GRANULATION OF LIGNOCELLULOSIC POWDERS

by

VIKRAMADITYA YANDAPALLI

(Under the Direction of Sudhagar Mani)

ABSTRACT

Lignocellulosic biomass required to be densified into pellets/granules to improve handling and storage properties and to reduce cost of transport and storage. A novel wet granulation technology was proposed to granulate pine and switchgrass powders with corn starch. The physical and flow properties of biomass powders were studied at five particle size levels and three moisture levels. Small size particles with high moisture content had lower flowability due to high angle of repose. Granulation of pine powders having a mean size of 135 μm with 5% (w/w) corn starch binder solution produced granules with highest density and hardness. Pretreated switchgrass powders with 20% quick lime loading rate had produced the highest density granules with the least amount of soldium alginate-corn starch binder requirement. Wet granulation of lignocellulosic biomass powders can produce high density granules for efficient handling, transport and storage.

INDEX WORDS: Pine and Switchgrass powders, binder, lime pretreatment, granule density, hardness.

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DEDICATION

To my parents and brother.

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CHAPTER 1

INTRODUCTION

The world's energy consumption is primarily dependent on non-renewable fossil fuels, which are not only decreasing at a rapid pace but also increasing the greenhouse gas emissions. Development of alternative fuel sources is critical to meet the future energy demand and to mitigate environmental emissions. Biomass is one of the traditional renewable energy sources that have been used worldwide to generate power, heat and liquid transportation biofuels in small scales (Matti, 2004; Caputo et al., 2005). Efficient handling, transport and storage of biomass from various sources such as agricultural residues, energy crops and forestry are still a challenge due to their high moisture content, low bulk and energy density (Sokhansanj and Turhollow, 2002; Mani et al., 2006). To overcome these problems biomass is mechanically densified into pellets, briquettes and cubes (Sokhansanj et al., 2005; Saracoglu and Gunduz, 2010). However, pelletization or briquetting of biomass demands high-energy input and cost that limits the growth of domestic pellet demand (Mani et al., 2006; Sokhansanj and Fenton, 2006). While the demand for densified biomass in the international market, specifically in Europe is growing continuously, it is critical to increase domestic utilization of biomass by reducing the cost of generating densified biomass to promote rural economic development, domestic energy security and to reduce local carbon footprints. Wet granulation technology can be a suitable alternative for biomass densification, as it demands less energy to increase biomass density at low cost. Granulation is a process of

agglomerating fine particles into self-organized granules with or without binding agents by applying shear/vibrational forces (Kadam, 1991; Pietsch, 2002).

Wet granulation process depends on number of powder properties such as particle size, shape, particle size distribution, surface properties, moisture content, chemical composition and binder properties to generate desirable granule properties (Pietsch, 2002;Pietsch, 2003; Ennis, 2010). Granulation process is also dependent on type of granulator used for agglomeration and each has its own pros and cons. Typically, wet granulation of powders for production of granules with a desired size range of 1-20mm can be performed by low agitation systems such as pan or drum granulators (Ennis and Lister, 1996; Ennis, 2010). Binder type and concentration can have significant effect on granule formation and final properties (Mort, 2005). Hence, it is important to identify suitable binder(s) for lignocellulosic biomass powders to produce high quality granules that are most suited for efficient handling, transport and storage (Veverka and Hinkle, 2001). The biomass powder particles below 500 μm size are suitable for generation of good quality granules as particles with smaller size tend to better adjust inside the wet granule (Pietsch, 2002; Ennis, 2010). The physical, chemical and flow characterization of granules are perceived as key parameters to determine granule qualities in addition to its final use (Baykal and Doven, 2000; Gluba, 2005; Probst and Ileleji, 2009; Sobczak et al, 2009).

Wet granulation technology is used in chemical, fertilizer, pharmaceutical, food and mineral industries for effective densification of fine powder materials (Kadam, 1991; Pietsch, 2002; Hoeung et al., 2011; Palzer, 2011; Saad et al., 2011). Wet granulation of food materials such as wheat powders, culinary powders, protein powders, starch and

flavor powders are performed for improvement of food product quality (Palzer, 2011). Wet granulation technology is also used in granulating animal feed material such as dried distillers grains with solubles (DDGS) for improving handling and flowability (Probst and Ileleji, 2009). In general, biomass powder materials can be granulated using a low-pressure mixer like pan granulator along with application of selective liquid binder. The biomass powder size, shape, flowability and wettability are critical properties that affect the granulation process. Lignocellulosic biomass consists of cellulose, hemi-cellulose and lignin polymers cross-linked to form a complex matrix (Howard et al., 2003). This complex matrix prevents the surface exposure of natural binding components like lignin, starch, protein and phenolic compounds reducing the cohesive strength of biomass powders. Typically, pretreatment methods such as alkaline, acidic, ammonia fiber explosion, microwave irradiation and steam explosion are applied to biomass to increase accessibility of cellulose by disrupting lignocellulosic matrix to extract sugars for biofuel production (Li et al., 2010; Pedersen and Meyer, 2010). Pretreatment methods could also be used to improve biomass granulation by increasing the surface exposure of biomass binding components by disrupting lignocellulosic matrix. Woody biomass material like sawdust is used as binding material in agglomeration process due its intrinsic binding property (Pietsch, 2002). Therefore, pretreatment methods are more suitable for fibrous biomass materials like switchgrass, wheat and barley straw. Kashaninejad and Tabil (2011) used the alkaline microwave pretreatment method for wheat and barley straw grinds to increase the surface exposure of natural binding components that had improved the quality of biomass pellets.

Proposed research objectives

The overall goal of this proposed research was to develop wet granulation technology for lignocellulosic biomass powders to produce high-density granules for efficient handling, transport and storage at low energy input and cost.

The specific objectives of this research were:

1) To determine the bulk flow properties of switchgrass and pine powders used for the granulation study.
2) To determine the effects of particle size and binder concentrations on producing high quality pinewood granules.
3) To investigate the effect of alkaline pretreatment conditions on producing high quality switchgrass granules.

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CHAPTER 2

REVIEW OF LITERATURE

Introduction

The major sources of biomass material are agricultural residues, energy crops and forestry (Tumuluru et al., 2010). Biomass mainly consists of cellulose, hemicellulose and lignin (Howard et al., 2003). Microscopic observation of lignocellulose structure reveals that cellulose, hemicellulose, lignin are bound tightly and form a rigid matrix (Murphy and McCarthy, 2005). Lignin is a thermosetting resin component, which is being used as a binder during high-pressure densification process (van Dam et al., 2004). Higher lignin content increases calorific value of biomass (Phanphanich and Mani, 2011). Several other natural binding components like protein, starch, and crude fat could help in densification process of biomass (Kaliyan and Morey, 2010).

Typically, biomass is size reduced to below 1 mm and 0.5 mm for pelletization and wet granulation process respectively (Kaliyan and Morey, 2009; Phanphanich and Mani, 2009). Physical, chemical and flow properties of powder materials are important for design and operation of equipment (Bodhmage, 2006). Physical properties of biomass powders such as bulk density, particle density, porosity, size and shape affect the flowability through various equipment's. In general, physical and flow properties of powders are also affected by temperature and relative humidity of ambient air, where the materials are stored or processed (Fitzpatrick et al., 2004; Bodhmage, 2006; Littlefield et

al., 2011). Typically, lower biomass powder particle size ranges at higher moisture contents had poor flowability (Littlefield et al., 2011).

Granulation

Granulation can be defined as development of products with desired size, shape and density from slurries or fine powder particles (Lachman et al., 1976). There are four main types of granulation technologies: they are agitation, heat bonding, compaction, and drop formation (Sherrington and Oliver, 1981).

Densification of material by agitation along with or without using binders is known as agglomeration. The granule size and quality obtained in this process is dependent on several machine and material variables. Agglomeration method of densification is most commonly used in fertilizer, mineral and metallurgy industries (Darcovich, 2000; Couper, 2005; Pietsch, 2005). Granulation through heat bonding can be achieved by nodulization and sintering method. In nodulization method, the material is agitated inside a hot kiln to form hard round granules. In sintering method, the material is made into a unified mass, which is further fragmented into required size. Ceramic, metallurgy and chemical industries commonly use this type of granulation technology (Sherrington and Oliver, 1981; Darcovich, 2000; Couper, 2005).

Compaction of material could be achieved by compression and extrusion. In compression process, material is shaped to a block or sheet, which is fragmented into desired size. Compression method of densification is mostly used in ceramic, mineral, automotive and plastic industries (Darcovich, 2000; Couper, 2005). In extrusion process a material is forced out through an orifice using an extruder. Lubricants and binding agents are also used for aiding the process. The properties of the final product are based

on the design of the orifice and type of extruder used. Extrusion method of densification is most commonly used in biomass, animal feed and chemical industries (Ennis and Lister, 1997; Darcovich, 2000; Couper, 2005). In drop formation method, material is developed into droplets of solution or slurry. Later these droplets are cured either by fluidized bed, prilling or spray drying. Drop formation method is usually used in food, pharmaceutical, ceramic and anhydrous chemical industries. (Kadam, 1991; Darcovich, 2000; Couper, 2005).

Traditional biomass densification methods are baling, pelletization and briquetting. Densification through these methods requires high pressure and energy. Low-pressure densification methods require relatively lower energy for compaction. These low-pressure systems can be further classified into high agitation and low agitation mixers (Figure 2.1). Therefore, low-pressure and agitation systems like fluidized bed, pan and drum granulators can be used for production of biomass granules with low energy consumption (Ennis and Lister, 1996).

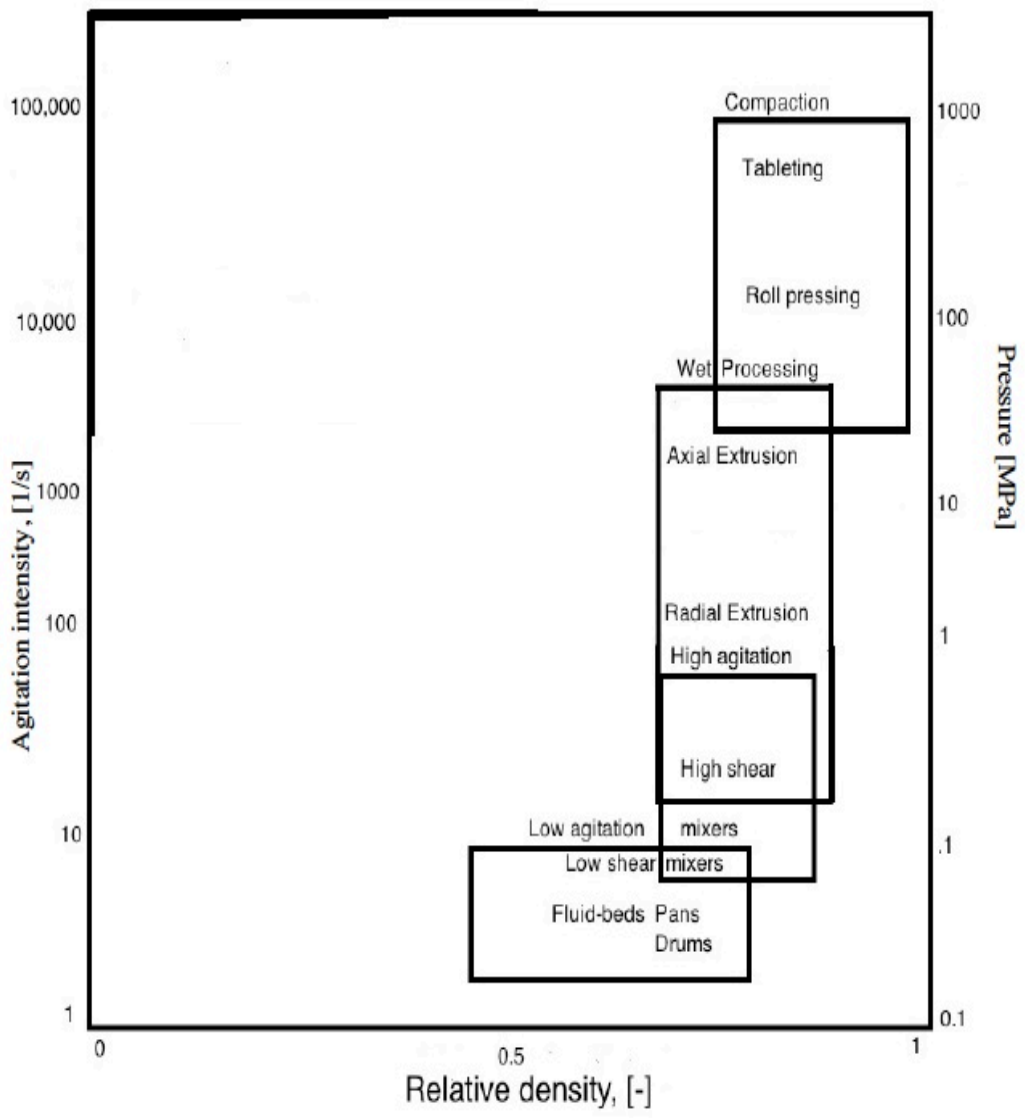

Figure 2.1. Classification of agglomeration processes by agitation intensity, compaction pressure and relative density (Ennis and Lister, 1996).

Note: Relative density in regard to initial particle density i.e (1 - ε) where ε is the solid volume fraction.

Wet Granulation/Agglomeration process

Wet granulation method does not use pressure for densification, which in turn helps in reduction of operating cost for densification process (Ennis and Lister, 1996; Pietsch, 2002). Hence, a detailed description of this method is given. In wet granulation process, fine powder particles were wetted by the help of a binding agent and mixed in a

granulator to produce granules (Darcovich, 2000). Granule quality is dependent on binding strength of fine powder particles, which is based on the type of binder and binding mechanisms applicable for that process (Kadam, 1991). There are three sets of rate processes that cause agglomeration they are wetting and nucleation, growth and consolidation, attrition and breakage (Figure 2.2) (Sastry and Fuerstenau, 1973; Ennis and Lister, 1997). In wetting and nucleation, a binding agent is thoroughly mixed with feed powder resulting in formation of nuclei granules. During growth and consolidation, these nuclei granules clash among themselves or with granulator and powder bed resulting in granule compression and further enlargement. Finally, in attrition and breakage, the product granules formed may reduce in size because of the collisions and friction that may occur in the granulating equipment and in product conveyance (Iveson et al., 2001).

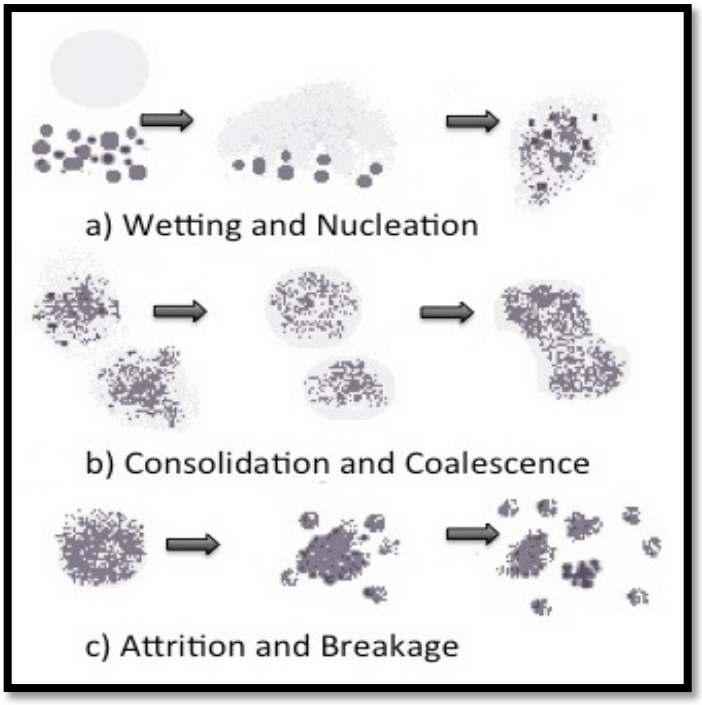

Figure 2.2. Schematic of agglomeration processes (Ennis and Lister, 1997)

Controlling agglomeration rate processes

As mentioned before there are three sets of rate processes in agglomeration, they are wetting and nucleation, growth and consolidation, attrition and breakage. Hence, it is important to control these rate processes for obtaining desired product granules.

Controlling wetting

It is important to characterize and control wetting, as improved wetting uniformity produces better quality granules. The rate process of wetting can be tested by different methods like washburn test, flotation tests, inverse gas chromatography and contact angle goniometer (Ennis and Lister, 1996; Ennis and Lister, 1997; Couper, 2005). Based on these tests and also required characteristics of product granules, modifications in material properties and operating variables for increasing wetting uniformity are done (Table A1) in Appendix A). Wetting of powder bed is mainly dependent on parameters like binder surface tension, binder viscosity and extent of binder distribution, which could be controlled by steam treatment of powder, change in binder concentration or type and variation in powder material particle size distribution (Ennis and Lister, 1996).

Controlling growth and consolidation

The rate processes of growth and consolidation includes nucleation, coalescence, layering, compaction and breakage. It is important to control these rate processes for production of desired granules. These rate processes are mainly dependent on stokes number (St) that could be increased by increasing binder viscosity or agitation intensity (Ennis and Lister, 1996). Further variables that are important in controlling these rate processes were given (Table A2 in Appendix A). Growth rate and consolidation of the nuclei granules is dependent on parameters like collision frequency, residence time, and

binder concentration, these parameters could be controlled by varying the spray rate, impeller or drum rotation speed, varying binder concentration (Ennis and Lister, 1996; Iveson et al., 2001).

Controlling breakage

The rate process of breakage is important to achieve the target granule size. The key variables to control breakage were given (Table A3 in Appendix A) (Ennis and Lister, 1996). Breakage and attrition of granules are dependent on parameters like granule hardness, binder plasticity, impact and wear during granulation and product handling. These parameters could be controlled by improving bond strength by varying binder concentration and agitation intensity, varying residence time and drying time, modifying scrapper or impeller design (Ennis and Lister, 1996; Iveson et al., 2001).

Agglomeration binding mechanisms

Granules are formed due to the bonding between powder particles and these bonds must have enough strength to produce better quality product granules (Sastry and Fuerstenau, 1973).

There are several binding mechanisms operating during the agglomeration process, but generally more than one will be applicable to any particular system (Pietsch, 2002). They are elaborated as follows.

A. Solid bridges (Pietsch, 2002)

1. Sintering: The sinter bridges will be forming between solid particles when the temperature of the system rises above the melting temperature of the feed material.

2. Partial melting: In this system the particles with uneven shape collide with each other and create friction, which leads to formation of liquid bridges by partial melting of the particles. The liquid bridges quickly solidify and form solid bridges.

3. Chemical reaction or Hardening binders: Addition of hardening binders or chemical reaction between particles could result in formation of solid bridges. Temperature, pressure and moisture are the important factors in this type of solid bridge formation.

B. Liquid bridges and capillary pressure: In general, liquid bridges develop between the particles due to the availability of free water or by capillary condensation. Negative capillary pressure that may exist at pore ends of particles will increase the strength of these liquid bridges (Pietsch, 2002). Newitt and Conway-Jones (1958) have further explained the different states of granule formation by mobile liquid binding based on the percentage of moisture content (mc) of granules and are explained as follows (Barlow, 1968; Rumpf, 1974)

    1. Pendular: The first state of granule formation and it is possible only if the moisture content of material is more than 0% and less then 13.6%. The granules that formed in this state are non-spherical and soft. They also have dry surface and low density.

    2. Funicular: The second state of granule formation and it is possible only if the moisture content of the soft and non-spherical granules were raised above

13.6% but below 100%. Firm granules of spherical shape are formed during this state and these granules are denser than pendular state.

3. Capillary: The third state of granule formation and to obtain this state, moisture content of 100% should be attained. Granules in this state are spherical and dense. Their surface is wet than funicular state.

4. Droplet or Suspension: The fourth state of granule formation. In this state all the particles are surrounded by liquid and it typically occurs during spray drying process.

C. Adhesion and Cohesion forces (Pietsch, 2002)

1. Highly viscous binders: The binders with high viscosity like honey, tar, pitch etc., when applied to a material, increases the adhesion forces between solid and binder interface. Highly viscous binders also improve the cohesion forces between particles.
2. Adsorption layers: The finely divided solid materials form adsorption layers. Adsorption layers, which are thinner than 3 nm help in enhancing adhesion forces that in-turn help in inter-particle binding.

D. Attraction forces between solid particles: The ultrafine or nanosized solid particles bind due to the attraction forces, which are explained below (Pietsch, 2002).

1. Electric and Magnetic forces: When ultrafine solid particles come in contact with each other, there is migration of electrons between them due to electrostatic forces this electron migration leads to formation of electrical double layers and thus

binding the solid particles. Ferromagnetic particles have the capability of binding by the help of magnetic forces, which are similar to electrostatic forces (Pietsch, 2002).

