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Understanding the Impacts of Ammonia Fiber Expansion (AFEX™) Pretreatment and Densification on Densified Products Quality and the Bioproducts Yield Through Enzymatic Hydrolysis and Fast Pyrolysis

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UNDERSTANDING THE IMPACTS OF AMMONIA FIBER EXPANSION (AFEX™) PRETREATMENT AND DENSIFICATION ON DENSIFIED PRODUCTS QUALITY AND THE BIOPRODUCTS YIELD THROUGH ENZYMATIC HYDROLYSIS AND FAST PYROLYSIS

BY

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This dissertation is approved as a creditable and independent investigation by a candidate for the Doctor of Philosophy and is acceptable for meeting the dissertation requirements for this degree. Acceptance of this dissertation does not imply that the conclusions reached by the candidate are necessarily the conclusions of the major department.

K. Muthukumarappan, Ph.D. Date

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Van Kelley, Ph.D. Date

Department Head, Department of Agricultural and Biosystems Engineering

Dean, Graduate School Date

I dedicate this dissertation to….

- My loving family – mom, dad, and to my brother.
- "Mother nature" - the god I believe in.

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LIST OF ABBREVIATIONS

AFEX	:	Ammonia Fiber Expansion
%	:	Percentage
°C	:	Degree Celsius
CBU	:	Cellobiose unit
CS	:	Corn stover
df	:	Degrees of freedom
DOE	:	Department of energy
EIA	:	Energy information administration
EPA	:	Environmental protection agency
FPU	:	Filter paper unit
FS	:	Feedstock
GLM	:	General linear model
h	:	hour
HP	:	Horse power
HPLC	:	High performance liquid chromatography
kg	:	Kilogram
l/d	:	Length to diameter ratio
MC	:	Moisture content
min	:	Minute
mm	:	Milli meter
MPa	:	Mega pascal

MSU : Michigan State University

N : Newton

PCG : Prairie cord grass

Proc : Procedure

RBPD : Regional biomass processing depots

rpm : Revolutions per minute

SAS : Statistical analysis software

SG : Switchgrass

TGA : Thermogravimetric analysis

US : United States

wb : Wet basis

Wt : Weight

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1. Sundaram, Vijay, Kasiviswanathan Muthukumarappan, and Srinivas Reddy Kamireddy. "Effect of ammonia fiber expansion (AFEX™) pretreatment on compression behavior of corn stover, prairie cord grass and switchgrass." Industrial Crops and Products 74 (2015): 45-54.
2. Sundaram, Vijay, and Kasiviswanathan Muthukumarappan. "Influence of AFEX™ pretreated corn stover and switchgrass blending on the compaction characteristics and sugar yields of the pellets." Industrial Crops and Products 83 (2016): 537-544
3. Sundaram, Vijay, and Kasiviswanathan Muthukumarappan. "Impact of AFEX™ Pretreatment and Extrusion Pelleting on Pellet Physical Properties and Sugar Recovery from Corn Stover, Prairie Cord Grass, and Switchgrass." Applied biochemistry and biotechnology (2016): 1-18.
4. Sundaram, Vijay, Kasiviswanathan Muthukumarappan, and Stephen Gent. “Understanding the impacts of AFEX™ pretreatment and densification on the fast pyrolysis of corn stover, prairie cord grass, and switchgrass”. Applied biochemistry and biotechnology (2016):1-20.
5. Sundaram, Vijay and Kasiviswanathan Muthukumarappan. “Effect Of Afex™ Pretreatment, Compressive Load, Screen Size, And Moisture Content On The Sugar Yields Of Corn Stover, Prairie Cord Grass, And Switchgrass”. Industrial Crops and Products (Manuscript submitted)

ABSTRACT

UNDERSTANDING THE IMPACTS OF AMMONIA FIBER EXPANSION (AFEX™) PRETREATMENT AND DENSIFICATION ON DENSIFIED PRODUCTS QUALITY AND BIOPRODUCTS YIELD THROUGH ENZYMATIC HYDROLYSIS AND FAST PYROLYSIS

VIJAY SUNDARAM

2017

Lignocellulosic biomass poses significant challenges during handling, transportation, and storage due to its low bulk density. Densification involves conversion of the low bulk density biomass into a highly compacted product which helps in improving the handling, transporting, and storage obstacles associated with biomass logistics. Besides the logistical challenges, the recalcitrant nature of the lignocellulosic biomass makes it even more challenging during the enzymatic hydrolysis. The carbohydrate components, cellulose and hemicellulose are not readily accessible by the enzymes during the hydrolysis process due to the presence of lignin. Pretreatment is the process to convert the native recalcitrant biomass in the form, which is effective to enzymatic hydrolysis. Numerous pretreatment technologies have been extensively studied on different lignocellulosic biomass using physical, chemical, and biological methods. Ammonia Fiber Expansion (AFEX™) is a promising pretreatment method, which involves treating the biomass with liquid ammonia at moderate temperature and pressure. The impacts of AFEX™ pretreatment include cellulose decrystallization, hemicellulose hydrolyzation, and lignin depolymerization. Due to these alterations, the

cellulose and hemicellulose components can be easily accessed by the enzymes during the hydrolysis step, resulting in increased sugar yields.

To address the logistical issues faced by the large-scale biorefineries, a concept called “Regional biomass processing depots” (RBPD) was developed. RBPDs involve procuring, pretreating, and densifying low density lignocellulosic feedstocks on a distributed scale to minimize the logistical challenges and carbon footprint. To make the RBPDs successful, it is imperative to understand the impacts of different preprocessing operations on the physical qualities of the densified products and the product yields. The increased lignin availability after AFEX™ pretreatment helps in better binding of the fibers during the densification process to produce well compacted products. Although, the densification produces compacted products, it is imperative to examine the effects of densification on the biomass conversion process. Hence, this study was designed to study the impacts of AFEX™ pretreatment and densification on the densified products quality and the product yields from the densified products. The lignocellulosic biomass corn stover, prairie cord grass, and switchgrass were selected for this research. The objectives of this research are: to understand the compression behavior of the AFEX™ pretreated biomass, to study the impacts of AFEX™ pretreatment and densification on the physical qualities of the densified products and sugars yields through enzymatic hydrolysis, and to understand the impacts of AFEX™ pretreatment and densification on the fast pyrolysis behavior. Five different researches were conducted and the brief summary of the individual studies is given below:

The objective of the first study was to understand the effect of (AFEX™) pretreatment on the compression behavior of selected lignocellulosic biomass. Size reduced (2, 4, and 8 mm) untreated and AFEX™ pretreated samples were moisture adjusted (8, 12, 16, and 20% wb) and were compressed using a single pelleting unit. AFEX™ pretreated corn stover with moisture content of 20% at screen size of 2 mm produced pellets with 21% higher unit density compared to untreated corn stover pellets. AFEX™ pretreated prairie cord grass and switchgrass with 20% moisture content at a screen size of 2 mm produced pellets having 25% and 21% higher unit density. The decrease in hammer mill screen size and the increase in moisture content and applied pressure increased the pellet unit density. Data obtained from the compression experiments were fitted with different compaction models. The Kawakita and Ludde model exhibited high degree of accuracy in all the samples. The constant value '1/b' in Kawakita and Ludde model represents the yield strength of the compacts, and the results showed that the AFEX™ pretreatment made the biomass easier to compress. Lower values of yield strength were obtained at high moisture content signifying that AFEX™ pretreated biomass at high moisture content leads to onset of deformation at relatively low pressure.

