it must be further studied to provide information on the selection of materials and operating parameters. This should include the further characterization of the binder solutions such as contact angle and surface tension. Further characterization of the binder solutions could explain the differences found in drop penetration times which did not correspond to differences in binder viscosity. Understanding the effect of binder solution properties on drop penetration times would enable the selection of a more ideal binder solution for the drum granulation of biochar powder into a soil amendment, (ii) the research was conducted using a lab scale granulator. Large amounts of biochar granules would be required for soil amendment and therefore scale-up research is required, (iii) only three binders were investigated. An ideal binder would provide sufficient yield of optimal size granules with specified strength. In addition, an ideal binder could provide essential nutrients and microorganisms for plant growth that would complement the biochar addition to the soils.

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