2. Molecular forces:
    a. Van-der-waals forces: These are the molecular attractive forces with a range of 100 nm. These forces arise due to the electric polarization that is induced in each of the particles by other particles.

    b. Valence forces: New surfaces with valences may be created during fine grinding of solids and these valences may bind among themselves by recombination bonding mechanism that increases the bond strength between particles.

    c. Non-valence associations like hydrogen bridges also cause binding between solid particles.

E. Interlocking bonds: These bonds are generally formed between solid particles that are in the shape of fiber or threads. Sometimes solid particles form agglomerates of weak strength. Hence, to strengthen these weak bonds fibrous binding additives that promote interlocking bonds are used (Pietsch, 2002).

The level of tensile strength given by each of the binding forces given above was illustrated in the below Figure 2.3 from which it could be understood that liquid and solid bridges are the significant binding forces in the particles with diameter above 10 μm (Rumpf, 1962; Rhodes, 1998).

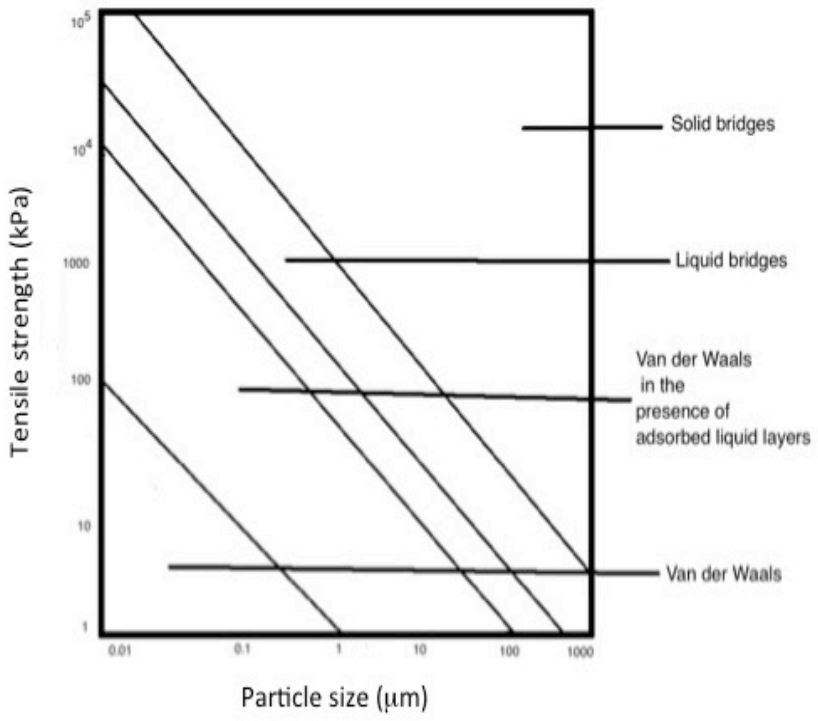

Figure 2.3. Tensile strength of agglomerates (Rumpf, 1962)

Granulation equipment

Wet granulation is the term generally used to describe the process of particle size enlargement by tumbling or agitating mechanism along with addition of liquid binders (Kadam, 1991). There are typically three main types of wet granulating equipment based on the agitation process (Ennis and Lister, 1996; Parikh, 2005), they are tumbling granulators (drum and pan granulators), fluidized granulators (fluidized beds, spouted beds and wurster coaters) and mixer granulators (high shear granulators). The agglomeration process in these granulators is dependent on material properties and process parameters. Typical characteristics of these granulators were given (Table A4 in Appendix A). Furthermore, tumbling granulators are typically used for production of granules in the size range of 0.5 to 20 mm with moderate density. Mixer granulators are commonly used for production of granules in the size range of 0.1 to 2 mm. The product

granule density varies from low to high according to the requirement. Typically fluidized granulators are used in production of granules in the size range of 0.1 to 2 mm, where the product granule density varies from low to moderate according to the requirement (Ennis and Lister, 1996). Therefore, it could be concluded that tumbling granulator like pan granulator is useful in production of lignocellulosic biomass granules in the size range of 5 to 20 mm.

Pan granulator

A typical pan granulator is shown in Figure 2.4 (Pan pelletizer, Feeco International Inc, WI, USA) and it consists of a round pan that rotates in an inclined angle that is generally tilted between 50 to 60 degress (Ennis, 2010). For production of granules by this granulator feed powder material is loaded onto the pan and later a binding agent is sprayed on it, which leads to formation of wet powder bed. Further addition of feed powder material to the wet powder bed leads to formation of granules due to tumbling action of pan. Scrapping blades are used for effective mixing of the material in the granulator (Pietsch, 2002). Granules after attaining the desired size and weight will be discharged from downside of the pan due to gravity (Saravacos and Kostaropoulos, 2002). These granules are later dried in a drying unit. The efficiency of the process and the product granule quality is dependent on the pan granulator parameters like inclination angle of the pan, speed of pan rotation, ratio of height and diameter of the pan, position for addition of binder and feed material. Mostly, these parameters for granulation of a specific feed material are experimentally determined (Pietsch, 2002; Saravacos and Kostaropoulos, 2002).

Pan granulators are useful in production of granules with more uniform size than drum granulator because in pan granulator granules with larger size tend to be discarded earlier than the fine powder particles, whereas in drum granulator a non-uniform product is ejected at the end of the process (Couper, 2005). Pan granulator also has several other advantages like ease of handling and cleaning, ability to be operated both as batch or continuous process, better control of the critical machine factors required for optimization of granulation procedure. The major disadvantage of pan granulator is that it is open system prone to effects of external environment (Saravacos and Kostaropoulos, 2002).

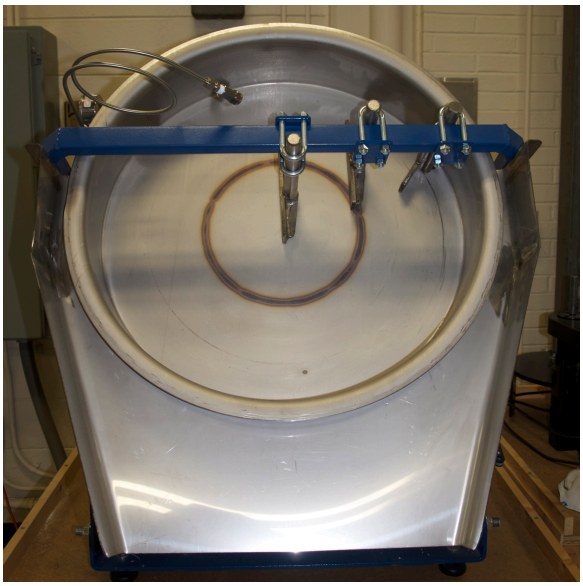

Figure 2.4. Pan granulator
(Pan pelletizer, Feeco International Inc, WI, USA)

Binders

Binding agents are used to reduce biomass springiness during densification process. Some of the commonly used binders in biomass densification are paper mill waste, lignin, bentonite, pyrolytic oil (char) and starch binders (Taylor, 1988; Becidan et al., 2007). Typically, binders can be added as a solution or in dry form with a concentration range of 2-10% w/w (Ghebre-Sellassie, 1989). There are many other types

of binders, which are been used in other industrial sectors like food, pharmaceuticals, mining, chemical and fertilizer apart from biomass densification industry. These binders list according to the industry were given (Table A5 in Appendix A). Pharmaceutical and food industries prefer to use expensive non-toxic binders whereas chemical, fertilizer, mining and cement industries prefer to use inexpensive industrial grade binders (Tabil, 1996; Parikh, 2005; Kadam, 1991; Pietsch, 2002).

Effects of binder on granulation

Typically, for densification of any non-elastic materials binding agents are used (Parikh, 2005). Binder solution surface tension plays a key role in granulation process by influencing the capillary pressure and frictional force between the powder particles (Iveson et al., 2001). The volume of binder solution required for granulation of specific powder mass could be known by plotting the cumulative granule size distribution against the mean granule size for given liquid binder at four different relative volumes (V_r) (Kadam, 1991). Large agglomerates can be formed when binder particle size is increased (Parikh, 2005). The size of binder spray droplets is also important in regulating the granule size. Hence droplet sizes are controlled through an atomizing spray nozzle (Kadam, 1991; Jinapong et al., 2008). Wetting and adhesive properties of the binder solution are significantly dependent on the binder solution concentration, temperature, solvent type and quantity (Kadam, 1991; Mort, 2005; Parikh, 2005). The viscosity of binder solution is also important for wet granule strength as it affects the strength of liquid bridges between powder particles (Parikh, 2005). Several binder addition methods like pouring, melting, spraying are currently being employed in different industries such as fertilizer, chemical, food and mineral (Parikh 2005; Kadam, 1991).

Pretreatment of lignocellulosic biomass

Lignocellulosic biomass is made of lignin, cellulose and hemicellulose (Howard et al., 2003). Lignin acts like a natural binding material that helps in maintaining the structural strength of the lignocellulosic material (van Dam et al., 2004). Several pretreatment methods were being used for disrupting the lignocellulosic structure. The main purpose of these pretreatments is to enhance the enzymatic hydrolysis by improving the accessibility of enzymes to cellulose, which is converted to monosaccharides that are fermented to biofuels (Mosier et al., 2005; Pedersen and Meyer, 2010). Typically used pretreatment methods are alkaline solution, alkaline wet oxidation, ammonia fiber explosion, microwave irradiation, dilute acid hydrolysis and steam explosion (Esteghlalian et al., 1997; Bura et al., 2002; Mosier et al., 2005; Pedersen and Meyer, 2010; Brodeur et al., 2011; Kashaninejad and Tabil 2011).

Pretreatment methods are also used for improving the densification process of biomass as they help in surface relocation of natural binding components of biomass (Kashaninejad and Tabil 2011; Rijal et al., 2012). Microwave irradiation and alkaline pretreatment were used for increasing the quality of wheat and barley straw pellets (Kashaninejad and Tabil 2011). Switchgrass material that was pretreated by acidic and alkaline pretreatments was not only able to produce good quality pellets but also improved the yield of monosaccharides by enzyme hydrolysis (Rijal et al., 2012). Pretreatments methods not only help in disruption of lignocellulosic matrix but also increase the internal surface area of biomass as these pretreatments are carried out in an aqueous environment (Kashaninejad and Tabil, 2011). The increase in internal surface

area and surface relocation of natural binding components can help in improvement of wet granulation process.

In general, the surface and structural changes of pretreated biomass material is accessed by microscopy techniques such as stereomicroscopy, autofluorescence microscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) (Donohoe et al., 2011). UV-autofluorescence microscopy is used for observing the surface relocation of natural plant binding components like lignin, chlorophyll, protein and phenolic compounds (Yeung, 1998; Kaliyan and Morey, 2010). Several studies have used scanning electron microscopy to observe the structural changes on an entire biomass particle (Singh et al., 2009; Kaliyan and Morey, 2010; Donohoe et al., 2011). Therefore, autofluorescence microscopy along with scanning electron microscopy is useful in observing the surface and structural changes of pretreated switchgrass powder material.

Granulation application

Agglomeration method of densification is used in several industrial sectors like mining, pharmaceutical, food, chemical and fertilizer. Several research studies were conducted on development of agglomeration process for the materials used in those industries (Table A6 in Appendix A). Typically, for production of granules in size range of 0.07 mm to 1 mm fluidized bed and high shear granulators are preferred (Jinapong et al., 2008; Chen et al, 2009; Hassanpour et al., 2009; Osborne et al., 2010). The product granule density and strength will be higher in the granules produced by high shear granulator when compared to fluidized bed granulator (Ennis and Lister, 1996). Typically pan and drum granulators are used to produce granules in size range of 5 mm to 15 mm.

The binder solution, binder addition method and scrapper blade design were varied according to the material and the expected product granule properties (Baykal and Doven, 2000; Watano et al., 2003; Gluba, 2005; Rahmanian, et al., 2009; Saad et al., 2011).

Discussion

Physical and flow properties of biomass powders at lower particle size ranges, below 1 mm along with their shape factors are not extensively studied. Understanding the physical and flow properties of these powders will not only be helpful in improving the biomass granulation process but also in design of equipment. Several granulation methods are available for densifying biomass but granulation through tumbling mechanism is believed to be suitable for biomass granulation. Tumbling granulators like pan and drum does not involve application of pressure for densification which helps in reducing the energy consumption and in turn cost of the densification process (Ennis and Lister, 1996; Pietsch, 2002). Tumbling granulators can produce granules in the size range of 0.5 to 20 mm, which could be easily transported. Pan granulator has several advantages over drum granulator such as production of granules with uniform size, ease of operation and cleaning (Saravacos and Kostaropoulos, 2002; Couper, 2005). Therefore, pan granulator can be ideal for biomass granulation.

Several binding agents are being used in wide variety of industries but considering the factors like binding capacity, calorific value, ash content, cost and availability it would be good to use cornstarch and sodium alginate-cornstarch as binders for biomass granulation (Veverka and Hinkle, 2001; Pietsch, 2002). Biomass pretreatment could be useful in surface relocation of natural binding components that

could reduce the binder percentage required for granulation and also improve the final granule quality. Lime pretreatment of biomass is a cost effective process, which can disrupt the lignocellulosic matrix and expose the natural biomass binding components improving the granulation process and granule quality.

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CHAPTER 3

EFFECTS OF PARTICLE SIZE AND MOISTURE CONTENT ON BULK FLOW PROPERTIES OF SWITCHGRASS AND PINE POWDERS

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Abstract

Physical and bulk flow properties of biomass powders are critical for designing and selecting suitable material handling, feeding and storage devices in a biorefinery. Powder particle size and moisture content are the main parameters that affect the bulk flow properties of lignocellulosic powders. The main objective of this study was to investigate the effects of particle size and moisture content on the bulk flow properties of switchgrass and pine powders. The bulk flow properties such as sphericity, aspect ratio, bulk density, particle density, Hausner Ratio (HR) and Angle Of Repose (AOR) were determined at five different particle sizes (894, 632, 354, 158 and 84 μm) with three different moisture contents (~ 1%, 7.5% and 15%, wb). Switchgrass powders with less than 354 μm particle size had low flowability at both ~ 1% and 7.5% moisture contents (wet basis). At ~15% moisture contents, switchgrass powders exhibited poor flowability at all studied particle size ranges. Pine powders with less than 354 μm particle size had low flowability at all three moisture content levels. Lower aspect ratio and sphericity reduced the flowability of switchgrass powders compared to that of pine powders.

Key words: Bulk flow properties, bulk density particle size, moisture content, angle of repose.

Introduction

Lignocellulosic biomass are one of the major renewable sources of energy to generate solid and liquid biofuels, power and chemicals. They are often delivered to a biorefinery in the form of bales, chops and chips and further preprocessed into specific particle size ranges depending on the downstream conversion technologies. For densification of biomass into pellets, biomass should be fine ground into an average particle size of 1 mm, whereas biochemical fermentation and pyrolysis technologies require less than 1 mm particle sizes. Physical and bulk flow properties of fine biomass particles are important for not only improving the conversion efficiency, but also designing and selecting suitable material handling, feeding and storage devices (Mani et al., 2006; Phanphanich and Mani, 2009; Bernhart and Fasina, 2009; Kaliyan and Morey, 2009; Luo et al., 2010; Tumuluru et al., 2010). Limited studies have been reported in the literature on the bulk flow properties of lignocellulosic powders below one mm size range (Mani et al., 2004; Chevanan et al., 2009; Chen et al., 2012). The combined effect of particle size and moisture content on bulk flow properties of lignocellulosic powders below 1 mm was also unknown. Typically, physical properties of biomass powders measured are aerated bulk density, tap density, particle density, particle size and shape (Mani et al., 2004; Lam et al, 2008; Bernhart and Fasina, 2009, Littlefield et al., 2011, Phanphanich and Mani, 2011). They have a significant impact on the flowability of powders (Mani et al., 2004; Lam et al, 2008; Bernhart and Fasina, 2009, Littlefield et al., 2011). Therefore, understanding the importance of physical properties that affect the flowability of biomass powders will be helpful in designing hoppers, conveyors, silos and feeding devices. Flowability of powders depends on number of physical, chemical and

environmental factors, hence multiple test parameters are required to gain a comprehensive understanding of powder flowability (Bodhmage, 2006; Krantz et al., 2009). In general, powder flow parameters that are evaluated for determining the flowability are Hausner ratio, compressibility index, angle of repose and internal friction (Santomaso et al., 2003; Ganesan et al., 2008).

Particle size has a significant effect on the aerated bulk density, tap density, particle density and surface area of powder materials (Mani et al., 2004; Lam et al, 2008; Littlefield et al., 2011). In general, lower particle sizes tend to have higher surface area, which results in decreased flowability due to increased frictional forces (Fitzpatrick et al., 2004). Small size powder particles also have intrinsic adhesivity and cohesivity caused by van der waals and electrostatic forces (Feng and Hays, 2003), which reduces the flowability. Another important parameter is the moisture content of the powders, as it is known to cause powder cakes or agglomerates by formation of liquid bridges and poor flowability (Goldszal and Bousquet, 2001; Fitzpatrick et al., 2004). Typically, an increase in moisture content of biomass powders decreases its bulk and tapped densities and particle density (Bernhart and Fasina, 2009; Littlefield et al., 2011).

The main objectives of this paper were to determine the effects of particle size and moisture content on the bulk flow properties of pine and switchgrass powders and to develop mathematical relationship among particle size, aspect ratio, moisture content to predict the bulk flow properties of powders.

Materials and methods

Materials

Switchgrass (var. Alamo) was harvested from the University of Georgia, experimental station study plots and was square baled and stored in the Bioconversion Research and Education Center, UGA. Southern pine wood chips were obtained from a local saw mill in Macon, Georgia and were dried to 10% (wb) moisture content prior to storage.

Material preparation and moisture conditioning

The raw samples were comminuted using two type of grinders: (1) a hammer mill (10HMBD, glenmills, NJ, USA) with a 1.58 mm screen and (2) a knife mill (SM 2000, Retsch, Germany) with 0.25 mm screen to generate various particle size range. The ground biomass powders were size separated into the following size ranges 1000-800, 800-500, 500-250, 250-100, <100 μm using sieves (ISO 3310-1, Retsch, Germany) and a sieve shaker (AS 200, Retsch, Germany). Three moisture levels (0, 7.5 and 15%, wb) selected were prepared by pre-conditioning of samples after oven drying at 103 °C ± 2 °C for 24 hr. Dry biomass powders were conditioned in air-tight plastic bags with pre-calculated amount of distilled water to achieve desired moisture content. For each preconditioning, a slightly more water was added to compensate moisture losses due to evaporation and stored at 4°C for 72 hrs. The final moisture content of the conditioned samples was determined before and after measuring various flow properties. The average moisture content at which all the experiments were conducted was reported as the sample moisture content.

Moisture content

Powder samples were oven dried at 103 °C ± 2 °C for 24 hr as per the ASAE S358.2 standard method (ASABE, 2006). Weight loss between wet and dry samples was recorded by a weighing balance (Mettler Toledo AL204, Mettler-Toledo Inc., OH, USA) and used in calculating the sample moisture content and reported on a wet basis.

Average particle size and sphericity

Geometric mean particle size of a sample was calculated for each size range based on ANSI/ASAE S319.4 standard test method (ASABE, 2008). Sphericity was determined using a camsizer system (Horiba Instruments, Inc. CA, USA). Initially, powder sample of 2-3 g weight was dispersed at a uniform rate by the help of a vibrating tray. Two high-speed cameras captured projections of the dispersed powder particles. Later, particle shape analysis software (Retsch technology GmbH and Jenoptik L.O.S GmbH, Version 4.3.14) was used to measure the dimensions of the particle projections, which were used to calculate area (a) and perimeter (p) of the powder particles and finally the sphericity (Eq. 1).

$$\text{Sphericity} = \frac{4\pi a}{p^2} \qquad \text{- (1)}$$

Sphericity values are represented in the scale from 0 to 1, where sphericity value of 1 indicates that particles are perfect spheres.

Microscopic analysis

A leica steromicroscope MZ6 with Camera (spot idea model 27.2-3.1 MP) in bright field transmitted light microscopy mode with a magnification of 4X and 0.63 X were used to capture the images of powder particles. These images were used to measure

breadth (b) and length (l) of powder particles by ImageJ software (Rasband, 1997-2012). The ratio of breadth by length of these powder particles is given as the aspect ratio. Twenty particles were chosen for these measurements from different images by considering their area, as it could be understood that even though small size range particles are more in number in an image, the area occupied by them will be significantly less when compared to large size particles. Aspect ratio values are represented in the scale from 0 to 1 and lower aspect ratio indicates that particles are higher in length than width. Same camera and microscope were used to take images of both switchgrass and pine powders with different mean sizes for illustration purpose.