The second study was intended to study the effects of AFEX™ pretreatment, feedstock moisture content, hammer mill screen size, compressive load on sugar recovery from corn stover, prairie cord grass, and switchgrass. Pellets were produced using a single pelleting unit from untreated and AFEX™ pretreated biomass. Then the pellets were subjected to enzymatic hydrolysis to determine the glucose and xylose yields. A significant increase in the glucose and the xylose recoveries was noted in all the feedstocks after AFEX™ pretreatment. Statistical analysis showed that only the screen size was significant ($p<0.05$) in controlling the sugar yields whereas compressive load and feedstocks moisture content were not (p>0.05) in the case of untreated feedstocks and for the AFEX pretreated feedstocks all the selected factors were not significant (p>0.05). These results indicate that the larger screen size AFEX™ pretreated samples can be densified to increase the bulk density of the feedstocks without affecting the sugar yields.

The blending effects of the AFEX™ pretreated corn stover and switchgrass was investigated in third study. AFEX™ pretreated corn stover and switchgrass were blended (25:75, 50:50 and 75:25 percent on dry weight) and compressed at different applied pressures. The impacts of blending ratio, screen size, and compressive pressure were studied on pellet unit density, pellet hardness, specific energy consumption for pellets and on the sugar yields. A single pelleting unit was employed the pellets produced from AFEX™ pretreated samples reached their maximum pellet unit densities at an applied pressure of 94.8 MPa. The pellets produced from the small screen size sample at a higher applied pressure required more force to break. Besides, blend with higher proportion of AFEX™ pretreated corn stover produced harder pellets (711 N). Specific energy consumption for the pellets production varied from 11.4 to 57.9 kW h t^{-1}, and due to low bulk density of switchgrass, blends with a higher proportion of switchgrass consumed more energy. Pelleting and biomass blending had no significant effects on sugar yields of the AFEX™ pretreated corn stover and switchgrass samples.

The effects of AFEX™ pretreatment, moisture content (5,10, and 15 % wb), particle size (2, 4, and 8 mm), and extrusion temperature (75, 100, and 125 °C) on pellet bulk density, pellet hardness, and sugar recovery from corn stover, prairie cord grass, and switchgrass were investigated in the fourth study. Pellets were produced using a laboratory-scale extruder. AFEX™ pretreatment increased the pellet bulk density for all the biomass. Maximum pellet hardness of 2342.8, 2424.3, and 1298.6 N was recorded for AFEX™ pretreated corn stover, prairie cord grass, and switchgrass, respectively. Glucose and xylose yields of AFEX™ pellets were not affected by the extruder barrel temperature and the screen size. The results obtained showed that low temperature and large particle size biomass can be employed for AFEX™ pretreated biomass without compromising sugar yields.

The fifth study was intended to study the effects of AFEX™ pretreatment and densification on the fast pyrolysis product yields. Untreated and AFEX™ pretreated feedstocks were moisture adjusted and were densified using a single screw extruder and ComPAKco densification technique. Results of the thermogravimetric analysis showed the decrease in the decomposition temperature of the all the feedstocks after AFEX™ pretreatment indicating the increase in thermal stability. Loose and densified feedstocks were subjected to fast pyrolysis in a lab scale reactor and the bio-char and bio-oil yields were recorded. Bio-char obtained from the AFEX™ pretreated feedstocks exhibited increased bulk and particle density compared to the untreated feedstocks. The properties of the bio-oil were statistically similar for the untreated, AFEX™ pretreated, and AFEX™ pretreated densified feedstocks. Based on the bio-char and bio-oil yields, the AFEX™ pretreated feedstocks and the densified AFEX™ pretreated feedstocks exhibited similar behavior. Hence, it can be concluded that densifying the AFEX™ pretreated feedstocks could be a viable option in the biomass processing depots to reduce the transportation costs and the logistical impediments without affecting the product yields.

1. INTRODUCTION AND LITERATURE REVIEW

1.1. Need for alternate energy sources

Dependence on the petroleum products imports threatens the United States security, economy, and the environment (Greene *et al.,* 2004). In the year 2015, more than 80 percent of the primary energy consumed in the United States was derived from the fossil fuels (USEIA, 2015). Transportation accounts for 26 percent of total U.S. greenhouse gas emissions and the emissions are due to the combustion of fossil fuels (USEPA, 2016). Fossil fuel based energy production is associated with a multitude of challenges including unsustainable nature, environmental pollution, global climate change, etc. Due to the finite fossil fuel resources, increasing energy demands, and increasing crude oil prices, the United States should make a transition from fossil fuel based development towards sustainable and alternate fuels based economy.

Application of lignocellulosic biomass for the biofuels production offers a renewable alternative (Kumar *et al.,* 2008) and according to the U.S. department of energy, generating power and fuels from biomass resources will have economic benefits including trade deficit reduction and new employment creation (USDOE, 2016). Biomass can be defined as any organic matter available on a renewable basis including, agricultural crops, trees, animal wastes, municipal wastes, grasses, etc. (Perlack *et al.,* 2011). The utilization of biomass to generate energy is termed as 'Bioenergy' and the resultant products can be used as a direct fuel or can be converted into liquids and gases (biofuels). Currently, we use first generation biofuels, produced from feedstocks that have been traditionally used as food. Due to the increasing food price and food vs. fuel debates, the focus has been shifted towards the second and third generation biofuels.

Second generation biofuels could be the viable resource to achieve the target of 36 billion gallons of renewable fuels by the year 2022 (Sissine, 2007). Second generation biofuels are produced from processing of cellulose present in the lignocellulosic materials like agricultural residues (corn stover, wheat straw, rice hulls, etc.), forest residues (roots, twigs, leaves, etc.), municipal residues (kitchen wastes, yard trimmings, paper products, etc.) and sustainable biomass (switchgrass, prairie cord grass, jatropha, etc.). The utilization of lignocellulosic biomass for the energy production does not compete with the food production besides developing the rural economy (Nanda *et al.,* 2015).

1.2. Lignocellulosic biomass

Lignocellulosic biomass covers a wide range of plants that is composed of cellulose, hemicellulose, and lignin. Due to its plentiful availability and renewable nature, lignocellulosic biomass have attracted much attention to produce fuels and chemicals (Binder and Raines, 2009). Biofuels production from lignocellulosic biomass are favored due to its high energy density, easy to transport and store, and its compatibility with the existing fuel combustion in the vehicles (Eranki, 2012). Lignocellulosic biomass can be converted into biofuels via biochemical and thermochemical conversion process. In biochemical conversion process, the lignocellulosic biomass will be hydrolyzed to convert the carbohydrate fractions into simple sugars. Fermentation is the subsequent process to convert the simple sugars into fuels and chemicals (Balan, 2012). In thermochemical conversion process, the lignocellulosic biomass will be subjected to pyrolysis or gasification to yield syngas, which in turn will be converted into fuels via Fischer-Tropsch process or by a biological conversion (Balan, 2014).