Aerated bulk density and Tap density

Aerated bulk density was measured with a modification to the procedure given by Bodhmage, (2006). The samples were poured through a funnel with an opening of 33 mm onto a 100 ml graduated cylinder. The excess powder in the cylinder was carefully removed and the remaining powder was leveled and volume occupied was noted. The funnel was placed just above the graduated cylinder. The weight of the powder sample inside the cylinder was measured using a weighing balance (GX-2000, A&D Engineering Inc, CA, USA) and used to calculate the aerated bulk density (ρ_a) of the powder material (Eq. 2). Later the same powder filled graduated cylinder was fitted on to a custom made tap density tester, which was built as per the ASTM B 527-06 Standard method (ASTM, 2006). This tester, which has a frequency of 270 drops/min, was operated for 4 min and change in powder volume was measured. The volume of the tapped powder was used to calculate the tap density (ρ_t) of the biomass powder (Eq. 3).

$$\rho_a = \frac{m_a}{v_a} \qquad \text{- (2)}$$

$$\rho_t = \frac{m_a}{v_t} \quad \text{- (3)}$$

Where, m_a is mass of powder sample inside the graduated cylinder, v_a is the volume of graduated cylinder and v_t is the volume occupied by the tapped powder.

Particle density

Particle density of the biomass powders was measured using a gas multi-pycnometer (MPV-D160-E, Quantachrome Corporation, FL, USA). Initially, helium gas was allowed to pass onto a reference cell and the pressure was noted as P_1. Later, the gas was pumped onto a sample cell with known amount of biomass sample and the change in pressure was noted as P_2. These pressure values were used to measure the true volume occupied by the biomass sample (Eq. 4).

$$v_p = v_c - v_R \left[\left(\frac{P_1}{P_2} \right) - 1 \right] \quad \text{- (4)}$$

Where, v_R denotes the reference cell volume and v_c denotes the volume of sample cell. v_p denotes the true volume occupied by the sample material. This true volume is used to calculate the true particle density (ρ_p) (Eq. 5).

$$\text{Particle density } (\rho_p) = \frac{M}{v_p} \quad \text{- (5)}$$

Where, M denotes the mass of the sample, v_p denotes the true volume of sample.

Hausner ratio and Angle of repose

Angle of repose is determined using an angle of repose tester (Mark 4, Powder Research Ltd, UK). This tester has a vibrating tray, funnel, chute and a measuring stand. A powder sample of 30 g was poured on the vibrating tray, which dispersed the sample

on to the measuring stand forming a semi cone of powder sample. Height (h_c) and average radius (r_c) of the semi cone were measured to calculate the angle of repose (Eq. 6).

$$\text{Repose angle}(\alpha) = \tan^{-1}\left(\frac{h_c}{r_c}\right) \qquad \text{-(6)}$$

In general, cohesive powders have higher angle of repose compared to free flowing powders.

Hausner ratio (HR) is another important powder flow property indicator widely used in relation to angle of repose to understand the powder flowability (Carr, 1965; Bodhmage, 2006; Geldart et al, 2006). Hausner ratio was given as the ratio of aerated bulk density and tap density. Tap density determination method significantly affects the hausner ratio (Santomaso et al., 2003). Therefore, in this study a wide range flowability indexes given by De Jong et al., (1999) was used to evaluate the powder flow property (Table 3.1).

Table 3.1. Powder flowability based on HR and angle of repose (AOR)

Flowability	HR	AOR
non flowing	>1.4	>60
cohesive	>1.4	>60
fairly free flowing	1.25-1.4	45-60
free flowing	1-1.25	30-45
excellent flowing	1-1.25	10-30
aerated	1-1.25	<10

Statistical analysis

The effects of particle size and moisture content (independent variables) on different physical and flow properties such as aerated bulk density, tap density, particle density and angle of repose (dependent variables), were determined by a two-way

analysis of variance (ANOVA) along with Tukeys multiple comparison test ($P<0.05$) using JMP Pro software (Version 9.0.2, SAS Institute Inc., Cary, NC, 2010) (JMP, 2010). A multiple regression analysis was performed to develop mathematical relationship between dependent and independent variables using JMP Pro software (Version 9.0.2, SAS Institute Inc., Cary, NC, 2010) (JMP, 2010).

Results and Discussion

Size and shape characteristics of powders

Switchgrass and pine powder size and shape properties are given in Table 3.2. Low aspect ratios of powders indicated the either stick or elongated particles (Bodhmage, 2006). It was further confirmed by microscopic images of switchgrass and pine powders (Figs 3.1 & 3.2). Switchgrass powders had lower aspect ratios compared to that of pine powders. Sphericity of switchgrass powders was less than that of pine powders at each particle size. Sphericity of particles less than 100 μm was difficult to measure using an image analyzer due to particle agglomeration and cohesion.

Table 3.2. Size and shape properties of switchgrass and pine powders

Size range (μm)	Geometric mean particle size d_{gw} (μm)	Switchrgass		Pine	
		aspect ratio (b/l)[a]	sphericity	aspect ratio (b/l)[a]	sphericity
800-1000	894	0.29 (0.23)	0.492 (0.021)	0.61 (0.26)	0.778 (0.009)
500-800	632	0.38 (0.16)	0.532 (0.008)	0.47 (0.23)	0.626 (0.012)
250-500	354	0.35 (0.13)	0.450 (0.047)	0.38 (0.18)	0.562(0.033)
100-250	158	0.36 (0.16)	0.533 (0.033)	0.37 (0.17)	-
<100	84	0.37 (0.17)	-	0.40 (0.25)	-

Note: [a] b is small dimension and l is large dimension of an individual powder particle
Standard deviations are given in brackets next to mean value

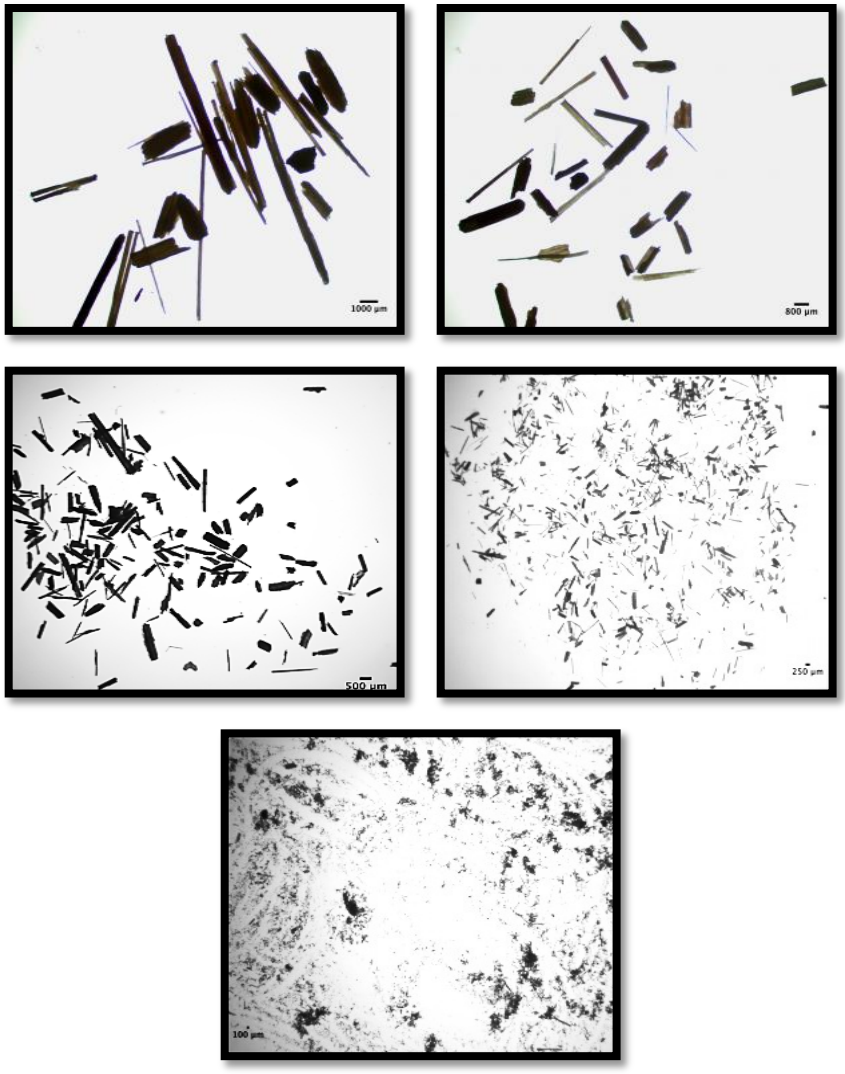
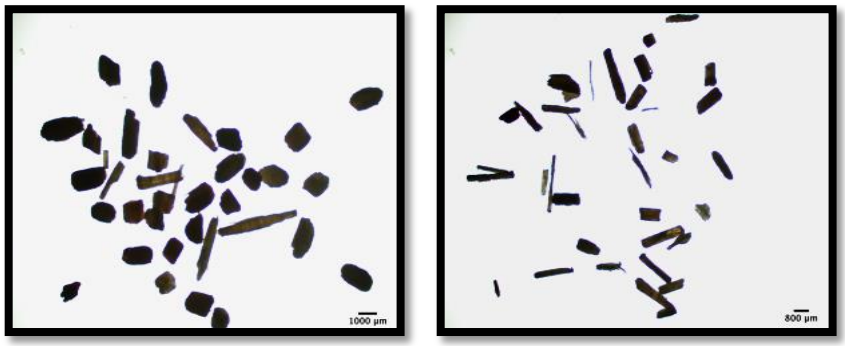


Figure 3.1. Microscopic images of switchgrass powders with mean particle sizes of 894, 632, 354, 158 and 84 µm



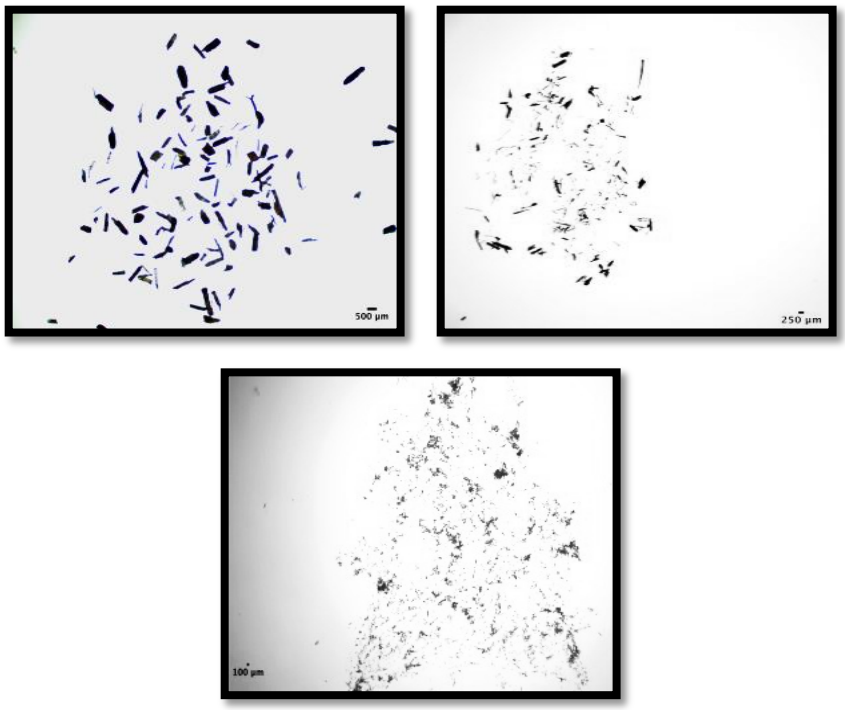


Figure 3.2. Microscopic images of pine powders with mean particle sizes of 894, 632, 354, 158 and 84 µm

Physical properties of switchgrass and pine powders

Physical properties of switchgrass and pine powders at all three moisture contents are given in Table 3.3 and 3.4 respectively. Particle size, moisture content and interactions had a significant effect on bulk density, tapped density and particle density ($P<0.05$) for switchgrass powder (Table B1 in Appendix B). Aerated bulk density and tap density were significantly affected by particle size, moisture content and interactions for pine powder. The interaction effect was not significant for particle density of pine powders. ($P<0.05$) (Table B2 in Appendix B).

A decrease in aerated bulk density, tap density and particle density of switchgrass and pine powders was observed with increase in moisture content, due to increase in powder volume compared to their mass and powder cohesion. A similar trend of decrease in aerated bulk density, tap density and particle density values with increase in moisture

content was observed in poultry litter, pecan shells, hemp seed and kenaf seed (Sacilik et al., 2003; Bernhart, and Fasina, 2009; Bakhtiari et al., 2011; Littlefield et al., 2011).

Aerated bulk density of switchgrass powder increased with decrease in powder size from 1000 μm to 250 μm. A similar trend was observed for pine powder between 1000 μm and 500 μm particle size, then aerated bulk density decreased until 100 μm. A similar trend was also observed for tapped density of both pine and switchgrass powders. Particle density values for switchgrass powder decreased with increase in particle size due to loss of intra-particle porosity in smaller size particles during comminution. Similar results were observed in pecan shells, wheat straw, barley straw, corn stover and switchgrass (Mani et al., 2004; Littlefield et al., 2011). Particle density values for pine powders at different sizes and moisture contents were in the range of 1311.48 to 1634.58 kg/m^3 and no trend was observed between mean particle size and moisture content.

Table 3.3. Physical properties of switchgrass powders

Mean moisture content (wb%)	Size range (µm)	Geometric mean particle size d_{gw} (µm)	Aerated bulk density (kg/m^3)	Tap Density (kg/m^3)	Particle density (kg/m^3)
2.27	800-1000	894	144.67^{i} (2.68)	169.54^{g} (3.50)	1522.32^{a,b,c} (60.76)
	500-800	632	152.97^{g,h,i} (2.93)	179.61^{f,g} (0.34)	1449.18^{b,c,d,e} (63.72)
	250-500	354	284.27^{b} (5.29)	328.62^{a,b} (3.82)	1574.22^{a,b,c}(50.01)
	100-250	158	263.13^{c} (8.96)	318.89^{b} (4.25)	1616.72^{a,b} (64.79)
	<100	84	189.37^{f} (3.30)	277.86^{d} (3.24)	1679.63^{a} (87.76)
7.69	800-1000	894	145.4^{h,i} (5.54)	177.74^{f,g} (4.96)	1240.86^{g,h} (64.57)
	500-800	632	161^{g} (2.72)	187.21^{f} (1.68)	1293.73^{e,f,g,h} (35.01)
	250-500	354	302.77^{a} (1.96)	338.29^{a} (2.24)	1435.15^{c,d,e,f} (16.26)
	100-250	158	277^{b,c} (4.56)	329.83^{a} (3.78)	1437.63^{c,d,e,f} (31.17)
	<100	84	212.33^{e} (3.78)	301.18^{c} (2.54)	1471.54^{b,c,d} (32.44)
14.4	800-1000	894	142.87^{i} (4.42)	174.23^{g} (2.17)	1136.51^{h} (29.12)
	500-800	632	158.9^{g,h} (3.63)	184.40^{f} (3.02)	1302.43^{d,e,f,g,h} (54.95)
	250-500	354	208.47^{e} (4.92)	251.79^{e} (5.58)	1274.61^{f,g,h} (62.18)
	100-250	158	227.03^{d} (4.44)	268.15^{d} (0.87)	1290.09^{e,f,g,h} (69.11)
	<100	84	184.27^{f} (6.45)	242.41^{e} (4.07)	1319.81^{d,e,f,g} (71.24)

Note: Mean values with same alphabet are not significantly different; standard deviation values are given brackets next to the mean values

Table 3.4. Physical properties of pine powders

Mean moisture content (wb%)	Size range (µm)	Geometric mean particle size d_{gw} (µm)	Aerated bulk density (kg/m^3)	Tap density (kg/m^3)	Particle density (kg/m^3)
1.13	800-1000	894	285.63^{b,c} (1.62)	313.92^{b,c,d} (3.58)	1529.51^{a,b,c} (30.91)
	500-800	632	308.43^{a} (7.94)	336.44^{a} (4.20)	1488.12^{b,c,d} (6.58)
	250-500	354	272.5^{c} (1.44)	323.77^{a,b,c} (1.54)	1560.01^{a,b} (42.71)
	100-250	158	214.63^{f} (4.04)	286.80^{f} (1.87)	1634.58^{a} (43.98)
	<100	84	178.67^{g,h} (3.18)	254.69^{g} (5.63)	1556.37^{a,b} (93.96)
7.6	800-1000	894	281.43^{b,c} (5.12)	302.09^{d,e} (6.41)	1488.92^{b,c,d} (56.65)
	500-800	632	292.33^{b} (10.33)	327.22^{a,b} (10.17)	1432.02^{b,c,d,e,f} (6.81)
	250-500	354	257.6^{d} (10.04)	311.59^{c,d} (3.99)	1430.39^{b,c,d,e,f} (5.21)
	100-250	158	217.23^{f} (1.62)	285.21^{f} (0.81)	1473.02^{b,c,d,e} (49.42)
	<100	84	180.13^{g,h} (3.67)	256.12^{g} (3.07)	1471.63^{b,c,d,e} (53.99)
15.83	800-1000	894	272.33^{c} (1.05)	296.02^{e,f} (2.37)	1410.18^{c,d,e,f} (40.39)
	500-800	632	285.73^{b,c} (0.06)	314.58^{b,c,d} (2.02)	1311.48^{f} (26.10)
	250-500	354	237.23^{e} (1.45)	283.07^{f} (5.47)	1368.99^{d,e,f} (16.79)
	100-250	158	187.83^{g} (0.81)	246.68^{g} (5.43)	1391.75^{d,e,f} (48.21)
	<100	84	167^{h} (2.31)	223.19^{h} (2.23)	1342.32^{e,f} (47.14)

Note: Mean values with same alphabet are not significantly different; standard deviation values are given brackets next to the mean values

Flow properties

Bulk flow properties of pine and switchgrass powders are given in Tables 3.5 and 3.6. Particle size, moisture content and interaction effect significantly affected the angle of repose (AOR) ($P<0.05$) for both switchgrass and pine powders (Table B1 and B2 in

Appendix B). AOR increased with increase moisture content for both switchgrass and pine powders due to moisture absorption and formation of liquid bridges between powder particles (Goldszal and Bousquet, 2001; Saad et al., 2011). In general, AOR values for both switchgrass and pine powders increased with decrease in particle size due to increase in inter-particle attraction forces of smaller particles (Feng and Hays, 2003; Jallo et al., 2010). One exception to this general trend were switchgrass powders at 14 (wb%) moisture content, where AOR values slightly increased with increase in particle size due to absorption of moisture and irregular shape characteristics.

Hausner Ratio (HR) is dependent on tap density measurement method and powder compaction (Santomaso et al., 2003). Biomass powders used in this study were highly compacted inside the cylinder by tapping them for 1080 times. Hence, no linear relationship between HR and AOR was observed. Similar results have been observed in barley, lactose and cellulose powders (Santomaso et al., 2003). Therefore, a wider range flowability index given by De Jong et al., (1999) was used in interpreting the flow property of biomass powders as given in Tables 3.5 and 3.6.

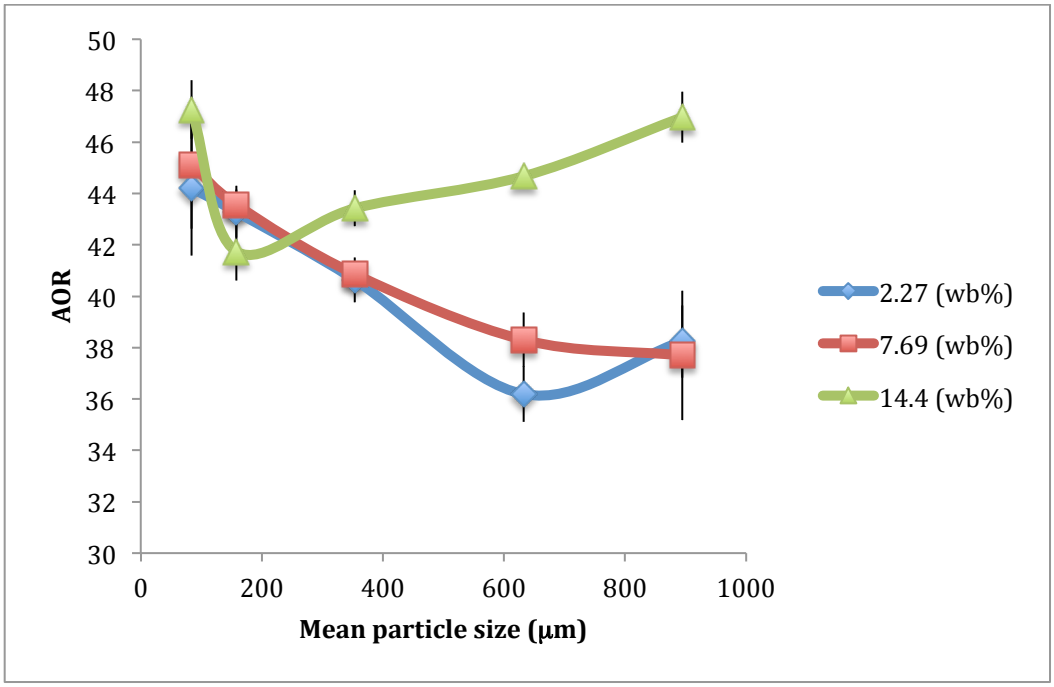


Figure 3.3. Angle of Repose (AOR) for switchgrass powders

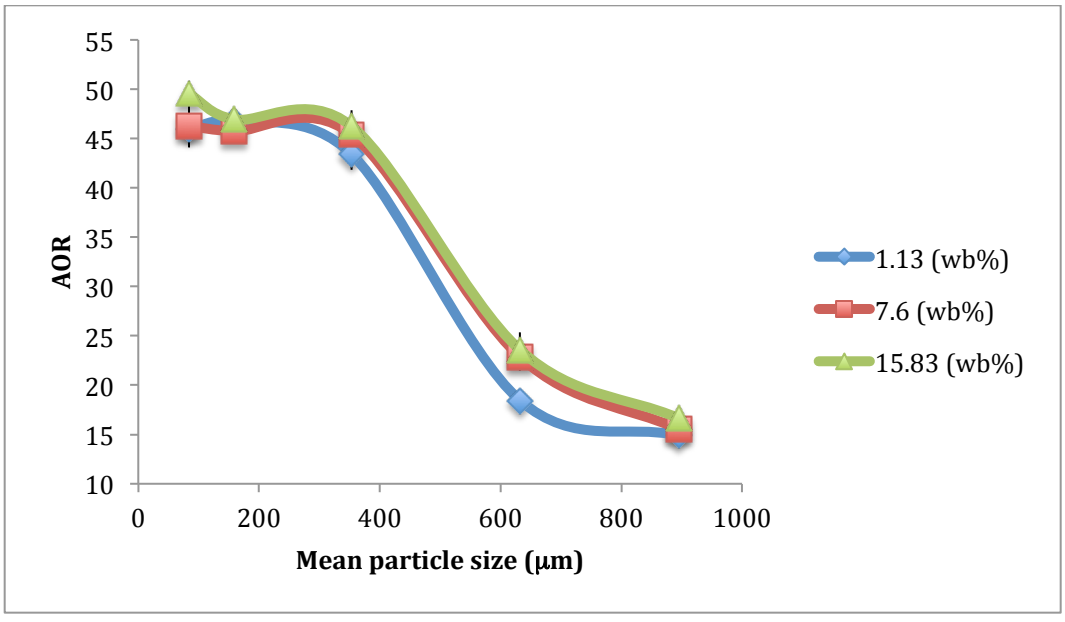


Figure 3.4. Angle of Repose (AOR) for pine powders

Table 3.5. Flow properties of switchgrass powders

Mean moisture content (wb%)	Size range (μm)	Geometric mean particle size d_{gw} (μm)	Angle of repose (degrees)	Hausner ratio	Flow property
2.27	800-1000	894	$38.24^{d,e}$ (1.41)	1.171 (0.011)	free flowing
	500-800	632	36.19^{e} (1.08)	1.174 (0.024)	free flowing
	250-500	354	$40.64^{c,d}$ (0.88)	1.156 (0.013)	free flowing
	100-250	158	$43.28^{a,b,c}$ (1.01)	1.212 (0.025)	free flowing
	<100	84	$44.21^{a,b,c}$ (2.63)	1.467 (0.041)	free flowing to fairly free flowing
7.69	800-1000	894	$37.69^{d,e}$ (2.52)	1.223 (0.049)	free flowing
	500-800	632	$38.30^{d,e}$ (1.06)	1.162 (0.018)	free flowing
	250-500	354	$40.86^{c,d}$ (0.48)	1.117 (0.006)	free flowing
	100-250	158	$43.56^{a,b,c}$ (0.59)	1.191 (0.032)	free flowing
	<100	84	$45.13^{a,b}$ (2.50)	1.418 (0.020)	fairly free flowing
14.4	800-1000	894	46.97^{a} (0.99)	1.220 (0.037)	fairly free flowing
	500-800	632	$44.67^{a,b,c}$ (0.10)	1.160 (0.007)	free flowing
	250-500	354	$43.42^{a,b,c}$ (0.70)	1.208 (0.047)	free flowing
	100-250	158	$41.74^{b,c,d}$ (1.13)	1.181 (0.022)	free flowing
	<100	84	47.27^{a} (1.14)	1.316 (0.025)	fairly free flowing

Note: Mean values with same alphabet are not significantly different; standard deviation values are given brackets next to the mean values.

Table 3.6. Flow properties of pine powders

Mean moisture content (wb%)	Size range (μm)	Geometric mean particle size d_{gw} (μm)	Angle of repose (degrees)	Hausner Ratio	Flow property
1.13	800-1000	894	14.91[d] (1.14)	1.099 (0.016)	excellent flowing
	500-800	632	18.44[d] (0.19)	1.091 (0.014)	excellent flowing
	250-500	354	43.41[b] (1.57)	1.188 (0.008)	free flowing
	100-250	158	46.74[a,b] (1.02)	1.336 (0.018)	fairly free flowing
	<100	84	45.97[a,b] (1.34)	1.425 (0.032)	fairly free flowing
7.6	800-1000	894	15.53[d] (0.51)	1.073 (0.003)	excellent flowing
	500-800	632	22.85[c] (1.36)	1.119 (0.009)	excellent flowing
	250-500	354	45.41[b] (0.18)	1.210 (0.040)	free flowing to fairly free flowing
	100-250	158	45.74[b] (0.62)	1.312 (0.009)	fairly free flowing
	<100	84	46.27[a,b] (2.19)	1.422 (0.025)	fairly free flowing
15.83	800-1000	894	16.65[d] (0.72)	1.086 (0.005)	excellent flowing
	500-800	632	23.56[c] (1.79)	1.100 (0.006)	excellent flowing
	250-500	354	46.25[a,b] (1.64)	1.193 (0.029)	free flowing to fairly free flowing
	100-250	158	46.95[a,b] (0.53)	1.313 (0.026)	fairly free flowing
	<100	84	49.54[a] (1.30)	1.336 (0.029)	fairly free flowing

Note: Mean values with same alphabet are not significantly different; standard deviation values are given brackets next to the mean values.

Powder bulk flow properties model

Multiple regression analysis models relating moisture content, aspect ratio and particle size were developed to predict the aerated bulk density, tap density, particle density and angle of repose of switchgrass and pine powders (Table 3.7). The goodness of fit was assessed based on R^2 (determination coefficient) and adjusted R^2 values and root mean square error. Aerated bulk density and tap density models for switchgrass powder had higher R^2 and adjusted R^2 values. Particle density and angle of repose models for switchgrass powders had lower R^2 and adjusted R^2 values. However, models predicting bulk flow properties of pine powder had higher R^2 and adjusted R^2 values. The plots of predicted versus actual experimental values for both switchgrass and pine powders aerated bulk densities are given in Figures 3.5 and 3.6 respectively. The plots of the actual experimental values versus the predicted values for all the bulk flow properties for both switchgrass and pine powders also confirmed the goodness of fit (Figure B1 and B2 in Appendix B).

Table 3.7. Regression models for bulk flow properties of switchgrass and pine powders

Biomass	Model	R^2	R_a^2	Root mean square error
Switchgrass	ρ_a= 4143.58-170.96m-4.59p+0.20mp-10655.09a+462.03ma+12.32pa -0.53mpa	0.92	0.91	16.33
	ρ_t = 3400.91-133.28m-3.59p +0.15mp-8360.31a+ 352.18ma+ 9.26pa-0.40mpa	0.94	0.93	16.50
	ρ_p= 1752.17-35.82m+0.64p-0.09mp +11.52a+12.26ma-2.97pa+0.33mpa	0.87	0.84	62.69
	AOR= 61.97-8.21m-0.01p+0.01mp-44.95a+22.45ma-0.02pa-0.02mpa	0.77	0.73	1.85
Pine	ρ_a= 350.99-13.31m+0.40p+0.004mp-485.71a+32.08ma-0.22pa-0.02mpa	0.99	0.98	6.05
	ρ_t = 465.92-13.05m+0.21p+0.01mp-550.11a+27.26ma-0.01pa-0.02mpa	0.96	0.95	6.94
	ρ_p= 2289.39-20.07m-0.99p+0.005mp-1743.87a+11.34ma+2.21pa+0.001mpa	0.81	0.78	44.19
	AOR= 166.63-2.71m-0.15p+0.004mp-300.91a+7.36ma+0.30pa-0.01mpa	0.96	0.95	3.02

Where, ρ_a= aerated bulk density; ρ_t = Tap density; ρ_p = Particle density; AOR = Angle of repose; m = Moisture content; p = Mean particle size; a = aspect ratio; R^2 = Determination coefficient; R_a^2 = Adjusted determination coefficient.

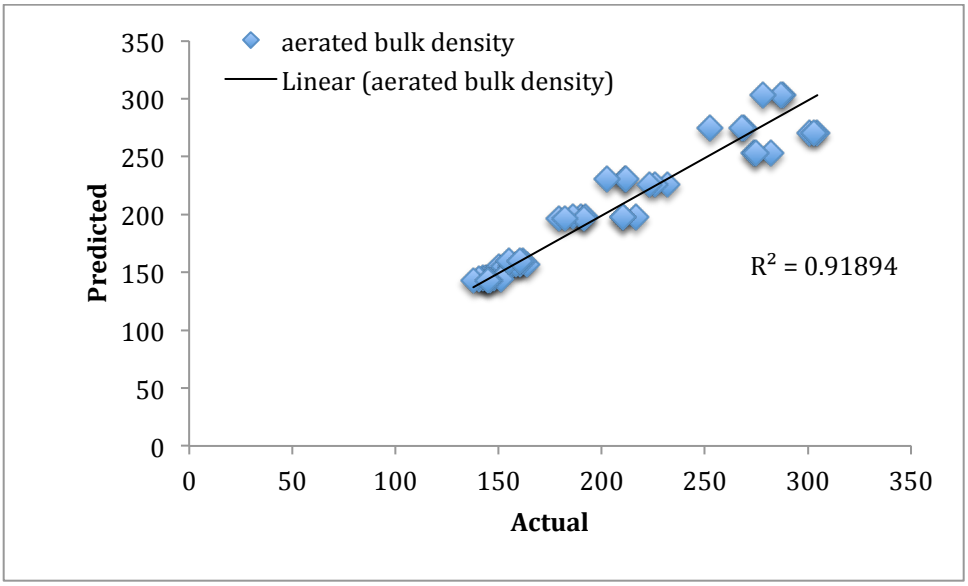


Figure 3.5. Switchgrass powders aerated bulk density predicted vs. actual data

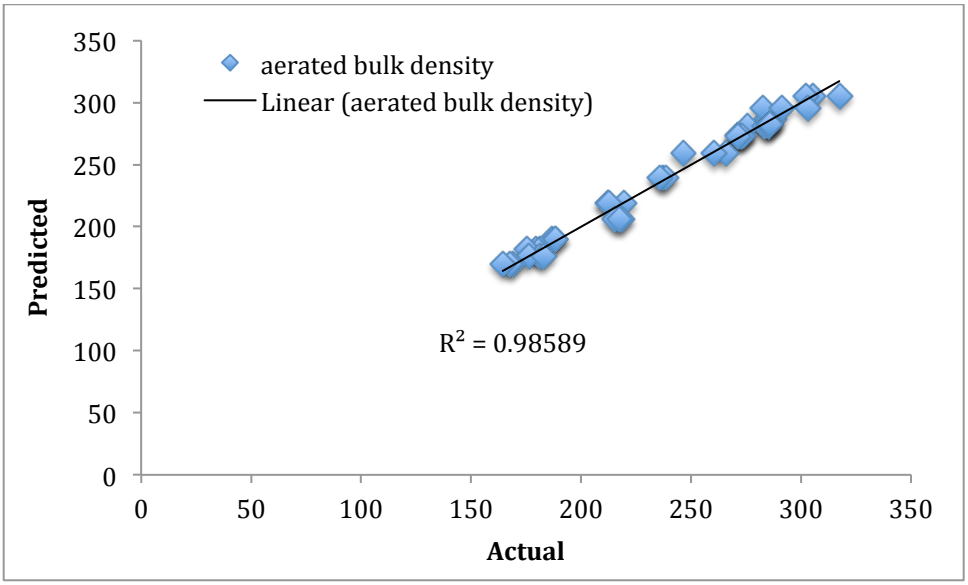


Figure 3.6. Pine powders aerated bulk density predicted vs. actual data

Conclusions

Physical and bulk flow properties of pine and switchgrass powders were significantly affected by particle size and moisture content. Flowability of switchgrass and pine powders decreased with decrease in particle size below 354 μm at all three moisture contents. Switchgrass powders had lower aspect ratio and sphericity compared to that of pine powder which decreased the flowability. Multiple regression models developed between particle size, aspect ratio and moisture content were effective in predicting the bulk flow properties of pine and switchgrass powders and they can be used for designing and selecting biomass handling and storage devices.

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CHAPTER 4

EFFECT OF BINDER CONCENTRATION AND POWDER PARTICLE SIZE ON GRANULATION OF PINE POWDERS

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Abstract

Wood chips and sawdusts are densified into pellets to increase bulk density and flowability and to reduce cost of handling, transport and storage. Domestic US market for wood pellets is limited due to high-energy input and cost of production and low price of alternative fuels. In this paper, granulation of pine powders was investigated using a pan granulator to evaluate the quality of granules at various liquid binder concentrations and particle sizes. Granulation is the process of agglomerating fine particles (typically, below 500 μm) into spherical granules by simultaneously wetting the particle surfaces with liquid binders and application of shear and rotational forces. A laboratory scale pan granulator was used to granulate pine powders at different mean particle sizes (397, 225, 135 μm) with an optimal corn starch binder concentration. Three levels of binder concentrations (2.5, 5, 7.5%) were tested to find an optimum binder concentration required to produce high density granules. The pine granule properties including granule size, size distribution, bulk density, angle of repose, hardness and chemical compositions were determined by standard protocols. Pine powder having a mean size of 135 μm produced with 5% corn starch binder concentration had the highest quality granules. Woody biomass can be successfully densified into high quality granules with limited binder concentration for efficient handling, transport and storage.

Key words: Pan granulation, pine powder, granule density, hardness, granule flowability.

Introduction

Lignocellulosic biomass after harvesting imposes major problems for efficient and economic transport, handling, storage and delivery to a large scale biorefinery due to low bulk density, high moisture content and poor flowability. Densification of biomass in the form of pellets and cubes has been previously studied to improve bulk density and to enhance efficient handling and storage (Mani et al. 2006a, b). Pelleting of woody biomass has been commercially used to produce wood pellets for export market in the Europe. Domestic markets for wood pellets in the US are relatively small but steadily growing for home heating applications. Industrial scale utilization of wood pellets in US that may create large market demand was limited due to high energy input and cost of pellet manufacturing and access to low cost fossil fuels (coal, natural gas). Production of densified biomass at low cost with less energy demand is critical for capturing US domestic and industrial utility markets.

Densification by a granulation technology can reduce process energy input and cost, while increasing biomass bulk density and flowability. Granulation is a process of agglomerating fine powders wetted with liquid binders into granules by mild application of shear and vibration forces. Granulation technology has been widely used in many industries like food, pharmaceutical, mining, chemical and fertilizer to develop formulations and to increase flowability and bulk density (Baykal and Doven, 2000; Veverka and Hinkle, 2001; Pietsch, 2002; Hoeung et al., 2011; Palzer, 2011). Granulation of lignocellulosic biomass particles will develop a controlled bulk density and uniform format feedstock to generate high quality biomass granules. Among various granulation equipment reviewed, granulation through tumbling was pre-screened to granulate

biomass particles. Each type of granulator produces various size ranges of granules. For example, a high shear granulator and fluidized bed granulator usually produce granules having a mean size range of 0.1 to 2 mm and rotating pan and drum granulators produce granules having a mean size range of 0.5 to 20 mm diameter (Ennis and Lister, 1996). Both rotating pan and drum granulators can be scalable to relatively large capacity (> 100 tonnes/h depending on the feedstock density) and can produce quality granules in the range of 5-15 mm. Pan granulator is commonly used for granulating lime, fly ash and food powders (Veverka and Hinkle, 2001; Harikrishnan and Ramamurthy, 2006; Palzer, 2011). In pan granulator, the pan angle, pan depth and pan speed are critical for forming initial granules (Pietsch, 2002; Ennis, 2010a).

A multitude of parameters including, biomass properties, type and concentration of binding agents and their surface adhesive properties in addition to granulator parameters affect the production of high quality granules from biomass powders (Pietsch, 2002; Mort, 2005; Ennis, 2010b). Liquid binder concentration is an important parameter that affects the granulation process (Parker et al., 1990; Tardos et al., 1997). In general, high concentration binders tend to have higher viscosity, which helps in better granule formation due to stronger liquid bridge formation, but may require higher pressure to spray whereas, low concentration binders may pose some challenges to form good quality granules as fewer liquid bridges are formed due to lower number of contact points between binder and particles (Tardos et al., 1997; Pietsch, 2002). There are many binding agents that were used for granulation of many industrial products such as starch, calcium lignosulfonate, sucrose, methyl cellulose etc. (Kadam, 1991; Pietsch, 2002; Parikh, 2005). The selection of an appropriate binding agent for biomass particle granulation is

critical for successful development of biomass granules and their end application. Among the biomass properties, particle size plays a critical role in forming granules with appropriate binders. For effective granulation, finer particles (less than 500 μm) are preferred with uniform size and shape parameters (Pietsch, 2002; Ennis, 2010a). Fine grinding of biomass is often energy intensive unit operation and may generate uneven particle shapes and particle size distributions (Mani et al., 2004; Kaliyan and Morey, 2009). Optimizing suitable particle size range or relatively larger particle size to generate good quality granules is critical for biomass to reduce grinding energy and cost of production. The quality of densified granules is determined based on granule size distribution, granule density, granule bulk density and hardness. The higher the granule density and hardness, the better are the granule quality (Pietsch, 2002; Ennis, 2010a).

The main objectives of this paper were to investigate the effect of binder concentration and particle size on generating high density pine granules using a pan granulator and to determine final granule size, single granule density, hardness, bulk density and flowability of pine granules.

Materials and Methods

Materials preparation

Southern pine chips at 50% (wet basis, wb) moisture content were obtained from a local saw mill in Macon, Georgia, USA and were dried to approximately 10% (wb) moisture content prior to storage. Wood chips were having the mean dimensions of 25.98 mm in length, 20.37 mm in width and 3.36 mm in thickness. Samples were ground using a hammer mill (10HMBD, Glenmills Inc, NJ, USA) with a sieve screen of 1.58 mm and further ground using a knife mill (SM 2000, Retsch, Germany) with a bottom sieve

screen of 0.25 mm. The knife mill ground samples having the mean particle size of 206 μm were directly used for determining optimum binder concentration to generate high density pine granules. The optimized binder concentration was used to investigate particle size effect on the pine granule quality. For particle size effect study, both hammer milled and knife milled samples were segregated into three average particle sizes (397, 225 and 135 μm) received from sieves 500 to 315 μm, 315 to 160 μm and <160 μm size ranges (ISO 3310-1, Retsch, Germany) using a sieve shaker (AS 200, Retsch, Germany).

Binder selection and preparation

Among several common binders used in granulation study, Pellet Bond™ modified corn starch (Matam Corp, IN, USA) was selected in this study based on two key factors: a) the binder should be derived from biomass source and low cost and b) the binder should pose no challenges during downstream conversion of granules into fuels, chemicals and power. Initial experiments were carried out to determine the solubility of a selected binder in water at room temperature 60°C (maximum binder temperature at which the binder can be sprayed in a pan granulator) and three binder solution concentrations (wt/wt) of 2.5%, 5%, 7.5% were prepared by mixing corn starch powder into distilled water at 60°C to determine the best binder concentration for pan granulation of pine particles.

Granulation experiment

A pan granulator (DP-14 agglomiser, Mars minerals, PA, USA) with 1/8 horsepower motor was used for granulation study (Figure 4.1a, 4.1b). Pine powder of 300g per run (based on the pan diameter) was used for the purpose of granulation. For every granulation run, pan granulator was set at 45° angle and the revolutions per minute

were set at 50. Pan depth was adjusted to 0.076 m (3 in) and two vane plow scrapers were used for uniform distribution of the material. The binder and dry feedstock powder were applied at 6° clock position. Binder was sprayed using a hand held sprayer.

Initially, binder solution was sprayed onto the surface of the pan granulator. Later, pine feedstock powder was added onto the pan granulator, resulting in formation of wet powder bed. Further addition of binder solution and pine feedstock powder to the wet powder bed had resulted in formation of granules. The wet granules formed were collected from the left side of the granulator or flown to the tray in front of the granulator due to gravity at the end of granulation run. Wet granules were oven dried at 103±2°C for 24 hours. Dry granules above 1 mm mean diameter were characterized by their physical, chemical and flow properties. The residence time and binder to pine feedstock powder content were measured for each granulator run. Granulation runs were done twice for each experiment.