1.3. Lignocellulosic biomass and its challenges

In the United States, the most common biofuel is ‘Ethanol’ produced from fermentation of biomass rich in carbohydrates (Tromly, 2001). Bioethanol production from fermentation of plant biomass has been well studied and various conditions like enzymes activity, range, genetics, etc. were optimized (Rabinovitch-Deere, 2013). Although lignocellulosic biomass appears to be the feasible alternative, the challenges involved in the conversion of biomass into biofuels must be resolved. Miao *et al* (2012) indicated that the primary challenge in biomass logistics involves transporting huge volumes of low bulk density materials in an effective and efficient manner. Developing uniform format solid feedstock is important for the consistent feedstock supply for the bioenergy production (Hess *et al.,* 2009). Densification process is one way to increase the bulk density of the biomass, which involves conversion of loose biomass into regular shape products like pellets, briquettes, and cubes (Kambo and Dutta, 2014). Besides the logistical issues, overcoming the recalcitrance of the lignocellulosic biomass is an another uphill task in biofuels production. The components of the lignocellulosic biomass cellulose, hemicellulose, and lignin) are arranged in a complex pattern to protect against the microbial attack. Hence, it poses significant challenges during the enzymatic hydrolysis process. Different pretreatment methods have been studied extensively to break the recalcitrance of the lignocellulosic biomass for low cost ethanol production. Table 1.1 shows the summary of different pretreatment technologies. Lignocellulosic biomass pretreatment is vital to improve the enzyme accessibility to the carbohydrate fractions, thus increasing the product yields and reducing the costs (Himmel *et al.,* 2007).

Pretreatment has an impact on the overall process, including the feedstock handling, conversion process, and in downstream processing (Yang and Wyman, 2007). On the other hand, lignin alternation during the densification process could impact the biomass reactivity to enzymatic hydrolysis (Rijal *et al.,* 2012). Hence, it becomes imperative to examine whether the pretreatment and densification impacts are valuable or detrimental to the biofuel production. This entire research work is based on the concept of investigating the impacts of pretreatment and densification on the biofuel product yields.

1.4. Pretreatment of lignocellulosic biomass

Lignocellulosic feedstocks are complex structured and made up of three major components, namely cellulose, hemicellulose, and lignin (Lange, 2007). Cellulose and hemicellulose make up two-thirds of cell wall dry matter and these components are polysaccharides that can be hydrolyzed to simple sugars and then can be fermented to produce ethanol. Lignin acts as a support to the cell structure embedding cellulose and hemicellulose. Fig.1.1 shows the structure of lignocellulosic biomass and the need for pretreatment. To convert the sugar components (cellulose and hemicellulose) of the lignocellulosic biomass into fuel and chemicals, the deconstruction of complex chemical structure is vital. The process involving the conversion of the native form of lignocellulosic biomass, which is recalcitrant to enzymatic hydrolysis into a form which is effective for enzymatic conversion is referred as “pretreatment in bioprocessing engineering” (Lynd *et al.,* 2002). The main aim of the pretreatment is to deconstruct the structure of lignocellulosic biomass, thus preparing the carbohydrate components in a form that can be easily accessed by the microorganisms during enzymatic hydrolysis.

Lignocellulosic biomass pretreatment methods include physical, chemical, biological methods and various combinations thereof (Harmsen *et al.,* 2010). Numerous pretreatment technologies have been studied to improve the production efficiencies and to reduce the cost involved in the production of cellulosic biofuel production (Lynd *et al.,* 2008).

1.5. Ammonia Fiber Expansion (AFEX™) pretreatment

Ammonia fiber expansion (AFEX™) is a promising method to pretreat agricultural materials for bioenergy production and the method involves treating the lignocellulosic biomass with liquid ammonia under mild temperature (70-200°C) and pressure (100-400 psi) for a specific time (Bals *et al.,* 2010). Swelling of cellulose fibers occurs, followed by the explosion when the pressure is rapidly released (Dale, 1986). This explosion results in several physical and chemical alterations in the structure of biomass. Some of the alterations include cellulose decrystallization, partial depolymerization of hemicellulose, cleavage of lignin-carbohydrate complex (LCC), and surface area increase due to structural disruption. Chundawat *et al* (2007) studied the effect of AFEX™ pretreatment on the enzymatic digestibility of corn stover. FTIR results confirmed the cleavage of lignin–carbohydrate complex (LCC) for AFEX™-treated fractions and spectroscopy results showed the extraction of cleaved-lignin phenolic fragments and other extractives to the biomass surface. Balan *et al* (2009) described the mechanisms involved in the AFEX pretreatment process.

- Ammonia added to the reactor penetrates the lignocellulosic biomass and reacts with the water present in the biomass to form ammonium hydroxide.

- The formation of hydroxide ion catalyzes various thermochemical reactions inside the biomass structure.
- As a result of the thermochemical reactions, the compounds lignin and hemicellulose will be extracted and redeposited on the surface of the biomass cell wall.
- These alterations in the lignocellulosic biomass structure enhances the accessibility of cellulose for the enzymes during the hydrolysis process.

Fig.1.2 shows the AFEX™ pretreatment reactor setup. AFEX™ pretreatment proved to increase the sugar yields of different lignocellulosic biomass due to the retention of sugar components. Lau *et al* (2009) reported preservation of plant carbohydrates when the corn stover was subjected to AFEX™ pretreatment. Biersbach *et al* (2015) showed the significant improvement in the ethanol yields from corn stover, prairie cord grass, and switchgrass pretreated through AFEX™. Alizadeh *et al* (2005) reported a 2.5 times increase in ethanol yield after the switchgrass was subjected to AFEX™ pretreatment. Similarly, Teymouri *et al* (2005) reported an increase in ethanol yield of 2.3 times after the corn stover was pretreated through AFEX™. Besides increasing the sugar yields a pretreatment, which alters the lignocellulosic biomass structure and mobilizes the lignin to the biomass surface can be potentially employed to densify the biomass without any external binders (Balan, 2014). During the AFEX™ pretreatment, the lignin is mobilized to the biomass surface which acts as a natural binder during the densification process.

1.6. Biomass densification

Bulk density of the lignocellulosic feedstocks ranges from 80-100 kg m^{-3} for agricultural straws and 150-200 kg m^{-3} for woody biomass (Sokhansanj and Fenton, 2006; Mitchell *et al.,* 2007). Due to its low bulk density, lignocellulosic biomass poses significant challenges in handling, transportation, and storage. It also presents challenges in coal co-firing and reduces burning efficiencies (Tumuluru *et al.,* 2010). Moisture content also plays a vital role in determining the heating value of the biomass and less moisture content feedstocks are preferable for the biofuel production. Hence, it is important to convert the lower bulk density lignocellulosic feedstocks to the higher density products with less moisture content to overcome the logistical issues and to make the biofuel production economical.