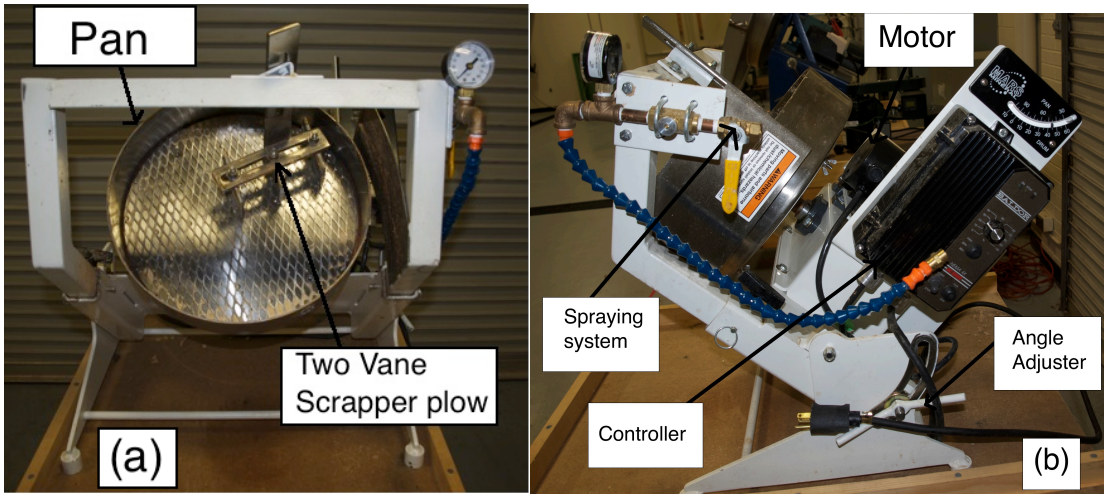

Figure 4.1. Pan granulator, (a) Front view, (b) Side view (Mars Mineral, Dp-14 agglomiser)

Binder properties

Corn starch binder density at 60°C was determined using a 2 ml pycnometer by completely filling the pycnometer with binder solution and calculating the ratio of weight of binder solution to the volume of the pycnometer. The apparent viscosity of the corn starch binder was determined using a rheometer (SR-5000, Rheometric Scientific Inc, NJ, USA) fitted with 40 mm parallel plate fixture by a shear rate test. The binder temperature was maintained at 60°C using a water bath (F25, Julabo USA Inc, PA, USA) attached to the rheometer. Each test measurement was repeated three times.

Wilhelmey plate method was used for determining binder surface tension. The platinum plate (19.62 mm × 10 mm × 0.11 mm) attached to force tensiometer (DCA-322, Cahn Instruments, WI, USA) was lowered into the corn starch binder solution that was maintained at a temperature between 50 to 60 °C. The interaction force (F) between platinum plate and corn starch binder solution was determined using a sensitive microbalance. Gravitational constant (g) was taken as 9.80665 m/sec^2 and used by the software given by manufacturer for calculating the corn starch binder surface tension (Eq. 1).

$$\gamma = \frac{F \times g}{PR \times \cos\theta} \qquad -(1)$$

Where, γ: surface tension, PR: wetted perimeter of platinum plate, θ (cos0=1): contact angle. Sample binder solution was stirred for each run to minimize the rate of sedimentation. Platinum plate was rinsed thoroughly with water and heated on a bunsen burner till red hot after each measurement run for effectively cleaning. Surface tension measurement was done thrice for each binder sample solution.

Powder and granule properties

Moisture content

The moisture content of pine powder and granule samples were determined according to the ASAE S358.2 standard method (ASABE, 2006). As per the standard method the sample was oven dried at 103±2°C for 24 hours and the weight difference between initial sample and final dried sample was measured using an analytical balance (GX-2000, A&D Engineering Inc, CA, USA) which is accurate to ±0.01 g. This weight difference was used for determining moisture content in wet basis. Moisture content measurement was replicated three times.

Mean size and size distribution

The geometric mean particle size and standard deviation of geometric mean particle size of pine powders was measured by ANSI/ASAE S319.4 standard test method (ASABE, 2008) using ISO standard sieves with a size range of 0.045 to 1.25 mm attached to vibratory sieve shaker (AS 200 control, Retsch Inc, PA, USA). Each run was repeated for three times.

Camsizer system (Horiba Instruments, Inc. CA, USA) was used for determining the mean size and size distribution of the pine granule samples. Typically, a sample material of 15-25 g was used for conducting the test according to ANSI/ASAE S319.4 standard test method (ASABE, 2008). Sieve size ranges from 1 to 30 mm were selected for this test. Initially, the sample material was dispersed through a vibrating tray and two high-speed cameras captured images of the dispersed sample projections. Later, the dimensions of sample projections were analyzed by the software given by the

manufacturer and were used to determine the size distribution, geometric mean diameter (d_{50} or d_{gw}), standard deviation of geometric mean diameter (S_{gw}) (Eq. 2)

$$s_{gw} = \frac{1}{2}(d_{84} - d_{16}) \qquad \text{-(2)}$$

Where d_{16}, d_{50} and d_{84} are the sample material diameter at 16%, 50% and 84% of cumulative distribution data respectively. This cumulative distribution was calculated based the shortest chord (x_{cmin}) of the sample material. Each run was replicated for three times.

Bulk density

The bulk density determination of pine powder and granule samples was performed in 5 replications according to modified ASTM E 873–82 standard method for densified particulate biomass fuels (ASTM, 2006). As per the modified process the pine powder and granule samples were poured freely by hand through a funnel placed just above the center of the container till it is over flown, excess sample was stricken off and leveled with the top edge of container using a ruler, then this container was dropped 5 times from a height of 0.05 m (2 in) onto a hard surface to allow settling. The empty volume created was refilled and leveled as per the above-mentioned process. The bulk density was then calculated by the ratio of sample mass to volume of the container.

Hardness

The hardness of the granules was measured according to ASAE S368.4 standard for compression test of food materials of convex shape (ASABE, 2000). As per the standard procedure granule was compressed between two parallel steel plates of Instron hardness tester (Instron 3344, MA, USA). The force in newtons (N) at which initial

fracture of granule occurs was considered as the hardness of the granule. The test was replicated for five times.

Single granule density

Single granule density of each biomass granule sample was measured by dividing the volume of each of the ten-biomass granules with their corresponding weights. The average of the values obtained was taken as single granule density.

Angle of repose

Pine powder and granule samples were poured through a funnel (30 mm diameter) clamped to a stand at 0.3 m (11.8 in) height from the base. After the formation of a symmetrical heap by the sample material, a digital camera was used to capture an image of sample heap. The still image was used to determine the angle between the surface of sample and horizontal plane, which is the angle of repose (Ileleji and Zhou, 2008; Chi-Ying Wong, 2000). Typically, angle of repose is represented in range of 25 to 66°, where 25° indicates excellent flowability and 66° indicates very low flowability (Carr, 1965; USP 29–NF 24, 2005; Geldart et al., 2006).

Chemical compositions

The adiabatic oxygen bomb calorimeter (IKA C2000, IKA Works Inc, NC, USA) was used for obtaining gross calorific value of the pine powder and granule samples according to the standard test method for coal and coke, ASTM D 5865–03 (ASTM, 2003). Gross calorific value measurements were conducted in triplicates.

Micro thermo-gravimetric analyzer (TGA-701, LECO Corporation, MI, USA) consisting of a muffle furnace was used for proximate analysis (moisture content, volatiles, fixed carbon and ash) of the pine powder and granule samples according to the

ASTM D 5142–04 standard method for coal and coke (ASTM, 2002a). Proximate analysis measurements were conducted in triplicates.

An Elemental analyzer (flash2000, Thermo scientific, MA, USA) was used for ultimate analysis (carbon, hydrogen, nitrogen and sulfur content) of pine powder and granule sample according to the ASTM D3176–89 standard test method for coal and coke (ASTM, 2002b). Ultimate analysis measurements were conducted in triplicates.

Statistical analysis

To determine the differences in granule qualities like hardness, bulk density and single granule density (dependent variables) made by different binder concentrations and powder particle sizes one way analysis of variance (ANOVA) and Tukeys multiple comparison test ($P<0.05$) was performed on JMP Pro software (Version 9.0.2, SAS Institute Inc., Cary, NC, 2010) (JMP, 2010).

Results and discussion

Physical and chemical properties of pine powder

The physical and flow properties of pine powders is given in Table 4.1. Bulk density of pine powders decreased with decrease in particle size. Angle of repose for pine powders indicates medium powder flowability (Carr, 1965; USP 29–NF 24, 2005; Santomaso et al., 2003; Geldart et al., 2006). Pine powders chemical composition is given in Table 4.2. Phanphanich and Mani (2011) reported similar chemical composition for pine chips. The low ash content and high calorific value indicate that pine powders are suitable for combustion applications.

Table 4.1. Physical and flow properties of pine powders

Sample preparation	Geometric mean diameter (d_{gw}) (µm)	Moisture content (wb%)[a]	Bulk density (kg/m^3)[b]	Angle of repose (degrees)[a]
Knife milled sample	205.97 (86.22)	5.14(0.09)	271.94(5.33)	42.16(2.57)
Particle segregation by sieves	396.86	5.12 (0.19)	331.43 (3.91)	38.85 (1.70)
	224.5	5.30 (0.25)	285.12 (1.74)	46.28 (0.59)
	134.54	5.36 (0.17)	208.57 (1.00)	48.17 (0.51)

Note: [a]Standard deviation is given in brackets for n = 3
[b]Standard deviation is given in brackets for n = 5

Table 4.2. Chemical composition of pine powders

Compositions	Average values
Moisture content (wb%)	5.56(0.02)
Volatiles (Dry %)	80.65(0.09)
Ash (Dry %)	0.24(0.02)
Fixed Carbon Dry(%)	18.05(0.09)
Nitrogen (Dry %)	0.71(0.21)
Carbon (Dry %)	47.98(0.39)
Hydrogen (Dry %)	6.13(0.07)
Sulfur (Dry %)	0
Gross calorific Value (MJ/kg)	18.82(0.09)

Note: Standard deviation is given in brackets for n = 3.

Binder properties

Pellet Bond™ modified corn starch binder solutions density, viscosity and surface tension at different concentrations is given in Table 4.3. Viscosity of binder solution is above 10 mPa implying that viscous forces play a critical role in granule consolidation (Knight and Seville, 1998). The viscosity of the binder solution was significantly increased with increase in concentration from 2.5 to 7.5 wt/wt%. Higher viscosity binder solution has lower spreading efficiency of binder droplets (Iveson et al, 2001). Lower surface tension of binder solution allows better rearrangement of particles due to reduced

capillary pressure, but if the surface tension of binder solution is too low then granules with have poor strength will be produced (Ouchiyama and Tanaka, 1980; Iveson et al, 2001). Variability in the corn starch binder solutions surface tension is due to sedimentation and dropping temperature of corn starch solution. Optimal viscosity and surface tension for binder solution is dependent on feedstock particle size distribution, shape and granulator operating conditions.

Table 4.3. Corn starch binder properties

Corn starch conc (wt/wt%)	Density (kg/m^3)	Apparent viscosity (Pa-S)	Shear rate (s^{-1})	Surface tension (mN/m)	Average Temperature °C[a]
2.5	1019.50 (4.69)	0.0113 (0.0071)	59.481 (0.027)	49.76 (2.13)	55.40 (5.19)
5	1039.20 (3.44)	0.0224 (0.0057)	59.459 (0.033)	56.80 (2.08)	53.95 (5.26)
7.5	1066.98 (5.90)	0.1766 (0.0072)	58.879 (0.257)	57.27 (3.06)	55.35 (6.11)

Note: Standard deviation is given in brackets for n = 3

[a]Average temperature at surface tension measurement

Granulation experimental runs

The residence time for most of the granulation runs using pine powders and corn starch binder was 25 min. The moisture content of the wet granules was in the range of 58.69 to 64.7 % (wet basis) (Table 4.4). Moisture in granules is useful in uniform dispersion of binder but it also increases the granule internal porosity when evaporated (Parker et al., 1990). Therefore, optimization of wet granule moisture content will improve the granule density.

Table 4.4. Pine granulation runs

Mean particle size (μm)	Binder concentration (wt/wt %)	Granulation time (min)	Wet granule moisture content (%wb)	Binder to powder % (wt/wt)
205.97 (86.22)	2.5	25	61.53 (0.36)	4.21
205.97 (86.22)	5	25	61.99 (1.02)	8.08
205.97 (86.22)	7.5	25	58.69 (1.90)	11.64
397	5	18 (2.83)	63.63 (0.18)	10.08
225	5	25	64.7 (0.10)	10.10
135	5	25	64.19 (0.99)	10.11

Note: Standard deviation is given in brackets next to the mean value of each property.

Effect of binder concentration

The pine granules produced from different binder concentrations are shown in below Figure 4.2.

a b c

Figure 4.2. Pine granules formed from different binder concentrations: a) 2.5% b) 5%, c) 7.5%

The size distribution of pine granules is given in Figure 4.3. The mean granule size of pine granules was in the range of 7.76 to 14.85 mm and all the granules were fairly round in shape. There was a significant effect of binder concentration on bulk density, single granule density and granule hardness of pine granules ($P<0.05$) (Table 4.5) (Table C1) (Appendix C). Pine granules made from 5% (wt/wt) binder concentration

were having highest bulk density, single granule density and granule hardness compared to granules made from other binder concentrations, which could be due to optimal binder wettability, adhesiveness, viscosity and surface tension that helped in better growth and consolidation of granules (Tardos et al., 1997; Iveson et al., 2001). Relatively, high viscous and concentration binder such as corn starch 7.5% (wt/wt) have poor spreading ability and binder droplet dispersion rate, which could lead to poor growth and consolidation stage of granule formation limiting the granule quality compared to 5% (wt/wt) binder concentration (Hapgood, 2000; Iveson et al., 2001; Mort, 2005). Relatively poor hardness and single granule density of granules made from 2.5% (wt/wt) binder concentration could be because of poor liquid bridge formation due to lower surface contact points between binder particles and granule powder particles (Tardos et al., 1997). Angle of repose values indicates excellent granule flowability (Carr, 1965; USP 29–NF 24, 2005; Geldart et al., 2006) (Table 4.5). The highest gross calorific value of pine granules was 19.80 MJ/kg. Ash content of these pine granules was low and it is in the range of 0.19 to 0.29 (dry%) (Table 4.6). Therefore, pine granules are suitable for heating applications.

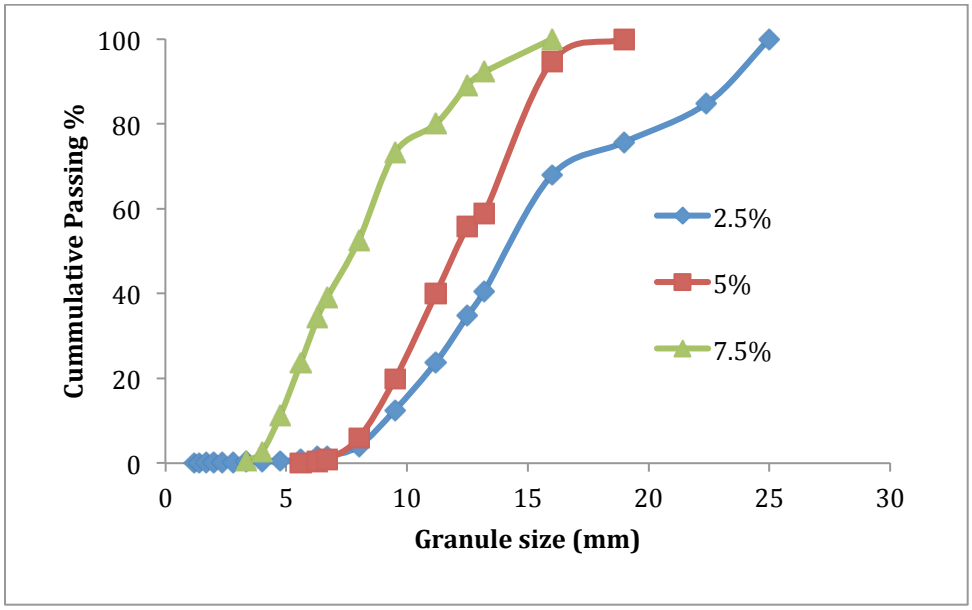

Figure 4.3. Size distribution of granules made with binder concentrations (wt/wt%) of 2.5%, 5%, 7.5%.

Table 4.5. Binder concentration effect on physical and flow properties of pine granules

Physical and flow properties	Corn starch concentration (wt/wt%)		
	2.5%	5%	7.5%
Geometric mean diameter d_{gw} (mm)	14.85 (5.31)	12.03 (2.96)	7.76 (3.35)
Hardness (N)	25.98^{b}(11.24)	71.45^{a}(27.37)	66.50^{a}(16.79)
Single granule density (kg/m3)	403.03^{b}(61.22)	488.99^{a}(59.11)	$469^{a,b}$ (91.49)
Bulk density (kg/m^3)	255.11^{c}(3.27)	278.63^{a}(3.72)	270.46^{b}(2.32)
Angle of repose (degrees)	23.67(3.51)	25.83(4.07)	23.33(3.79)

Note: Standard deviation is given in brackets next to the mean value of each property; Values with same alphabet are not significantly different

Table 4.6. Binder concentration effect on pine granules chemical properties

Chemical properties	Corn starch concentration (wt/wt%)		
	2.5%	5%	7.5%
Moisture (wb %)	2.9(0.03)	3.19(0.03)	0.03(0.02)
Volatiles (Dry %)	80.66(0.12)	80.90(0.21)	81.37(0.02)
Ash (Dry %)	0.19(0.07)	0.21(0.05)	0.29(0.05)
Fixed Carbon (Dry %)	18.59(0.10)	18.29(0.21)	18.32(0.03)
Nitrogen (Dry %)	3.26(3.57)	7.71(1.91)	4.59(3.28)
Carbon (Dry %)	76.56(1.22)	73.99(6.49)	77.03(7.53)
Hydrogen (Dry %)	5.70(0.01)	5.76(0.05)	7.24(2.66)
Sulfur (Dry %)	0	0	0
Gross calorific Value (MJ/kg)	19.01(0.13)	19.80(0.10)	19.40(0.20)

Note: Standard deviation is given in brackets for n = 3

Effect of particle size

Pine powders with different mean particle sizes were successfully granulated by using corn starch binder (Figure 4.4). The granule size distribution for these granules is given below (Figure 4.5).

a b c

Figure 4.4. Pine granules made with various mean powder particle sizes: a) 397 µm, b) 225 µm, c) 135 µm

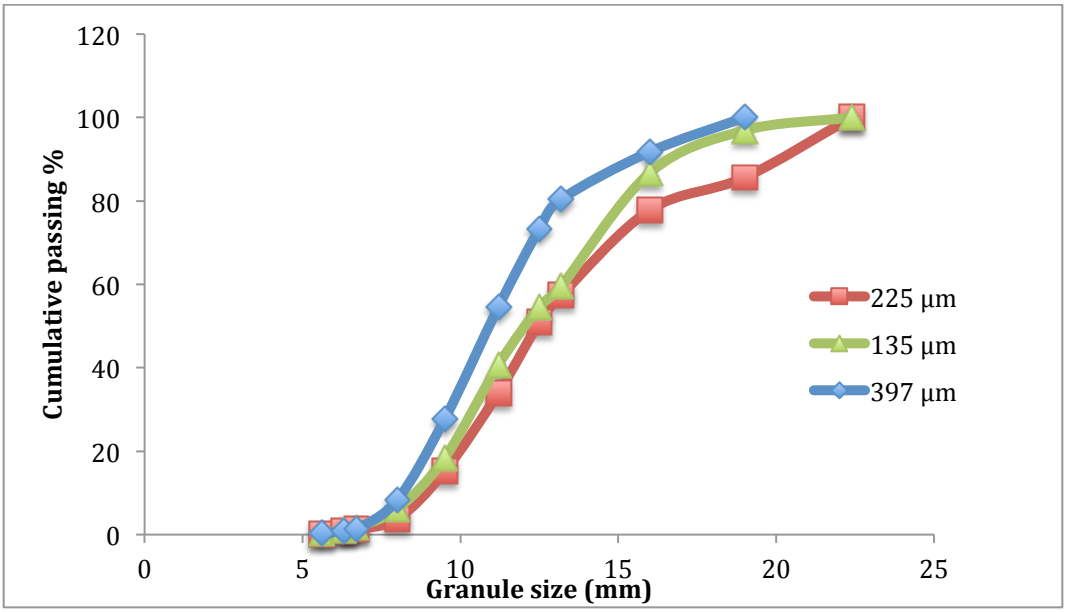

Figure 4.5. Size distribution of granules made with mean powder particle sizes of 397 µm, 225 µm, 135 µm

The physical, chemical and flow properties of pine granules made with different mean powder particle sizes were given in Table 4.7. There was a significant effect of powder particle size on bulk density, single granule density and granule hardness of pine granules ($P<0.05$) (Table C1 in Appendix C). The mean granule size of pine granules made from different powder sizes are from 10 to 12 mm. Hardness for granules made with mean powder size of 135 µm was 117.29 N, this indicates that powder particles at lower size ranges help in production of stronger granules. There is increase in single granule density and bulk density with a decrease in mean powder particle size. This could be due to uniform and tight mechanical interlocking of powder particles resulting in formation of granules with low intragranular porosity (Ennis and Lister, 1997; Schær, et al., 2004; Palzer, 2011; Ramachandran et al., 2012). Smaller powder particles tend to have higher surface area, which helps in better distribution of binder solution during pan rotation, this helps in increasing the granule strength (Iveson et al., 2001). Angle of repose values indicates that granules produced with different mean powder sizes are

having good flow properties (Carr, 1965; USP 29–NF 24, 2005; Geldart et al., 2006). The pine powder with mean particle size of 135 μm produced highest quality granules but it may be suitable to use 397 μm size powder for production of granules if the energy required for fine grinding and also the difficulty in handling the fine powder is considered.

Table 4.7. Particle size effect on physical, chemical and flow properties of pine granules

Physical, chemical and flow properties of granules	Geometric mean powder size (μm)		
	397	225	135
Geometric mean diameter d_{gw} (mm)	10.98 (2.44)	12.36 (4.31)	12.07 (2.94)
Hardness (N)	50.74[b] (17.24)	41.96[b] (4.61)	117.29[a] (20.44)
Single granule density (kg/m^3)	374.86[b] (59.60)	437.34[a] (58.32)	452.12[a] (45.64)
Bulk density (kg/m^3)	259.53[b] (4.03)	269.58[a] (4.09)	272.58[a] (2.39)
Angle of repose (degrees)	28.67 (4.04)	25.67 (3.79)	32 (3.61)
Gross calorific Value (MJ/kg)	18.28 (0.41)	17.33 (0.17)	18.04 (0.16)

Note: Standard deviation is given in brackets next to mean value of each property; Values with same alphabet are not significantly different.

Discussion

Typically, wood pellets have a bulk density and single pellet density of 600-800 kg/m^3 and 1030-1230 kg/m^3 respectively (Kaliyan and Morey, 2009; Yazdanpanah, 2009). In this study, pine granules produced nearly half the bulk density and single granule density of pellets. Further, improvement in granule densities may be possible using a custom binder with good adhesive and wetting properties. Granule hardness was not as high as wood pellets, but are above the minimum acceptable range for 4-5 mm

feed pellets (Major, 1984; Tabil, 1998; Kaliyan and Morey, 2009). Therefore, pine granules can be used for long distance transportation with minimum breakage. The ash content and calorific value of pine granules are similar to good quality wood pellets (Lehtikangas, 2001). Flowability of pine granules are superior than that of wood pellets, which helps in better conveyance and handling and bin storage of granules in the heat and power generation plants.

Conclusions

Pine powders can be densified into granules with a starch binder using a pan granulator. Binder concentration and particle size have a significant effect on granule density and hardness. Five percent (w/w) corn starch and a mean particle size of 135 μm produced high density and hardness granules for effective transport and storage. Despite low bulk density of granules compared to pellets, granules can be produced at low cost with optimized custom binders to promote domestic use of biomass for producing power, heat and biofuels.

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CHAPTER 5

EFFECT OF LIME PRETREATMENT ON GRANULATION OF SWITCHGRASS POWDERS

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Abstract

Switchgrass is a dedicated energy crop for generation of renewable energy. Densification of switchgrass will reduce the transport, storage and handling problems in the biorefinery logistic supply system by improving the physical and flow properties. Conventionally, switchgrass is densified using pelleting and briquetting technologies but these densification methods require high pressure, energy and cost for compaction. Hence, a novel low-pressure wet granulation method of densification is proposed in this study. Wet granulation process is agglomeration of powder particles into round granules by addition of liquid binders and application of shear/vibrating force. Switchgrass straw were ground into fine powders and pretreated with calcium oxide at 5%, 10%, 20% loading rates (0.05, 0.1, 0.2 g/g of biomass) at 121°C for 30 min and at room temperature (25°C) for 72 hours. Pretreated powders were granulated using cornstarch and sodium alginate combination binder in a pan granulator with standard operating conditions. Pretreated switchgrass powders structural changes were analyzed by scanning electron microscopy and autofluorescence microscopy. The physical, flow and chemical properties of pretreated switchgrass granules were determined and compared with untreated switchgrass granule samples. Granules made from switchgrass powder pretreated with 20% calcium oxide loading rate (0.2 g/g switchgrass powder) at both autoclave and room temperature conditions are having higher single granule density and lower binder to powder percentages compared to untreated switchgrass granule samples.

Key words: Switchgrass, pretreatment, wet granulation, binders.

Introduction

Switchgrass is a dedicated, perennial energy grass native to North America. Upon harvesting, switchgrass is often chopped and densified into bales, compressed into chops or pellets to improve bulk density and to reduce cost of handling, transport and storage (McLaughlin and Kszos, 2005; Kaliyan and Morey, 2009; Tumuluru et al., 2010). Switchgrass bales often require further processing (de-baling and grinding) at the biorefinery for further conversion into fuels and chemicals. Manufacturing of good quality switchgrass pellets are often challenging due to fibrous nature of a grass unlike wood pellets and demand significant energy input leading to high cost (Sokhansanj et al., 2009). Alternatively, densification by granulation is proposed to improve bulk density and flowability of switchgrass. Granulation is a process of producing spherical granules from fine powder particles by application of liquid binders and shear/vibrating forces (Pietsch, 2002). A multitude of parameters determines the quality of the final granules such as granule size, strength and bulk density (Pietsch, 2002; Mort, 2005). In this study a pan granulator was used for granulation. Therefore, the important machine parameters are the pan rotational speed, angle, depth and scrapper. The key material variables are switchgrass powder particle size, shape, binder concentration and percentage of binder to biomass powder.

Lignocellulosic biomass is often pretreated by several methods like ammonia fiber explosion, steam explosion, microwave, autoclave, alkaline and acidic pretreatments to reduce recalcitrant by delignification, dissolution of hemicellulose, decrystallization of cellulose to produce liquid transportation and solid fuels (Pedersen and Meyer, 2010; Brodeur et al, 2011; Donohoe et al, 2011; Rijal et al., 2012). Pretreatment methods also

facilitate increase in particle surface area and natural binding components surface relocation, which can improve binding of particles during densification (Kashaninejad and Tabil, 2011; Rijal et al, 2012). Several studies have shown effective lignocellulosic matrix disruption of switchgrass by alkaline pretreatment either by sodium hydroxide or calcium hydroxide at different time and temperature conditions (Xu et al., 2010; Donohoe et al, 2011; Samuel et al., 2011; Wang et al., 2012). Lime or calcium hydroxide pretreatment method was proposed for switchgrass granulation study as lime may pose limited constraints during downstream conversion of switchgrass granules unlike sodium salts causing corrosion and ash smelting (Siagi et al., 2007). Lime loading rate and operating temperatures are critical for relocation of natural binding components (lignin, protein and phenolic compounds etc.) or disrupting lignocellulose matrix during alkaline treatment. It is expected that surface relocation of these natural binding components during alkaline pretreatment will facilitate natural agglomeration with limited use of liquid binders.

The main objectives of this study were to determine the effect of lime pretreatment on the granulation of switchgrass powders and to evaluate the quality of switchgrass granules to optimize lime pretreatment conditions.

Material and preparation

Switchgrass (var. Alamo) was harvested and collected from the experimental plots of the University of Georgia and was square baled and stored at bioconversion research and education center (University of Georgia, Athens, GA, USA). Initially, these bales were ground by hammer mill (10HMBD, Glenmills Inc, NJ, USA) attached with a

bottom sieve screen of 1.58 mm and then with knife mill (SM 2000, Retsch GmbH, Germany) fitted with a bottom sieve screen of 0.25 mm.

Binder selection and preparation

Even though switchgrass could be granulated with several different binders a combination binder solution made of Pure-Dent® B700 Food Corn starch (GPC, IA, USA) and sodium alginate (WillPowder LLC, FL, USA) was used based on two key factors they are a) The reaction between alginate in sodium alginate and calcium ions in lime pretreated switchgrass will improve adhesiveness b) Starch will be useful in improving the strength of dry granules. Based on the viscosity of combination binder solution the concentration of sodium alginate was selected as 0.5 % (wt/wt) and Pure-Dent® B700 Food Corn starch concentration as 5% (wt/wt). Pre-calculated amounts of corn starch and sodium alginate powders were added into the distilled water and mixed uniformly by using a high shear mixer (GLH-115, PG700, Fischer scientific, PA, USA) to obtain the binder solution.

Lime pretreatment

Switchgrass powders were pretreated with 5%, 10% and 20% calcium oxide or quick lime loading rates (0.05, 0.1 and 0.2 g quick lime per g of switchgrass powder) at two operating conditions (autoclaving at 121°C and 15 psi for 0.5 h and at 72 h at room temperature 25°C). A known amount of quick lime was added to 350 g of switchgrass powder with a moisture content of ~6%, wet basis and mixed thoroughly with addition of ~307 g of distilled water to obtain a mixture with a ratio of 1:1 of switchgrass powder and total moisture. Hydration of calcium oxide will result in production of calcium hydroxide or lime by release of heat, which effectively disrupts lignocellulosic matrix.

The samples were pretreated in an autoclave (SR-24A, Consolidated sterilizer systems, MA, USA) at 121°C and 15 psi for 0.5 h. The samples were recovered from autoclave and cooled for 2 h to reach a stable temperature. Another set of lime added samples were preconditioned at room temperature (25°C) for 72 h in sealed plastic bags. Control samples (no lime addition) were also prepared under similar operating conditions prior to granulation study.

Granulation experiment

A pan granulator (DP-14 agglomiser, Mars minerals, PA, USA) with a diameter of 0.3556 m (14 in) and depth of 0.0762 m (3 in) fitted with two-vane plow scraper was used for granulation of both untreated and pretreated switchgrass powder material (Figure 5.1a, 1b). The pan speed was fixed at 50 RPM and pan angle at 45° for all the runs. Initially, corn starch and sodium alginate combination binder solution was sprayed using a hand held sprayer onto the granulator surface. Later, granulation powder material (untreated or pretreated switchgrass powder material) was added to the wet surface resulting in formation of a wet bed. 600 g of wet granulation powder was used for each run. Further, addition of binder and granulation powder material at 5 to 7° clock position to the rotating pan granulator helped in formation of granules. Granulation time and binder content sprayed were measured and used for calculation of binder to granulation powder percentages for each granulation run.

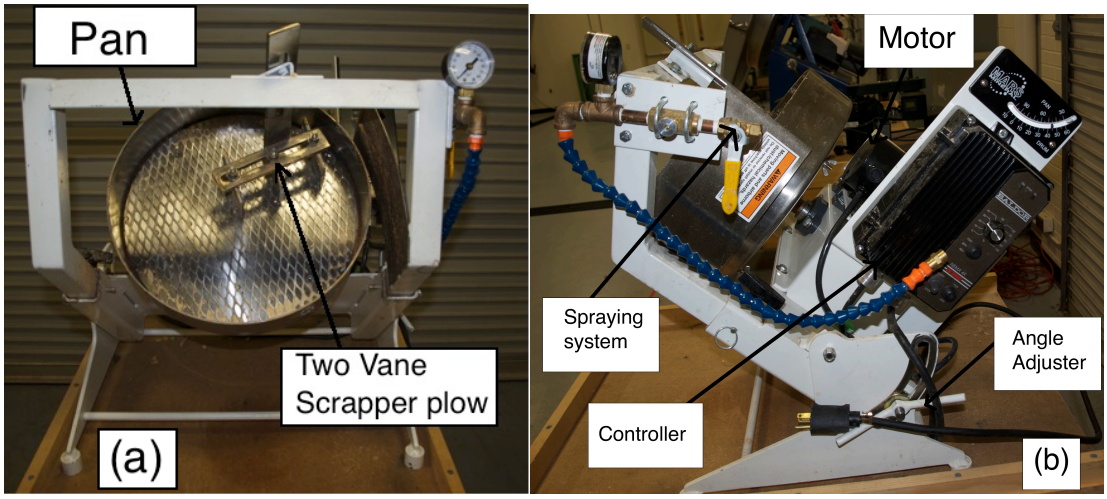


Figure 5.1. Pan granulator, (a) Front view, (b) Side view (Mars Mineral, Dp-14 agglomiser)

Moisture content

Moisture content of untreated and pretreated switchgrass powder and granule samples was determined according to ASAE S358.2 standard method (ASABE, 2006). Wet sample material was dried at 103°C ± 2 °C for 24 hours in a convection oven (FED 115-UL, Binder inc, NY, USA). The difference in weight between wet sample and dry sample was measured by an analytical balance (GX-2000, A&D Engineering Inc, CA, USA) and was used for calculating moisture content of the sample in wet basis. The test was replicated three times for each sample material.

Geometric mean size, size distribution and shape

Untreated switchgrass powder sample geometric mean particle size (d_{gw}) and standard deviation of geometric mean particle size (s_{gw}) were determined by following ANSI/ASAE S319.4 standard test method (ASABE, 2008) using a vibratory sieve shaker (AS 200 control, Retsch Inc, PA, USA) attached with ISO standard sieves in the size ranges of 0.045 to 1.25 mm. Sieve analysis test was repeated for three times.

The untreated and pretreated granule sample materials average size, size distribution and sphericity was determined using camsizer system (Horiba Instruments, Inc. CA, USA) based on ANSI/ASAE S319.4 standard test method (ASABE, 2008). Sieves in size range of 1 to 30 mm were selected for this test. Granule samples were dispersed from a vibrating tray onto a collection bin passing through measurement field of the two high-speed cameras, which determines the dimensions of granule samples. Furthermore, the data was analyzed by camsizer software (Retsch technology GmbH and Jenoptik L.O.S GmbH, Version 4.3.14, Germany) to determine cumulative passing percentage according ANSI/ASAE S319.4 standard test method (ASABE, 2008) and used in calculating geometric mean diameter (d_{gw} or d_{50}), standard deviation of geometric mean diameter (s_{gw}) (Eq.1) and sphericity (Eq. 2).

$$S_{gw} = \frac{1}{2}(d_{84} - d_{16}) \quad \text{-(1)}$$

$$SPHT = \frac{4\Pi a}{p^2} \quad \text{-(2)}$$

Where, d_{16}, d_{50} and d_{84} are the granule diameters at 16%, 50% and 84% in cumulative distribution. Cumulative distribution was calculated based on the smallest chord dimension (x_{cmin}) of the sample material. The roundness of the sample material was given by sphericity that was measured by the help of area (a) and perimeter (p) of the sample material projections. The roundness values were represented with a range from 0 to 1, where the value of 1 indicates perfect sphere. Test was repeated three times.

Bulk density

Untreated switchgrass powder sample material along with pretreated and untreated granule sample materials bulk density was determined according to modified

ASTM E 873–82 standard test method for densified particulate biomass fuels (ASTM, 2006). Both powder and granule samples were poured by hand through a funnel placed just above the container. After the sample material was overflown a ruler was used to level the top. The container was dropped onto a hard surface for 5 times from a height of 0.03 m (3 cm). The change in volume was refilled with sample material and the top is leveled with a ruler. Bulk density was calculated based on the ratio of sample mass present inside the container to the volume of container. Bulk density test was replicated three times for each sample material.

Chemical compositions

The gross calorific values of untreated and pretreated switchgrass powder and granule samples were determined according to ASTM D 5865–03 standard test method for coal and coke (ASTM, 2003). An adiabatic oxygen bomb calorimeter (IKA C2000, IKA Works Inc, NC, USA) was used for this test. Gross calorific test was repeated three times for each sample material.

Untreated and pretreated switchgrass powder and granule sample materials moisture content, volatiles, fixed carbon and ash content were determined using a thermo-gravimetric analyzer (TGA-701, LECO Corporation, MI, US) according to the ASTM D 5142–04 standard method for coal and coke (ASTM, 2002a). Nearly 1-2 g of sample materials was loaded into ceramic crucibles that were subsequently placed inside a muffle furnace. The furnace was heated and the loss of sample weight was used to determine the moisture content in wet basis and volatiles, fixed carbon and ash content in dry basis. Test was done three times for each material.

An elemental analyzer (flash2000, Thermo scientific, MA, USA) was used to determine the carbon, hydrogen, nitrogen and sulfur content of untreated and pretreated switchgrass powder and granule sample materials according to the ASTM D3176–89 standard test method for coal and coke (ASTM, 2002b). Ultimate analysis test was repeated three times for each material.

Binder properties

Corn starch and sodium alginate combination binder solution density was measured using a 2 ml glass pycnometer. Binder solution was completely filled into the pycnometer and weight of the solution was measured. Ratio of weight of the binder solution to the volume of pycnometer was used to calculate the density of the binder solution. The procedure was replicated three times.

Viscosity of cornstarch and sodium alginate combination binder was measured using a viscometer (lvdv-I, Brookfield Engineering Laboratories, MA, USA). Binder solution in a cylindrical beaker (1L) at 25 °C (room temperature) was used for measuring the viscosity. Initially, sample beaker is placed below the spindle (diameter of 25.12 mm) attached to viscometer. Height of the beaker is adjusted till the spindle was immersed into the sample solution. Speed of the spindle was set at 10 RPM for measuring the viscosity of the binder solution. The procedure was repeated three times.

Surface tension was determined using force tensiometer (DCA-322, Cahn Instruments, WI, USA) by wilhelmey plate technique. A platinum plate (19.62 mm × 10 mm × 0.11 mm) was lowered into the cornstarch and sodium alginate combination binder solution that was at 24.5 °C (room temperature). Interaction force between the platinum

plate and binder solution was measured using a sensitive microbalance and used by the software given by the manufacturer to calculate the surface tension (Eq. 3).

$$\gamma = \frac{F \times g}{PR \times \cos\theta} \qquad \text{-(3)}$$

Where, F is the interaction force between platinum plate and binder solution, g is gravitational constant (9.80665 m/sec^2), γ is surface tension of binder solution, PR is wetted perimeter of platinum plate, θ (cos0=1) is contact angle between platinum plate and sample solution. The procedure was replicated three times.

Auto-fluorescence microscopic analysis

Auto-fluorescence images of untreated and pretreated switcgrass powders were obtained using an upright Leica fluorescence microscope (Leica DM6000 B, Leica Microsystems Inc, IL, USA) with DAPI (excitation 360/40 nm and emission 460/50 nm) and GFP (excitation 485/20 nm and emission 530/25 nm) filters sets at a magnification of 5x.

Scanning electron microscopic analysis

Untreated and pretreated switchgrass powder samples images were obtained using scanning electron microscope (Zeiss 1450Ep, Carl Zeiss Microimaging Inc, NY, USA) at a magnification of 600x and beam accelerating voltage of 20 kV. The powder samples used for conducting SEM analysis were mounted on stubs and then sputter coated with gold.

Single granule density

Single granule density of granules obtained from untreated and pretreated switchgrass powder material was calculated as ratio of each granule mass to its volume. Fifteen granules for each material were used for determining the single granule density.

Granule hardness

Untreated and pretreated switchgrass granule hardness was determined according to ASAE S368.4 standard for compression test of food materials of convex shape (ASABE, 2000). Single granule was placed between two parallel steel plates of Instron hardness tester (Instron, MA, USA). The upper steel plate moving at a rate of 3 mm per min was used to compress the granule. The force in newtons (N) required for fracturing the granule was taken as the hardness of the granule. Ten granules were used for determining granule hardness for each material.

Angle of repose

Angle of repose for untreated switchgrass powder along with untreated and pretreated switchgrass granule samples were measured by pouring the sample material through a 0.033 m (3.3 cm) wide opening funnel attached to a stand located at a height of 0.108 m (10.8 cm) from the base. A picture of the pile formed by the sample material was taken and used for determining the angle of repose. Generally, lower the angle of repose higher is the flowability (Carr, 1965; USP 29–NF 24, 2005; Geldart et al., 2006; Ileleji and Zhou, 2008).

Statistical analysis

Granule bulk density, single granule density and hardness data for untreated and pretreated switchgrass granules were compared using one-way ANOVA and Duncan

multiple comparison test ($P<0.05$) on SAS software (Version 9.3) (SAS, 2011).