Biomass densification is one of the promising options to overcome the limitations associated with the biomass logistics (Tumuluru *et al.,* 2010). Densification involves application of pressure to the biomass, thus making the loose biomass into a highly compacted product. As a result of the densification, the compacted products will be easy to handle, transport, and store. Increase in the bulk density of the biomass not only reduces the space required for transportation and logistical costs, but also increases the energy density of the products. Besides, the densification also reduces the fines produced making the environment safe for the workers. Different researches have been carried out to understand the mechanisms involved in the biomass densification process. Rumpf (1962) explained the possible mechanisms involved in the densification process. The author divided the densification process into five different stages which are as follows:

1. The attraction force causes the solid particles to adhere to each other. The attractive force may be an electrostatic or magnetic force in nature.
2. The presence of water or moisture during the compression process produces cohesive forces between the particles. With the increase in applied pressure, the interfacial space between the particles is filled with the liquid. During this stage, the particles will experience the force of attraction, surface tension, and capillary forces.
3. Viscous binders and thin adsorption layers provide bonds that are immobile and forms strong bonds between the particles. The area of adsorption contact increases when the solid particles are subjected to high pressure.
4. Solid bridges formation in this stage determines the strength of the compacted products. The strength of the compacts can be attributed to the crystallization of dissolved substances, melting and hardening of binders, sintering, and chemical reactions at high temperatures.
5. Mechanical interlocking of particles may occur during the agitation and compression of fibrous, flat-shaped and bulk biomass particles. Interlocking plays a minor role to the strength of the compacted products.

Mani *et al* (2002) hypothesized the three different stages involved in the densification process and are as follows:

1. With the application of pressure particles rearrange themselves to form a closely packed mass. During this stage, most of the particles retain their properties and the energy dissipation will be due to the inter-particle and particle-to-wall friction.

2. During the second stage, particles undergo plastic and elastic deformation with the increase in applied pressure. These deformations increase the inter-particle contact promoting bonding of particles through van der Waal's and electrostatic forces.
3. In the third and final stage, reduction in the volume of the biomass continue until the biomass approach the true density. The particles cannot regain their position at the end of this stage.

Traditional densification methods include baling, pelletization, extrusion, and briquetting and the respective densified products are called as bales, pellets, extrudates, and briquettes. It is important to produce the densified biomass with higher quality in order to have better logistics and ease of handling. The quality of the densified biomass includes unit density, bulk density, durability, hardness, calorific value, etc. The quality of the densified products depends on various factors like feedstock particle size, temperature, moisture content of the feedstock, chemical constituents of the feedstock, applied load, die geometry, etc. It is vital to optimize the factors to produce quality densified products. Abundant studies have been carried out to study the factors affecting the quality of the densified products (Tumuluru, 2014; Hoover *et al.,* 2014; Shaw, 2008; Adapa *et al.,* 2013).

1.7. Regional biomass processing depots

Bringing low bulk density biomass from the agricultural fields to the biorefineries makes the biomass transportation expensive. This will also increase the number of trips from the fields to the biorefineries producing more carbon emissions. To make the biomass logistics economical and to reduce the carbon emissions, biomass feedstocks should come from the fields situated around 50 miles radius to the biorefineries (Broeren, 2011). The researchers at the Michigan State University (MSU) proposed the concept called ‘Regional Biomass Processing Depots’ (RBPD) to overcome the concerns associated with biomass logistics. Fig.1.3 shows the concept of regional biomass processing depots**.** Conventional biorefining involves collecting and preprocessing the biomass at the front end of biorefineries. This method requires huge storage space and higher transportation costs due to the low bulk density of the lignocellulosic biomass. In contrasts, RBPDs involves collection and preprocessing of biomass from the fields to produce uniform densified product suitable to handle, transport, and store with the conventional systems. Eranki and Dale (2011) showed that RBPDs yield same total energy and produces 3.7% greenhouse gas emission lesser than the conventional biorefining.

To make RBPD concept successful, adequate amount of research works are needed to develop the economical and robust processing technologies (Hess *et al.,* 2009). Preprocessing operations involves feedstock collection, size reduction, pretreatment, and densification. To make the RBPD effective, it is vital to optimize the preprocessing conditions to produce the quality densified products suitable for cheaper logistics and cost effective biofuel production. Several studies have been carried out to optimize the preprocessing parameters on densified products qualities and sugar yields. Hoover *et al* (2014) studied the impacts of AFEX™ pretreatment and pelleting variables on the physical properties and sugar yields from corn stover. Durability of the pellets produced in the study was >97.5% which exceeds the standard durability (97.5%) set for handling and transportation of pellets. Die speed and grind size did not influence the sugar yields of the corn stover and the authors concluded that the AFEX pretreatment in combination with pelleting may be helpful to solve the issues associated with biomass logistics. Sundaram and Muthukumarappan (2016) studied the impacts of AFEX™ pretreatment and extrusion pelleting on the pellet physical properties and fermentable sugar yields of corn stover, prairie cord grass, and switchgrass. Glucose and xylose yields were not affected by the extruder barrel temperature and hammer mill screen size for the feedstocks. The authors concluded that, AFEX™ pretreated feedstocks can be pelleted using a single screw extruder at low barrel temperature and even large particle size feedstocks can be densified without compromising sugar yields. Eranki and Dale (2011) emphasized that RBPDs can be configured to supply the feedstocks in the form best suitable for biochemical and thermochemical conversion process. This research was intended to understand the impacts of AFEX™ pretreatment and densification on the densified products qualities and products yield through biochemical and thermochemical conversion process.

1.8. Objectives

The principal objective of this research was to understand the impact of ammonia fiber expansion (AFEX™) pretreatment and densification on the pellet properties, sugar yields, bio-oil, and bio-char yields from corn stover, prairie cord grass, and switchgrass. The specific objectives of the research were examined and presented as a chapter from 2 to 5. Following are the detailed objectives of the research:

1. To study the impact of AFEX™ pretreatment and densification variables (applied pressure, biomass moisture content, hammer mill screen size) on the compression behavior of corn stover, prairie cord grass and switchgrass.
2. To study the impact of AFEX™ pretreatment and densification variables (applied pressure, biomass moisture content, hammer mill screen size) on sugar yields of corn stover, prairie cord grass, and switchgrass.
3. To understand the influence of AFEX™ pretreated corn stover and switch grass blending on the compaction characteristics and sugar yields of the pellets
4. To study the impacts of AFEX™ pretreatment and extrusion pelleting on pellet physical properties and sugar recovery from corn stover, prairie cord grass, and switchgrass.
5. To understand the impacts of AFEX™ pretreatment and densification on the fast pyrolysis of corn stover, prairie cord grass, and switchgrass.