Results and Discussion

Switchgrass powder physical, flow and chemical properties

The geometric mean particle size of untreated switchgrass powder was 176 μm and standard deviation of geometric mean particle size was 82 μm, which is a suitable particle size for wet granulation (Ennis, 2010). The bulk density of untreated switchgrass powder was 286 kg/m^3 and is more than that of switchgrass bale (100-200 kg m^{-3}) but it is very difficult to handle, transport and store cohesive fine powders (Geldart et al., 1984; Shinners et al., 2006; Kaliyan and Morey, 2009). The angle of repose of untreated switchgrass powder was 44 degrees with medium flowability (Geldart et al., 2006). Low flowability materials are difficult to granulate because of poor mixing condition (Chen et al., 2009). The chemical properties of untreated and pretreated switchgrass powder are given in Table 5.1. Untreated switchgrass powder has higher calorific value compared to pretreated powder this is due to lower ash content. A similar relationship between ash content and calorific values were observed in microwave-chemical pretreated wheat straw and barley straw powders (Kashaninejad and Tabil, 2011). Several studies have reported that higher lignin content had increased calorific values of the biomass (Kashaninejad and Tabil, 2011; Phanphanich and Mani, 2011). Gross calorific values for switchgrass powder pretreated at room temperature was slightly higher than that of autoclave pretreated materials. Carbon and hydrogen content of untreated switchgrass powder was higher than that of pretreated switchgrass powder. An increase of lime content in pretreated material decreased the carbon and hydrogen contents causing lower gross calorific values (Demirbaş,2001).

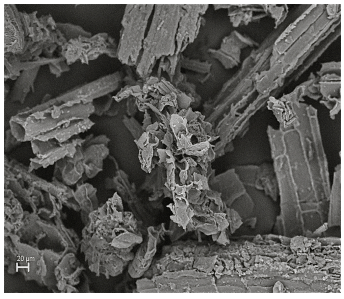
Table 5.1. Chemical composition of treated and untreated switchgrass powder

Quick lime loading rate[a]	Treatment condition[b]	Moisture (wb %)[c]	Volatiles (Dry %)[c]	Ash (Dry %)[c]	Fixed Carbon (Dry %)[c]	Nitrogen (Dry %)[c]	Carbon (Dry %)[c]	Hydrogen (Dry %)[c]	Gross calorific Value (MJ/kg)[c]
0	Untreated	3.63 (0.02)	80.50 (0.16)	1.40 (0.07)	17.44 (0.23)	1.25 (0.17)	45.41 (0.19)	5.40 (0.03)	18.62 (0.06)
0.05	25°C for 72 h	2.85 (0.04)	80.03 (0.23)	5.05 (0.17)	14.50 (0.17)	1.06 (0.23)	43.63 (0.94)	5.10 (0.22)	18.03 (0.03)
0.1		3.15 (0.01)	74.88 (0.09)	8.33 (0.21)	16.26 (0.26)	1.02 (0.30)	41.90 (0.74)	4.96 (0.20)	16.98 (0.19)
0.2		2.81 (0.06)	72.13 (0.55)	13.47 (0.52)	13.99 (0.21)	1.28 (0.03)	38.44 (0.64)	4.82 (0.10)	15.24 (0.20)
0.05	Autoclaving at 121°C for 0.5 h	6.40 (0.04)	80.37 (0.66)	4.65 (0.39)	14.03 (0.30)	1.11 (0.09)	43.79 (0.30)	5.07 (0.06)	17.09 (0.28)
0.1		4.28 (0.03)	75.21 (0.81)	8.29 (0.10)	15.80 (0.72)	0.93 (0.09)	43.78 (0.23)	5.00 (0.06)	16.75 (0.08)
0.2		6.46 (0.09)	73.87 (1.32)	14.59 (0.79)	10.80 (0.63)	0.80 (0.19)	40.34 (0.24)	4.80 (0.06)	14.85 (0.14)

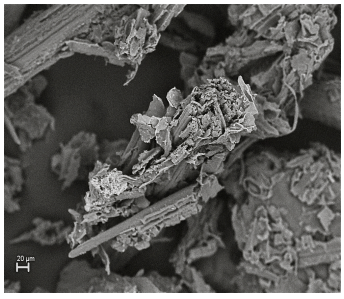
Note: [a] Ratio of calcium oxide with switchgrass on g per g basis
[b] Sulfur content was not detected
[c] Number enclosed in the parenthesis were standard deviations with n = 3.

SEM analysis of treated switchgrass

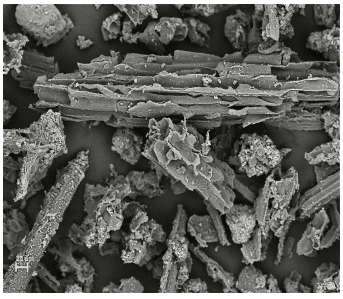
Scanning electron microscopic (SEM) analysis of untreated and pretreated powder shows a significant disruption of particle surface due to size reduction by grinding and lime pretreatment (Figure 5.2). Disruption in lignocellulosic matrix was more in pretreated powder compared with untreated switchgrass powder. During lime pretreatment, the surface porosity of particles increased compared to untreated sample (Singh et al., 2009; Donohoe et al., 2011). Complete disruption of cellular matrix due to lime pretreatment was not observed as reported by Donohoe et al., (2011) but relocation of cellular components to surface was observed due to low severity of pretreatment conditions.



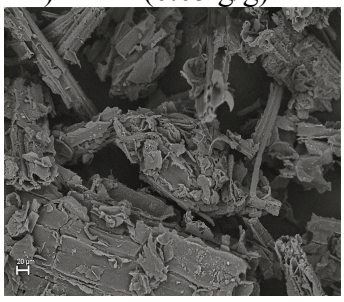
A) AT-L (0.05 g/g)



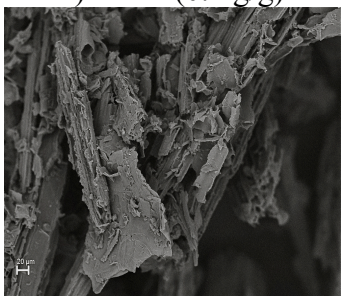
B) AT-L (0.1 g/g)



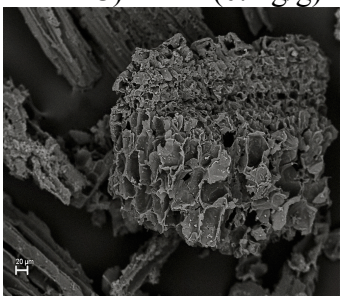
C) AT-L (0.2 g/g)



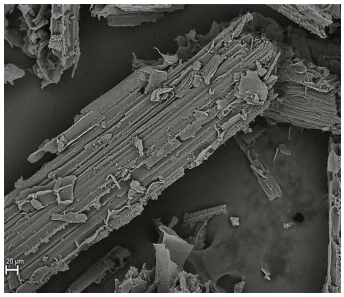
D) RT-L (0.05 g/g)



E) RT-L (0.1 g/g)



F) RT-L (0.2 g/g)



G) Untreated

Figure 5.2 SEM Images of pretreated and untreated switchgrass powder
Where, L is calcium oxide; AT is autoclave; RT is room temperature.

Auto-fluorescence analysis of switchgrass powder

Switchgrass has natural binding components like lignin (7.43 % dry matter), protein (1.59 % dry matter) and crude fat (1.87 % dry matter) (Mani et al., 2006; Kaliyan and Morey, 2010). Typically, plant cellular components like lignin, protein compounds, chlorophyll and phenolic compounds can emit fluorescence when excited with UV-blue light (350-480 nm) (Yeung, 1998; Kaliyan and Morey, 2010). Observation of lime treated sample with auto-fluorescence microscope exhibited blue fluorescence for lignin, green to blue for phenolic compounds and white for cutin and suberin (Rost, 1995; Yeung, 1998; Kaliyan and Morey, 2010).

Autofluorescent images of untreated and pretreated switchgrass powder are given in Figure 5.3. Untreated switchgrass powder had many particles with dominant blue fluorescence and few particles with dominant green fluorescence, indicating higher lignin content and lower protein content. Similar results were reported by Kaliyan and Morey, (2010) for size reduced switchgrass powders. Pretreated switchgrass powder particles had several particles with dominant green fluorescence, green to blue fluorescence indicating protein and phenolic compounds (except lignin) were relocalized to the particle surface. Particles with dominant blue fluorescence are fewer in pretreated material compared to untreated material due to disruption of lignin into smaller phenolic compounds

(Kashaninejad and Tabil, 2011). Kashaninejad and Tabil, (2011) reported that disruption of lignin into smaller components had improved the quality of pellets made from pretreated wheat and barley straw. In general, pretreated particles have brighter fluorescence than untreated particles. Therefore, relocalization of natural binding components like protein, lignin and phenolic compounds onto particle surface could improve the binding ability and densification of pretreated switchgrass material.

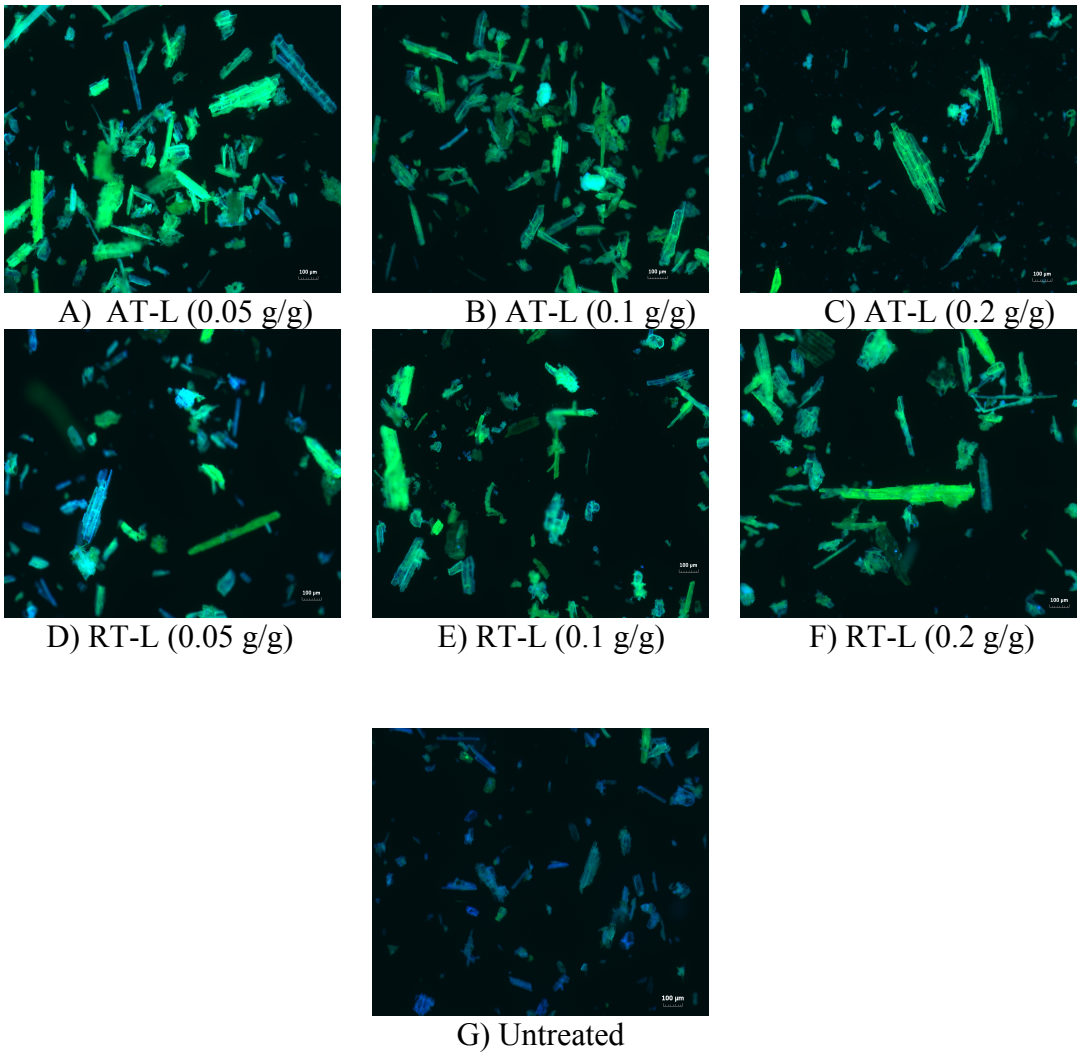


Figure 5.3. Auto-fluorescence images of pretreated and untreated switchgrass powder
Where, L is calcium oxide; AT is autoclave; RT is room temperature.

Cornstarch and sodium alginate binder properties

The density of binder was 1034 kg/m^3. Cornstarch and sodium alginate combination binder viscosity was 36 mPa.s at a shear rate of 10 RPM and was similar to the viscosity of poly ethylene glycol binder at 90°C (Johansen and Schæfer, 2001). Optimal binder viscosity typically above 10 mPA will be helpful in better consolidation of wet granules (Iveson et al., 2001). Surface tension of cornstarch and sodium alginate binder was 58 mN/m and similar to polyvinylpyrrolidone (1 % w/v) binder (Parker et al., 1990). Optimal binder surface tension will reduce the interparticle friction and improve the consolidation rate without weakening the granule strength (Iveson et al., 2001).

Granulation experimental runs

Granulation experimental conditions for untreated and pretreated switchgrass powder are given in Table 5.2. Typically, granulation time for each run was 60 min. Granules were formed during the first 30-40 min of granulation run and was further extended by reloading the granules for improved consolidation and binding of wet granules. Moisture content of wet granules and binder to powder percentages decreased with increase in lime content in pretreated powders. An increase in availability of natural binding components and also strong affinity between calcium-lignin and calcium-sodium alginate increased the binding ability of pretreated powder (Kim, 1990; Torre et al., 1992; Xu et al 2010; Yang et al., 2013). Percent binder to powder was slightly lower for autoclave pretreated materials compared to room temperature pretreated materials due to relocation of cellular components.

Table 5.2. Granulation run data

Quick lime loading rate[a]	Treatment condition	Moisture content of powder (wb%)[b]	Granulation time (min)[c]	Moisture content of granules (wb%)[b]	Binder to powder % (wt/wt)[c]
0	Untreated	44.21 (0.85)	60	68.87 (0.16)	9
0.05		48.16 (0.43)	60	68.49 (0.55)	8.39 (0.03)
0.1	25°C for 72 h	47.55 (0.44)	60	65.86 (0.92)	6.89 (0.05)
0.2		44.18 (0.21)	60	64.30 (0.680)	6.53 (0.02)
0.05		47.56 (0.52)	67.50 (10.61)	68.52 (0.22)	7.82 (0.09)
0.1	Autoclaving at 121°C for 0.5 h	47.15 (0.47)	60	63.25 (0.66)	4.96 (0.02)
0.2		43.57 (0.93)	60	60.03 (1.02)	4.04 (0.05)

Note: [a] Ratio of calcium oxide with switchgrass on g per g basis
[b]Number enclosed in the parenthesis were standard deviations with n = 3
[c]Number enclosed in the parenthesis were standard deviations with n = 2

Switchgrass granules physical, flow and chemical properties.

Wet granules were dried in oven at 103°C for 24 hours and were sieved through 1 mm sieve. Pretreated material produced relatively smaller size granules below 1 mm than untreated material due to over wetting of untreated powder caused by higher binder to powder percentage. Dry granules above 1 mm size were used for measuring physical and flow properties. Switchgrass granules images and size distribution are given in Figure 5.4 and 5.5 respectively. The granules formed from autoclave pretreated materials were darker in color compared to room temperature pretreated materials and control due to different relocation of cellular components.

A) AT-L (0.05) B) AT-L (0.1) C) AT-L (0.2)

D) RT-L (0.05) E) RT-L (0.1) F) RT-L (0.2)

G) Untreated

Figure 5.4. Switchgrass granules
Where, L is calcium oxide; AT is autoclave; RT is room temperature.

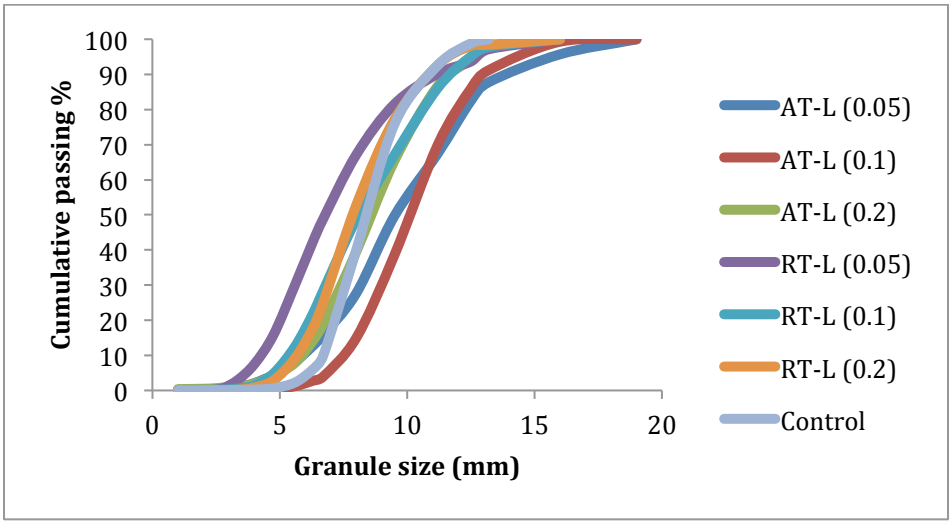


Figure 5.5. Switchgrass granules size distribution
Where, L is calcium oxide; AT is autoclave; RT is room temperature.

The physical and flow properties of switchgrass granules are given in Table 5.3. The geometric mean granule size of untreated and pretreated switchgrass granules is from 6 to 10 mm and is similar to diameter of biomass pellets (Saracoglu and Gunduz, 2010). Sphericity of switchgrass granules was significantly high and the granules can be effectively handled and stored. The effect of lime pretreatment on switchgrass granule properties such as single granule density, bulk density and hardness was analyzed by ANOVA ($P<0.05$) (Table D1 in Appendix D). Autoclave and room temperature pretreated powder with 20% calcium oxide loading rate (0.2g per g switchgrass) were able to produce granules with highest single granule density compared to untreated switchgrass granules. The bulk density of the untreated granules was slightly higher than pretreated granules due to uniform size and shape, which helps in better packaging of granules in the bulk density-measuring container. The angle of repose values for switchgrass granule show that granules have good flowability (Geldart et al., 2006). Hardness values of granules indicate that granules were not strong due to low binder percentage in dry granules (Pietsch, 2002; Simons et al., 2005).

The chemical properties of switchgrass are given in Table 5.4. Higher ash content and lower gross calorific values of granules formed from pretreated material were observed similar to the switchgrass powder material. Sulfur content was absent in all the granules similar to the switchgrass powder material. Pretreated granules can also be efficiently used for enzymatic hydrolysis step of biofuel production process, as the granules contain corn starch and lignocellulosic matrix disrupted powder material.

Table 5.3. Physical and flow properties of switchgrass granules

Quick lime loading rate[a]	Treatment condition	Geometric mean diameter d_{gw} (mm) [c]	Sphericity [c]	Hardness (N) [b, c]	Single granule density (kg/m^3) [b, c]	Bulk density (kg/m^3) [b, c]	Angle of repose (degrees) [c]
0	Untreated	8.37 (1.60)	0.89	5.18[a] (5.93)	352.40[b,c] (24.77)	194.61[a] (0.61)	24.67 (0.58)
0.05	25°C for 72 h	6.78 (2.55)	0.862 (0.01)	2.12[b] (0.08)	339.09[b,c,d] (21.10)	187.45[c] (1.35)	27.50 (0.50)
0.1		8.12 (2.48)	0.870 (0.01)	2.10[b] (0.01)	336.55[b,c,d] (29.62)	179.44[d] (0.64)	25.33 (0.58)
0.2		7.90 (1.96)	0.862	2.29[b] (0.39)	365.33[b] (48.21)	192.98[b] (0.42)	27.33 (0.58)
0.05	Autoclaving at 121°C for 0.5 h	9.53 (2.99)	0.849 (0.02)	2.16[b] (0.07)	312.57[d] (32.23)	175.19[e] (1.06)	26.33 (2.52)
0.1		10.00 (2.00)	0.859 (0.02)	2.18[b] (0.05)	326.99[c,d] (39.50)	180.51[d] (1.72)	27.17 (0.76)
0.2		8.62 (2.23)	0.865 (0.01)	2.07[b] (0.04)	396.40[a] (54.06)	188.81[c] (1.26)	27.5 (1.73)

Note: [a] Ratio of calcium oxide with switchgrass on g per g basis
[b]Values with same alphabet are not significantly different.
[c]Standard deviation is given in brackets next to average values of measured properties

Table 5.4. Chemical properties of switchgrass granules

Quick lime loading rate [a]	Treatment condition [b]	Moisture (wb %) [c]	Volatiles (Dry %) [c]	Ash (Dry %) [c]	Fixed Carbon (Dry %) [c]	Nitrogen (Dry %) [c]	Carbon (Dry %) [c]	Hydrogen (Dry %) [c]	Gross calorific Value (MJ/kg) [c]
0	Untreated	3.54 (0.05)	80.48 (0.53)	1.46 (0.13)	17.42 (0.42)	1.11 (0.07)	45.14 (0.89)	5.46 (0.09)	18.73 (0.11)
0.05	25°C for 72 h	2.40 (0.04)	81.05 (1.16)	4.08 (0.58)	14.52 (0.58)	1.00 (0.24)	42.76 (1.23)	5.27 (0.19)	17.58 (0.07)
0.1		3.46 (0.07)	76.61 (0.53)	7.29 (0.35)	15.54 (0.46)	1.13 (0.26)	41.53 (0.61)	5.18 (0.12)	16.77 (0.21)
0.2		2.42 (0.03)	73.42 (0.26)	11.99 (0.45)	14.24 (0.40)	0.92 (0.19)	39.91 (0.46)	5.04 (0.07)	15.57 (0.07)
0.05	Autoclaving at 121°C for 0.5 h	4.49 (0.04)	79.23 (0.65)	4.37 (0.21)	15.65 (0.44)	0.92 (0.12)	44.26 (1.62)	5.18 (0.02)	17.69 (0.39)
0.1		4.06 (0.01)	75.81 (0.31)	7.66 (0.06)	15.85 (0.30)	0.75 (0.18)	44.45 (0.72)	5.08 (0.09)	16.91 (0.12)
0.2		4.49 (0.05)	74.34 (1.70)	12.7 (0.68)	12.38 (0.99)	0.86 (0.10)	39.52 (1.04)	4.72 (0.07)	15.01 (0.09)

Note: [a] Ratio of calcium oxide with switchgrass on g per g basis
[b] Sulfur content was not detected
[c] Number enclosed in the parenthesis were standard deviations with n = 3.