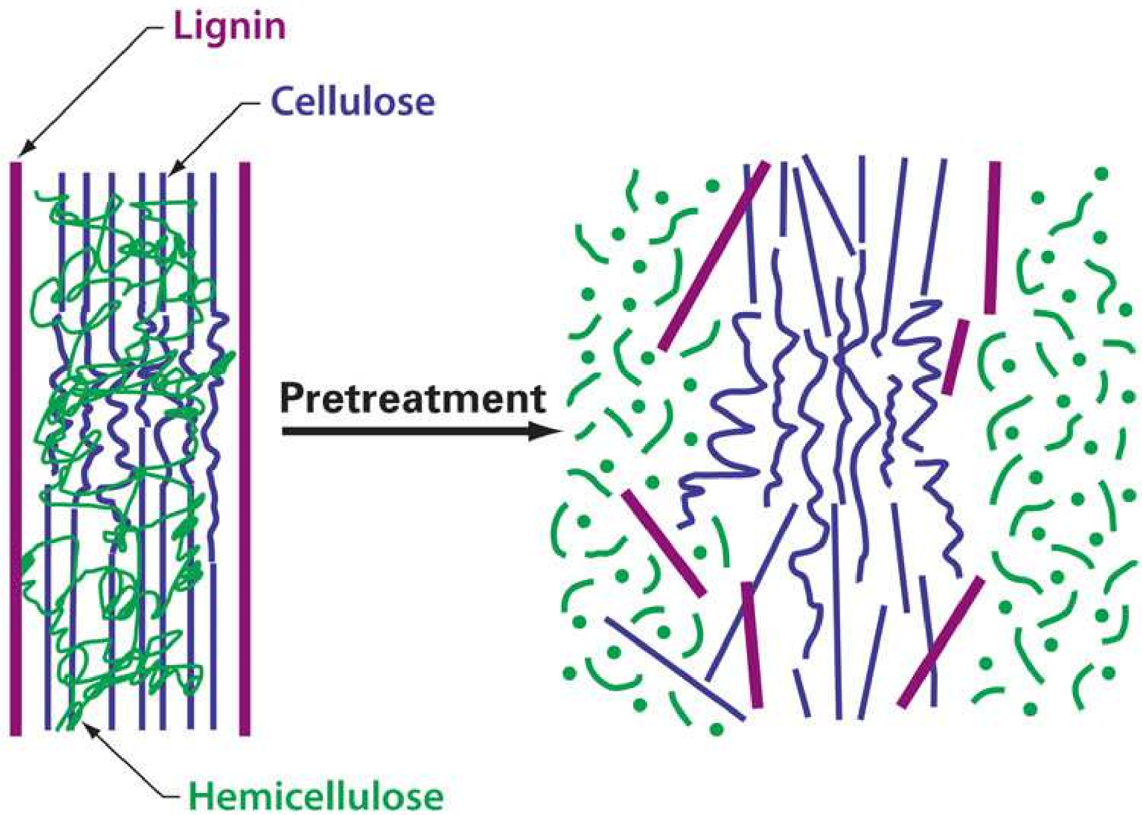


Fig. 1.1. Significance of lignocellulosic biomass pretreatment (USDOE, 2007)

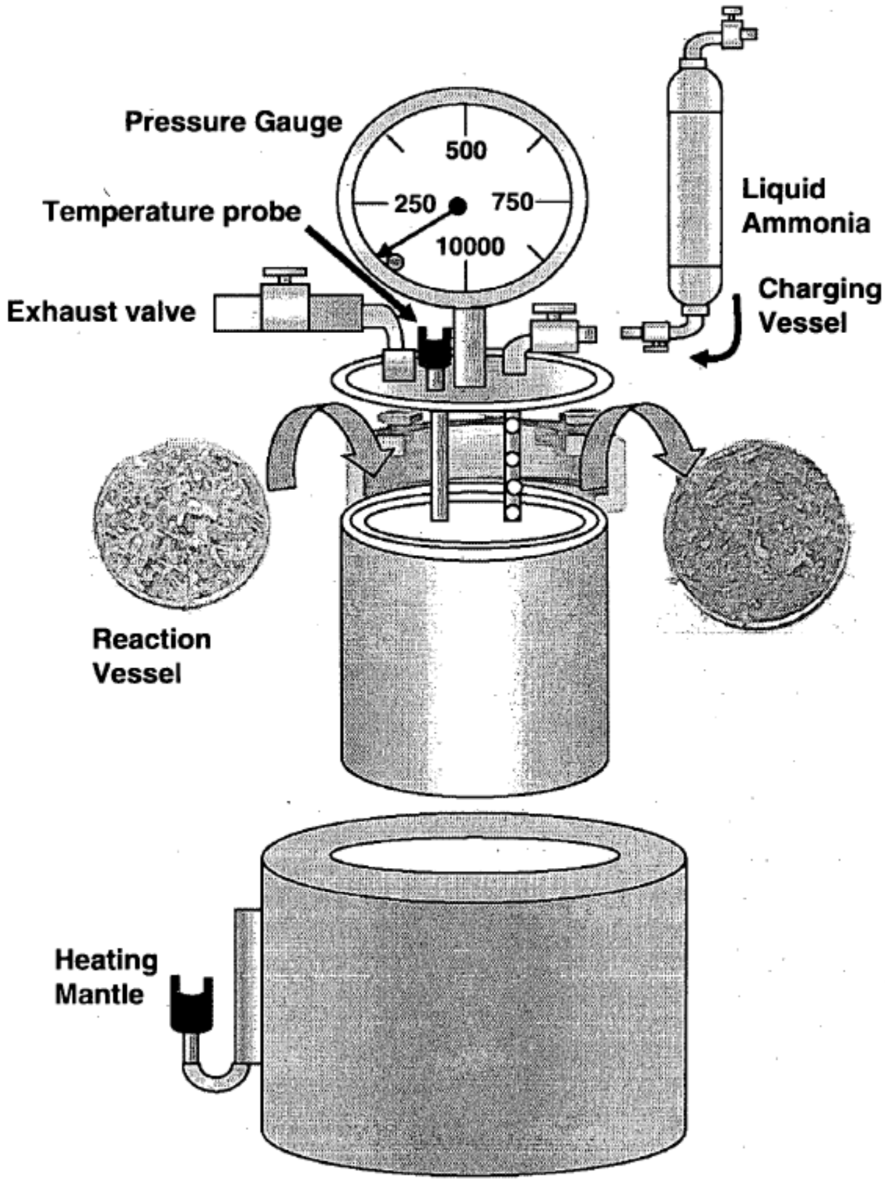


Fig. 1.2. Ammonia fiber expansion reactor (Balan et al., 2009).

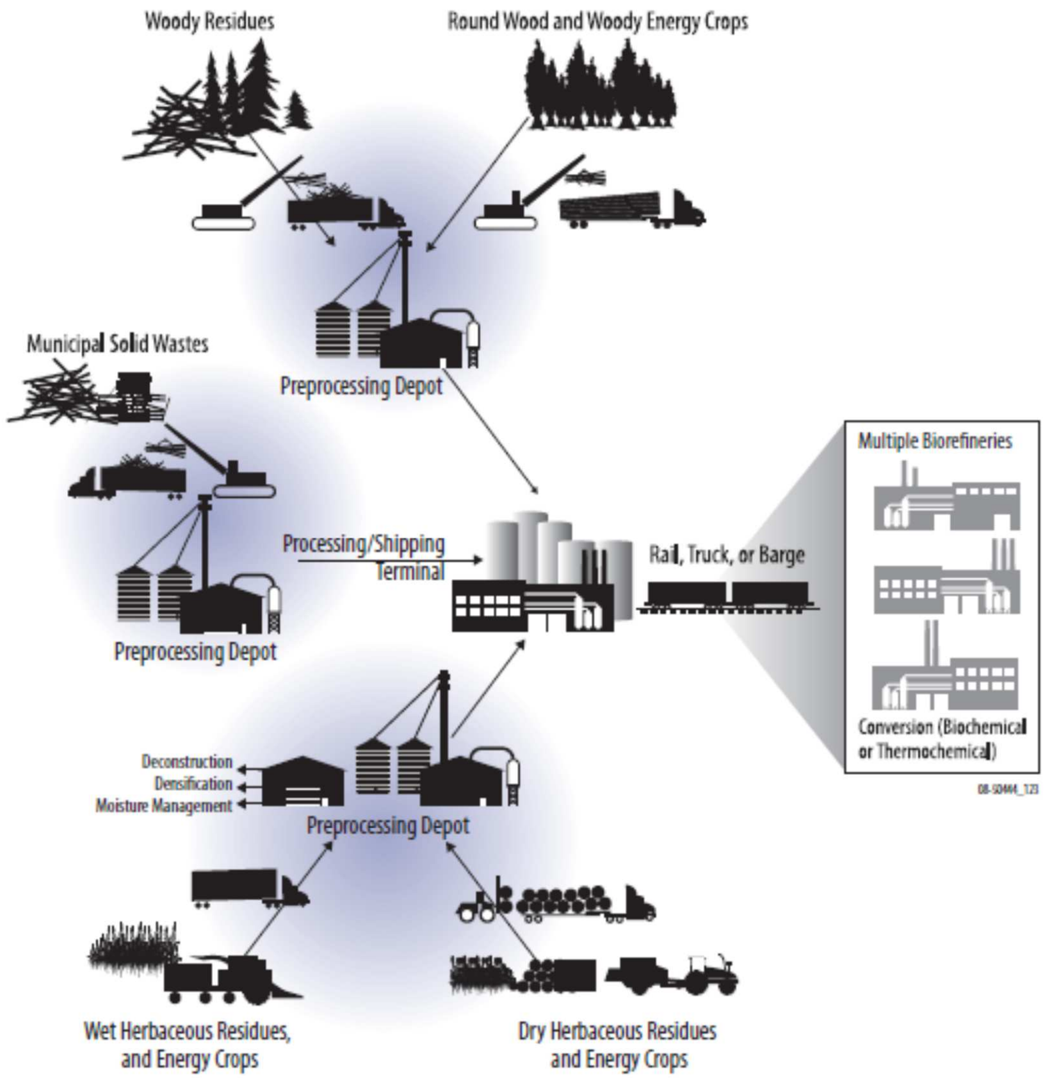


Fig. 1.3. Concept of regional biomass processing depots (Hess *et al.,* 2009).

Table 1.1. Summary of different lignocellulosic biomass pretreatment methods (Healey *et al.*, 2015)

Pretreatment	Summary	Advantages	Drawbacks
Grinding and milling	Size reduction of the biomass to increase the surface area	• No toxic compounds generated • No chemicals required	• Energy intensive operation • No alterations in the complex chemical structure remains the same
Concentrated acid	Reaction of biomass with concentrated hydrochloric or sulfuric acids.	• Low inhibitory product formation under low temperature conditions • Complete biomass hydrolysis	• High cost of acid • High cost of corrosive-resistant reactor • Production of inhibitory compounds
Dilute acid	Reaction of biomass with dilute acid at high temperature to solubilize hemicellulose	• Low acid concentration required (<1%) • Short reaction times	• Degradation of sugar and loss • Phenolics release
Alkaline	Cleaves linkages within lignin and between the hemicellulose and lignin	• Low pressure and temperature • Mobilizes the lignin to the cell wall surface	• Requires neutralization • Low recovery
Organosolv	Reaction of biomass with organic or aqueous organic solvent mixture and with inorganic catalysts	• Partial hydrolyzed cellulose • Recovery of hydrolyzed hemicellulose	• High temperature • Expensive organic solvents
Steam explosion	Reaction of biomass with steam at high temperature (up to 240°C)	• Hemicellulose solubilization and reduced cellulose crystallinity • No chemicals required • Short reaction time	• Partial destruction of xylan fraction • Inhibitory compounds generation
Autohydrolysis	Reaction of biomass with hot water or saturated steam	• No chemicals required • Low environmental pollution	• High pressure and temperature • Degradation of sugars at high temperature

2. EFFECT OF AMMONIA FIBER EXPANSION (AFEX™) PRETREATMENT ON COMPRESSION BEHAVIOR OF CORN STOVER, PRAIRIE CORD GRASS AND SWITCHGRASS

2.1. Abstract

Understanding the fundamental mechanisms involved in densification of bulky lignocellulosic feedstocks is imperative. This study was carried out to understand the effect of ammonia fiber expansion (AFEX™) pretreatment on the compression behavior of corn stover, prairie cord grass, and switchgrass. Samples were ground using three different hammer mill screen sizes (2, 4, and 8 mm) and were subjected to AFEX™ pretreatment. Untreated and AFEX™ pretreated samples were moisture adjusted to four levels (8, 12, 16, and 20% wb) and were compressed using a single pelleting unit. Physical properties comprising bulk density, particle density of the samples and unit density of pellets were determined for each combination. AFEX™ pretreated corn stover with moisture content of 20% at screen size of 2 mm produced pellets with 21% higher unit density compared to untreated corn stover pellets. AFEX™ pretreated prairie cord grass and switchgrass with 20% moisture content at a screen size of 2 mm produced pellets having 25% and 21% higher unit density. The decrease in hammer mill screen size and the increase in moisture content and applied pressure increased the pellet unit density. Data obtained from the compression experiments were fitted with different compaction models *viz.* Jones, Walker, and Kawakita and Ludde. The Kawakita and Ludde model exhibited high degree of accuracy (R^2 – 0.99 and 1.00) in all the samples. The constant value '$1/b$' in Kawakita and Ludde model represents the yield strength of the compacts, and the lower $1/b$ values were obtained for AFEX™ pretreated samples

compared to untreated samples. This implies the impact of pretreatment, which in turn made the biomass easier to compress. Lower values of yield strength were obtained at high moisture content (16–20% wb) signifying that AFEX™ pretreated biomass at high moisture content leads to onset of deformation at relatively low pressure to produce highly compacted pellets.

2.2. Introduction

The supply of sustainable and economical energy is a primary concern for many nations. One alternative solution is to make use of abundantly available renewable lignocellulosic materials to produce biofuels. According to studies, there are approximately 1.3 billion tons of biomass available annually from both harvested agricultural lands and forests in the United States (U.S. Department of Energy, 2011). Furthermore, the production of biofuels from lignocellulosic materials may lead to a reduced dependency on fossil fuels and lower greenhouse gas emissions (Degenstein *et al.,* 2013 and McKendry, 2002). Developing technologies to produce cost effective biofuels are a key challenge and biofuels production from lignocellulosic feedstocks poses several impediments.

One of the limitations of employing lignocellulosic feedstocks for biofuel production is its low bulk density. It leads to handling, storage, and transportation issues that can directly dictate the cost of the feedstock leading to high production cost (Hoover *et al.,* 2014). To maintain an economic and sustainable feedstock supply to the biorefineries, the compaction of low bulk density biomass is crucial (Adapa *et al.,* 2010). Besides, understanding the biomass compaction mechanisms will aid in the design of energy efficient compaction equipment, reducing the production cost, and increasing the quality of compacted products (Mani *et al.,* 2004a). Theerarattananoon *et al* (2011) stated that the densification of biomass feedstocks can assist in increasing the bulk density, reducing the transportation costs, improving the storability, and creating better environment to handle the feedstocks using existing grain handling equipments. The quality of the densified feedstocks depends on the feedstock characteristics (moisture content, chemical composition, particle size, etc.) and process variables (temperature, pressure retention time, etc.).