Conclusions

Switchgrass powder was effectively agglomerated into densified granules by starch-sodium alginate binder in a pan granulator. Pretreatment of switchgrass powder improved the surface relocalization of natural binding components but increased the intra-particle porosity. Percent binder to powder were low for pretreated granules due to lignin disruption to smaller phenolic components, relocalization of natural binders, calcium binding affinity to alginate and lignin. Granules made from switchgrass powder pretreated with 20% calcium oxide loading rate (0.2 g per g of powder) at both autoclave and room temperature conditions had the higher single granule density and lower percent binder to powder compared to that of untreated switchgrass granules. High ash content and lower granule strength may further study to improve granule quality.

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CHAPTER 6

CONCLUSIONS

Wet granulation of switchgrass and pine powders were densified into high density granules for efficient and economic handling, transport and storage. Physical and flow properties of pine and switchgrass powders at different particle sizes and moisture contents indicated that smaller particle sizes at higher moisture content had the lowest flowability. Wet granulation of pine powders at three different particle sizes and three different corn starch binder concentrations were experimentally investigated using a laboratory pan granulator. High density pine granules were successfully produced with a mean particle size of 135 μm and 5% (wt/wt) optimal corn starch binder concentration. The chemical compositions and heating values of pine granules did not change significantly compared to raw pine powders. However, the bulk flow properties of granules were superior compared to raw powders. Untreated and pretreated switchgrass powder material was successfully granulated with sodium alginate-corn starch binder. Pretreated switchgrass granules from 20% quick lime loading rate both at autoclave and room temperature conditions produced the highest density granules. Percent binder to powder required for pretreated switchgrass powders were minimized due to affinity in binding of calcium-alginate and calcium-lignin and relocation of natural binding components (lignin) during lime pretreatment. Pretreated switchgrass granules can be efficiently used in direct enzymatic hydrolysis of pretreated granules into biofuels. In general, pine and switchgrass granules exhibited excellent flowability and met targeted

bulk density for economic long-distance transport as similar to biomass pellets. Overall, wet granulation of lignocellulosic biomass can produce high quality granules at low liquid binder use and can be integrated with a large scale biorefinery.

Further research is required to demonstrate wet granulation technology at pilot scale before commercialization. Understanding granulation mechanisms of biomass to liquid binders, development of costume binders for biomass and design modification of pan/drum granulators at pilot scale can enhance the commercial viability of this technology. Wet biomass granulation technology has a great potential to be commercially competitive to wood pellet industries by significantly reducing cost and energy required for densification.

APPENDICES

Appendix-A

Table A1. Controlling variables for increasing wetting uniformity (Ennis and Lister, 1996)

Modifications in material or operating variables for wetting uniformity	Formulation changes effecting wetting uniformity	Process changes effecting wetting uniformity
Increase in surface tension and adhesion tension. Lowering contact angle	Change in surfactant concentration and type. Coating powder with monolayer of steam	Altering impurity levels in particle formation and reducing surface roughness in milling
Increase or decrease pore size for altering fluid penetration rate.	Modify feed material particle size distribution	Modify formation or milling conditions for obtaining feed material
Improve solid mixing	Increase feed powder flowability	Increase impeller or drum rotational speed
Increase spray distribution	Reduce binder viscosity for enhancing atomization	More spray nozzels operating at low spray rate
Reduce binder viscosity	Decrease binder concentration or change binder	Modify the temperature of processes to alter binder viscosity

Table A2. Controlling variables for optimizing growth and consolidation (Ennis and Lister, 1996)

Modifications in material or operating variables for optimizing growth and consolidation	Formulation changes effecting growth and consolidation	Process changes effecting growth and consolidation
Growth rate (minimum deformability): Increase residence time, rate of nuclei formation and collision frequency	Enhance wetting properties and binder distribution.	Increase spray rate, impeller or drum rotational speed and batch time.
Growth rate (high deformability): Reduce binder viscosity, Improve agitation intensity and particle density	Reduce binder concentration or change binder. Decrease thickener's concentration	Modify the temperature of processes to alter binder viscosity. Increase impeller or drum rotational speed
Growth extent: Maximize binder viscosity. Reduce agitation intensity and particle density	Increase binder concentration and add thickeners	Reduce temperature, impeller or drum rotation speed
Consolidation rate: Increase particle size and agitation intensity and reduce binder viscosity	Size of particles and binder viscosity are varied.	Increase the bed weight and change the impeller or scrapper blade design

Table A3. Controlling variables for minimizing breakage (Ennis and Lister, 1996)

Modifications in material or operating variables for minimizing breakage	Formulation changes effecting breakage	Process changes effecting breakage
Reduce impact velocity to reduce fragmentation	Lowering formulation density	Reduce bed-agitation intensity and also modify impeller design
Reduce wear by increasing hardness. Minimize binder plasticity and agglomerate voidage	Improve binder concentration or change binder. Binder plasticity is dependent on binder type	Alter process temperature to enhance agglomerate consolidation, increase granulation-residence time and minimize drying time
Maximize fracture toughness and overall bond strength. Reduce agglomerate voidage	Improve binder concentration or change binder. Bond strength is dependent on the compatibility of binder with primary particles	Increase bed-agitation intensity and granulation-residence time
Reduce load to decrease wear	Lowering formulation density	Reducing compaction and bed-agitation intensity
Decrease contact displacement to minimize wear		Reducing contacting by lowering mixing and collision frequency
Reduce fragmentation by decreasing hardness Maximize binder plasticity and agglomerate voidage	Binder change. Altering surface hardness by coating	Reverse above mentioned effects to maximize agglomerate voidage

Table A4. Typical characteristics of wet granulation equipment (Ennis and Lister, 1996; Ennis, 2010).

Equipment	Granule size (mm)	Density	Flowability	Capacity	Comments	Applications
Fluidized granulators (fluidized beds, spouted beds and wurster coaters)	0.1 to 2	Low to moderate	Moderate to high	Up to 50ton/hr	Easily scalable, good for coating application and not preferred for cohesive powders	Fertilizers, inorganic slats, detergents, pharmaceuticals and agricultural chemicals
Mixer granulators (high shear granulators)	0.1 to 2	Low to high	Moderate	Up to 50ton/hr	Preferred for cohesive materials	Chemicals, detergents, clays, carbon black, pharmaceuticals, ceramics
Tumbling granulators (drum and pan granulators)	0.5 to 20	Moderate	Moderate to high	0.5 to 800 ton/hr	Spherical granules	Fertilizers, iron ore non-ferrous ore, agricultural chemicals

Table A5. Industrial application of binders (Tabil, 1996; Parikh, 2005; Kadam, 1991; Pietsch, 2002).

Food and Pharmaceutical	Mining and cement	Chemical and fertilizer	Biomass Densification
Sucrose	Potassium silicate	Hydrated lime	Collagen protein
Acacia	Gypsum	Bentonite	Lignosulfonate
Methyl cellulose	Magnesia	Starch paste	Starch binders
Ethyl cellulose	Sodium borate	Fuller's earth	Bentonite
Hydroxypropylmethyl cellulose	Attapulgite	Sodium silicate	Crude glycerin
Hydroxypropyl cellulose	Alum	Potassium silicate	Paper mill waste
Polyvinyl pyrrolidone	Dolomite		
Polyethylene glycol	Metal fibers		
Tragacanth			
Gelatin			
Starch paste			
Pregelatinized starch			
Sodium alginate			
Collagen protein			

Table A6. Applications of granulation process

Feed material	Feed material size	Equipment	Operating conditions	Binder	Final granule size distribution	Reference
Durum wheat semolina powder	0.35 mm	Low shear mixer Labo 25 (Mahot, France) consisting of a bowl of 10.5 liters	Binder was sprayed using a standard nozzle attached to the binder tank. Bowl mixing speed was 9.2 rpm	Water	0.3 to 8mm	Saad et al., 2011.
Calcium carbonate powder	0.06mm	Cyclomix high shear mixer granulator (Hosokawa Micron B.V, Netherlands) with a capacity of 5 liters attached with an impeller made of four sets of blades and a pair of knifes.	Mixer was operated at speeds of 230, 300 and 350 rpm, binder was added gradually.	65 wt.% aqueous solution of polyethylene glycol (PEG 4000)	0.5 to 0.6 mm.	Rahmanian, et al., 2009.
Corn starch powder	0.015mm	The rotating fluidized bed consisting of a plenum chamber attached with two binder spray nozzles and a pulse air-jet nozzle	Air spray pressure and temperature of 0.3 Mpa and 333 K. Air flow rate of 0.596 m/s, binder feed rate of 10 g/min and rotational speed of 5.57 rps	10% hydroxypropylecellulose	0.05mm	Watano et al., 2003.
Fine dolomite powder	Mean particle size distribution from 0.0106 to 0.0349 mm	Rotating drum granulator with a diameter of 0.5m and length of o.4m	Drum rotational speed of 20 rpm, binder sprayed by the help of two pneumatic nozzles	Distilled water	<12mm	Gluba, 2005.
Fly ash	0.024mm	Rotating pan granulator with a (Intek, Istanbul) diameter of 0.4m, scrapping blades were located at interval of 0.06m.	Pan angle 43° and pan rotational speed 45rpm	Water	4.75-19 mm	Baykal and Doven, 2000

Appendix-B

Table B1. Two way ANOVA for switchgrass powder physical and flow properties

	DF	Sum of Squares				Pr > F			
Parameter		**Aerated bulk density (kg/m^3)**	**Tap Density (kg/m^3)**	**Particle density (kg/m^3)**	**Angle of repose (degrees)**	**Aerated bulk density (kg/m^3)**	**Tap Density (kg/m^3)**	**Particle density (kg/m^3)**	**Angle of repose (degrees)**
Moisture content	2	9632.98	14523.69	708473.43	163.12	<.0001	<.0001	<.0001	<.0001
Particle size	4	109843.44	153050.11	215049.13	175.91	<.0001	<.0001	<.0001	<.0001
Interaction	8	10795.12	10896.38	67450.93	151.36	<.0001	<.0001	0.0243	<.0001

Table B2. Two way ANOVA for pine powder physical and flow properties

	DF	Sum of Squares				Pr > F			
Parameter		**Aerated bulk density (kg/m^3)**	**Tap Density (kg/m^3)**	**Particle density (kg/m^3)**	**Angle of repose (degrees)**	**Aerated bulk density (kg/m^3)**	**Tap Density (kg/m^3)**	**Particle density (kg/m^3)**	**Angle of repose (degrees)**
Moisture content	2	3837.73	7664.98	267265.40	54.63	<.0001	<.0001	<.0001	<.0001
Particle size	4	91692.73	36927.93	39122.00	8407.79	<.0001	<.0001	0.0033	<.0001
Interaction	8	1038.33	1347.46	22149.16	35.12	0.0003	<.0001	0.231	0.0148

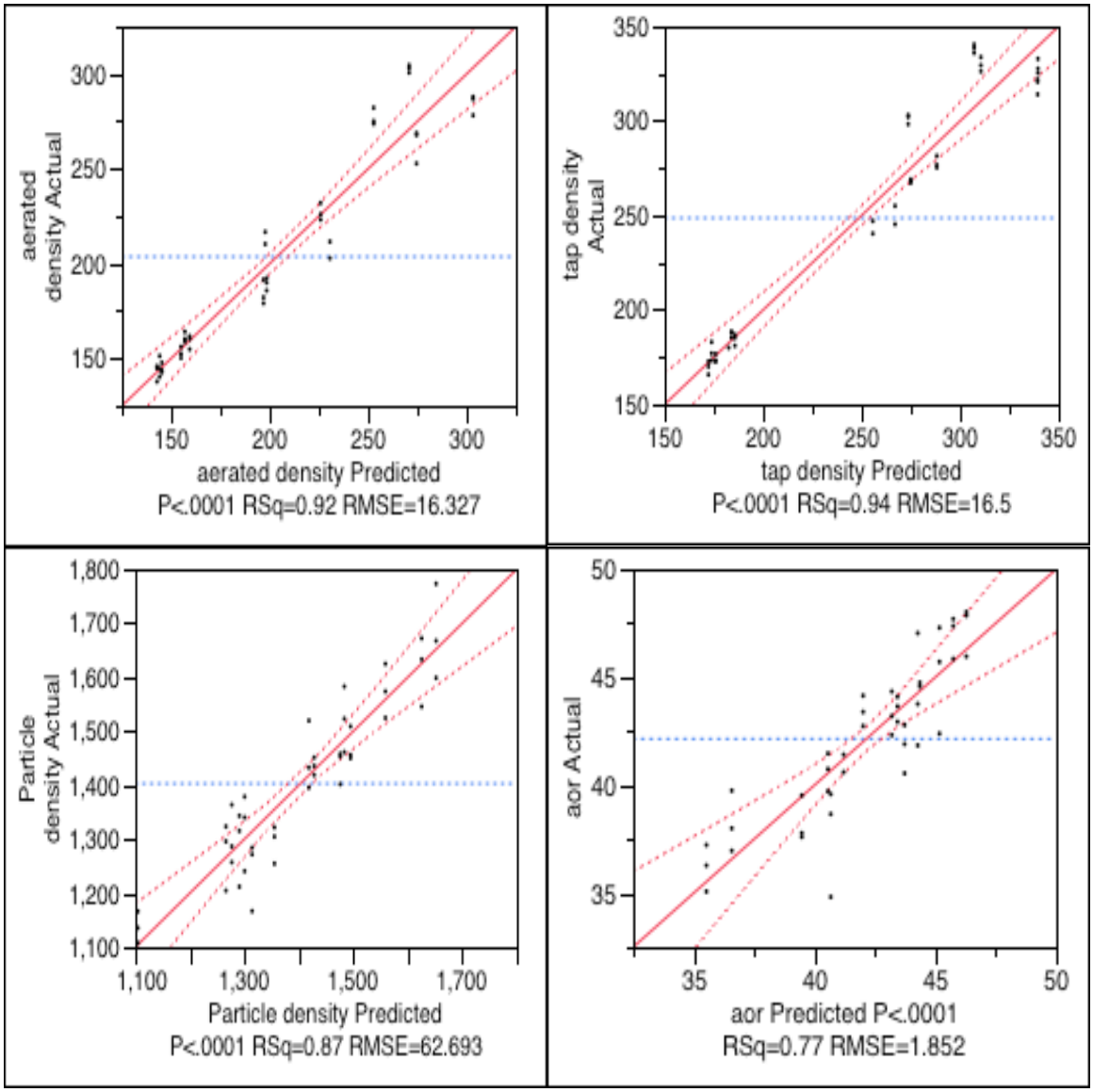

Figure B1. Actual vs. predicted plots for bulk flow properties of switchgrass powders

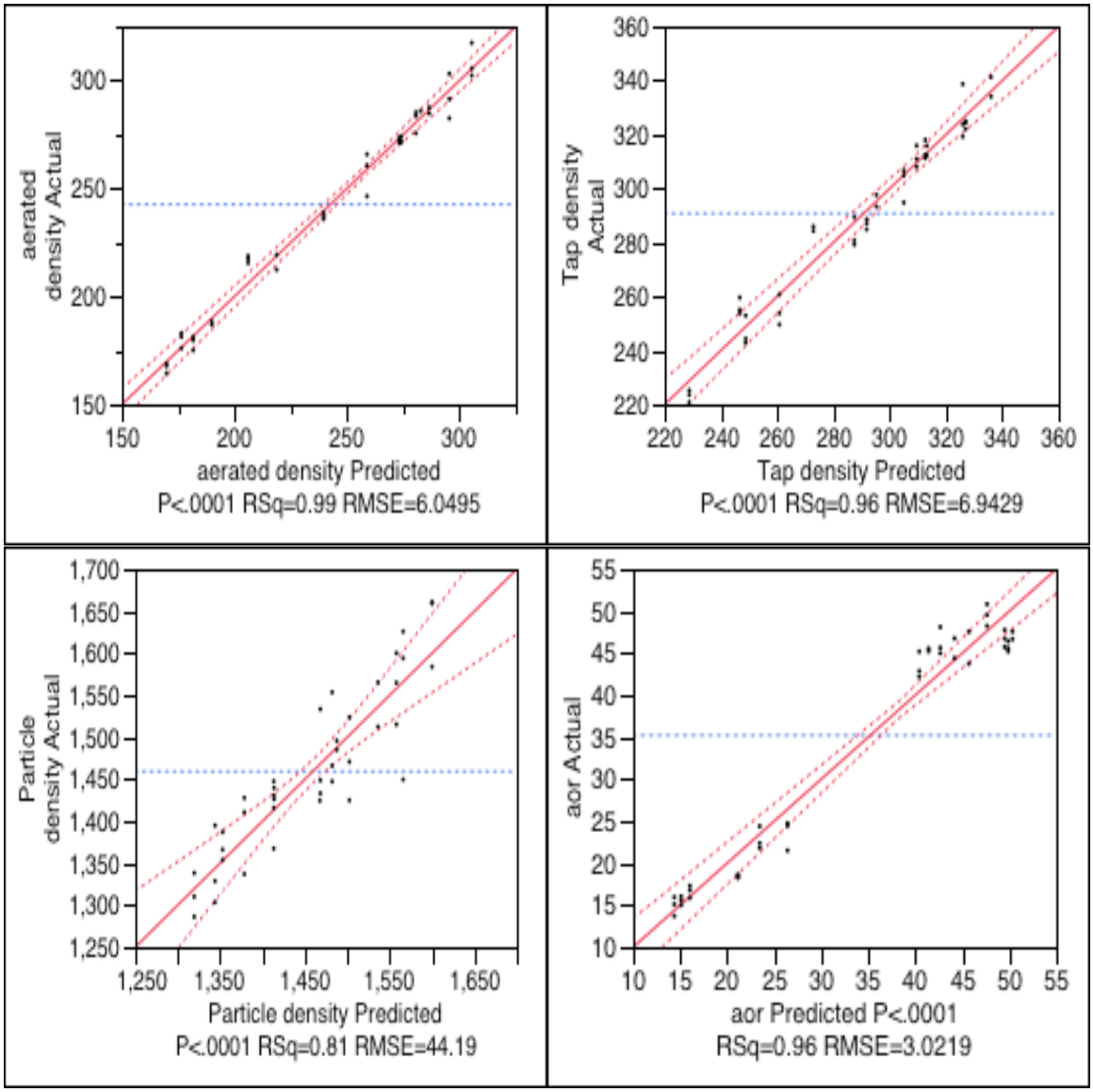

Figure B2. Actual vs. predicted plots for bulk flow properties of pine powders

Appendix C

Table C1. ANOVA table for pine granulation

Independent variable	Dependent variable	F value	P>F
binder conc	bulk density	71.3564	<.0001
binder conc	single granule density	3.8882	0.0328
binder conc	granule hardness	8.0681	0.006
mean particle size	bulk density	18.1319	0.0002
mean particle size	single granule density	5.5843	0.0093
mean particle size	granule hardness	34.5601	<.0001

Appendix D

Table D1. ANOVA table for untreated and pretreated switchgrass granulation

Independent variable	Dependent variable	F value	P>F
Treatment	Bulk density	222.72	<.0001
	Single granule density	8.16	<.0001
	Granule hardness	2.48	0.0324