The lignocellulosic biomass structure is composed of a highly complex matrix of cellulose, hemicellulose, and lignin. These components are interlinked by ether, ester, carbon–carbon, and hydrogen bonds (Faulon and Carlson, 1994). Among these components, lignin allows the particles to stick together during the densification process. Lignin softening will take place when the biomass is compacted under high temperature and pressure exhibiting thermosetting properties (van Dam *et al.,* 2004). Kaliyan and Morey (2010) studied the significance of natural binders (lignin and protein) present in corn stover and switchgrass at a microscopic level. Solid bridges were formed when the natural binders were subjected to melting and cooling. The study concluded that the activation of natural binders by regulating moisture and temperature is vital to produce durable densified products.

The interlinkage between the components makes the feedstock recalcitrant and several physical, chemical, physicochemical, and biological pretreatment methods have been extensively studied to alter this complex structure (Brodeur *et al.,* 2011). Sokhansanj *et al* (2005) implied that the recalcitrant structure of lignocellulosic biomass should be altered to activate the natural binders to enhance the densification process, and this can be achieved by the application of pretreatment. Adapa *et al* (2010) attributed the enhancement in the compact density of canola, oat, and wheat straw to the melting and depolymerization of lignin during steam explosion pretreatment.

Ammonia fiber expansion (AFEX™) is a promising technology for pretreating agricultural residues for bioenergy production (Bals *et al.,* 2010a). The method encompasses treating biomass with anhydrous ammonia in a high pressure Parr reactor for a short residence time before explosively releasing the pressure (Dale, 1986). This instantaneous drop in pressure results in solubilization and redeposition of lignin components on the biomass surface after ammonia is evaporated (Dale, 1986 and Chundawat *et al.,* 2011). AFEX™ pretreatment involves treating biomass with liquid ammonia at a moderate temperature (80–150 °C) and pressure (200–400 psi) in an enclosed stainless steel reactor for a short residence time (5–30 min) before releasing the pressure (Bals *et al.,* 2010a). This rapid drop in pressure results in physical disruption of the biomass structure; thus, exposing the cellulose and hemicellulose fibers (Dale, 1986, Balan *et al.,* 2009, Chundawat *et al.,* 2011 and Kumar *et al.,* 2009). The important impacts of this pretreatment include cellulose decrystallization, hemicellulose hydrolyzation, and lignin depolymerization (Bals *et al.,* 2010b and Chundawat *et al.,* 2011). Campbell *et al* (2013) investigated the packed bed AFEX™ reactor for pretreatment of corn stover and wheat straw. Durable pellets were formed from AFEX™ pretreated corn stover and wheat straw without any external binding agents. The lignin in the biomass acts a natural binding agent in sticking the fibers together during the densification process. The results of the study showed that the pelleting operations can be made efficient after biomass is subjected to AFEX™ pretreatment. Hoover *et al* (2014) studied the impact of the AFEX™ pretreatment and pelleting variables on pellet quality and sugar yield of corn stover. The results of the study showed that the pelleting of AFEX™ pretreated biomass produced pellets with durability of more than 97.5%.

Mani *et al* (2003) emphasized the requirement of research works on compression characteristics of different biomass to develop a cost effective compaction process. It is imperative to understand how the pretreated biomass behave during densification. The objective of the work is to study the impact of AFEX™ pretreatment and the effect of three variables, namely biomass moisture content, applied pressure, and hammer mill screen size on the responses namely bulk density, particle density, and pellet unit density. The feedstocks selected were corn stover, prairie cord grass, and switchgrass and a single pelleting unit was employed for pelleting. In addition, the results obtained experimentally were rigorously tested using three different compaction models, namely Walker (1923), Jones (1960), and Kawakita and Ludde (1971) to examine the compression characteristics of the untreated and AFEX™ pretreated biomass feedstocks such as corn stover, prairie cord grass, and switchgrass.

2.3. Materials and methods

2.3.1. Feedstock preparation

The feedstocks corn stover (2008), prairie cord grass, and switchgrass (2009) obtained from local farms in Brookings, South Dakota were ground with three different screen opening sizes viz. 2, 4 (Hammer Mill, Thomas Wiley Laboratory Mill, Swedesboro, NJ) and 8 mm (Speed King, Winona Attrition Mill Co., Winona, MN). The ground materials were sealed in plastic bags and sent to the biomass conversion research laboratory (BCRL, Michigan State University, MI) for AFEX™ pretreatment. The pretreatment conditions were optimized individually for each feedstock based on the recalcitrant nature of lignocellulosic biomass (Balan *et al.,* 2009) by BCRL. The key variables employed during the AFEX™ process were pretreatment time, ammonia–biomass ratio, temperature, and feedstock moisture content. The AFEX™ pretreatment conditions used for different feedstocks are given in Table 2.1. The pretreated materials were sealed in plastic bags and stored in a refrigerator at 4 °C until further use.

2.3.2. Moisture conditioning

The moisture content of the samples was determined using ASABE Standards (2006) standard and was reported in percent wet basis. The initial moisture content of the stored untreated feedstocks varied from 4% to 8%, and for the AFEX™ pretreated feedstocks the moisture content varied from 5% to 8% on a wet basis. Moisture content was varied at four different levels (8, 12, 16, and 20% on wet basis) and the selection of moisture content range was based on Kaliyan and Morey (2009) study. In their study, the authors optimized the conditions to produce durable briquettes from corn stover and switchgrass by varying the moisture content from 8% to 20%. To achieve the desired moisture levels, a calculated quantity of water was added to the samples in a plastic container, and the contents were tumbled manually. Moisture adjusted samples were stored in sealed plastic bags at 4 °C overnight, and the samples were brought to room temperature prior to the beginning of experiments.

2.3.3. Compression test using single pelleting unit

To study the compression performance of the AFEX™ pretreated and untreated biomass grinds, tests were carried out in a single pelleting unit (Mani *et al.,* 2002, Tabil and Sokhansanj, 1996 and Tabil and Sokhansanj, 1997). The unit consists of a piston and cylinder assembly with a base plate resting on the platform. The piston was connected to the crosshead of the texture analyzer (TA HD plus, Texture Technologies Corp., NY) as shown in Fig.2.1. Internal diameter and height of the cylinder were 6.35–76.2 mm, respectively. The cylinder was wrapped with a heating element to heat the contents of the cylinder during the compression. Thermocouples were attached to the cylinder, and the temperature was regulated by a temperature controller (SDC 120KC-A, Brisk Heat Corp., OH). The cylinder section was rested on the base plate, which had an internal diameter matching the diameter of the cylinder. Feedstocks with different combinations of moisture contents (8, 14, 16 and 20% w.b) and hammer mill sizes (2, 4, and 8 mm) were pelleted at different loading conditions (1000, 2000, 3000, 4000, and 5000 N) with corresponding pressure (31.6, 63.2, 94.8, 126.4 and 158.0 MPa) using the single pelleting unit. Samples of a quantity of 0.5–0.7 g were loaded into the cylinder, and the piston was allowed to compress in a single stroke. The temperature of the cylinder was maintained at 100 ± 2 °C to mimic the commercial pelleting process (Mani *et al.,* 2004b). Experimental variables selected and the levels of each variable are given in Table 2.2. The crosshead speed of the texture analyzer was set at 50 mm min^{-1}. After reaching the preset load, the piston was allowed to detain at an indicated preset load for a period of 30 s to avoid the spring back effect. The piston was raised, and bottom plate was attached to the cylinder to eject the pellet produced by lowering the piston. Five replications were produced for each combination.

2.3.4. Physical properties

The physical properties estimation of the untreated, AFEX™ pretreated, pelletized untreated and pelletized AFEX™ pretreated samples were carried out. Physical properties include bulk density, particle density, and pellet unit density were calculated and the values were fitted with different compaction models. The procedures adopted for determination of different physical properties are given below.

2.3.4.1. Bulk density of feedstocks

Bulk density is the important characteristic of the biomass as it directly influences the delivery cost of the feedstock to a biorefinery. Besides, it also impacts the storage and material handling system (Lam *et al.,* 2008). Bulk density is the ratio of mass of biomass to the total volume they occupy. It is used as a measure to determine the material flow consistency. The bulk density of the samples was determined using a hopper and stand (Product code 151, Seedburo Equipment Co*.,* Des Plaines, IL) apparatus. A cylindrical metal container with a known volume of 0.5 L was placed below the hopper to collect the samples fed into the hopper. The mass of the sample present in the container was measured for each feedstock, and the bulk density of feedstocks was calculated by dividing the mass of the sample by the volume of the vessel.

2.3.4.2. Particle density of feedstocks

Gas pycnometer is widely used to determine and characterize solids in powder form. In this study, micrometritics multivolume gas pycnometer (1305, Norcross, GA) was used to determine the particle density of the samples. The total pore volume was measured by passing the medium gas to fill the void spaces in the cell containing the sample. Helium gas was used as a medium gas, and the volume of the sample was calculated from the drop in pressure when the known amount of gas was allowed to expand into the cell containing the sample. Sample volume was calculated using the formula specified in the instrument manual.

$$\mathbf{V_{sample}} = \mathbf{V_{cell}} - \frac{\mathbf{V_{exp}}}{\left[\left(\frac{\mathbf{P_1}}{\mathbf{P_2}}\right) - \mathbf{1}\right]}$$

2.3.4.3. Pellet unit density

The dimensions (height and diameter) of the pellets were measured using a digital vernier caliper (Digimatic, Mitutoyo Corp., Japan) and the mass of pellets using a digital balance (Mettler PM 2500, Delta range, Columbus, OH). The ratio of mass of a pellet to its volume provided the pellet unit density, and three replications were performed under each condition.

2.3.5. Analysis of variance (ANOVA)

Regulating the process and feedstock parameters support the production of quality compacted products. Carone *et al* (2011) represented a simplified model for an industrialization process and the study results showed the influence of temperature, moisture content and hammer mill screen size and their interactions on density and hardness of the pellets. The study concluded that, high temperature, low moisture content, and reduced biomass size, in the same order governed the model in determining the pellets quality. In this study, the effects of moisture content, screen size, and applied force on compression characteristics of corn stover, prairie cord grass, and switchgrass were carried out using the analysis of variance (ANOVA) method. Least significant difference (LSD) at 0.05 level of significance was also carried out using SAS software (SAS 9.3, Cary, NC). The data were analyzed with PROC GLM procedure to determine the main and interaction effects, and the level of significance was set at 5%. Model parameters of Walker, Jones, and Kawakita and Ludde model were estimated using Microsoft Excel 2010 (Microsoft Corp., Seattle, WA 2010).

2.3.6. Compaction equations

2.3.6.1. Walker model (1923)

Walker, based on a series of experiments on powder compressibility proposed the relationship of volume ratio (V_R) as function of applied pressure (P) as mentioned in Eq. (2.1).

$$\mathbf{V_R = m_1 . In\ P} + z_1 \qquad \text{---------} (2.1)$$

Where V_R: volume ratio (V/V_s); m_1&z_1: model constants; P: applied pressure (Pa); V: volume of compact at pressure P (m^3); V_s: void free solid material volume (m^3).

2.3.6.2. Jones model (1960)

Jones studied the compression behavior of industrial metal powders and used the Eq. (2.2) to express the relationship between density and pressure data obtained.

$$\mathbf{In\ \rho = m_2 . In\ P + z_2} \qquad \textbf{-------- (2.2)}$$

Where,

ρ: Packing density (kg/m^3); m_2: model constant (compressibility); z_2: model constant; P: Applied pressure (Pa)

2.3.6.3. Kawakita and Ludde model (1971)

Kawakita and Ludde evaluated the relationship between pressure and volume change in compaction of powders to ascertain the behavior of materials during compaction. The model is given by Eq 2.3

$$\frac{\mathbf{P}}{\mathbf{C}} = \left(\frac{\mathbf{1}}{\mathbf{ab}}\right) + \left(\frac{\mathbf{P}}{\mathbf{a}}\right) \qquad \textbf{------- (2.3)}$$

Where,

C: Degree of volume reduction [$(V_0-V)/V_0$]; a & b: Model constants;

V_0: Volume of compact at zero pressure (m^3); P: Applied pressure (MPa)

2.4. Results and discussion

2.4.1. Bulk and particle density

Bulk and particle densities of the untreated and AFEX™ pretreated biomass samples are given in Table 2.3. Table 2.4 shows the ANOVA test results for factors affecting bulk and particle density of both untreated and AFEX™ pretreated samples. The outcomes of the analysis showed the significant effect ($p < 0.0001$) of moisture content, hammer mill screen size, feedstock type, and their interactions on bulk and particle density of the samples. Bulk density and particle density of untreated and AFEX™ pretreated biomass samples decreased with an increase in hammer mill screen size. Larger screen size particles tend to occupy more pore volume than the smaller particles (Mani *et al.,* 2004a), leading to decrease in bulk and particle densities. AFEX™ pretreatment increased the bulk and particle density of all three biomass samples, and this can be attributed to the brittle and friable nature of biomass after AFEX™ pretreatment (Hoover *et al.,* 2014). The highest bulk density was observed for prairie cord grass for both untreated (199.5 kg m^{-3}) and AFEX™ pretreated (232.0 kg m^{-3}) samples. The reason could be due to the grinds from prairie cord grass may have been finer than other biomasses (Mani *et al.,* 2006). The bulk density of the biomass also increased with increase in moisture content as the addition of water increases the weight. Besides, moisture conditioned AFEX™ pretreated corn stover had shown significant increase in bulk density as compared to moisture conditioned untreated corn stover. Particle density of all three AFEX™ pretreated biomass increased significantly compared to the untreated samples. Adapa *et al* (2010) attributed the increase in particle density of canola, oat, and wheat straw after steam explosion pretreatment to the disintegration of long chain lignocellulosic structure into short chains during pretreatment. In the case of AFEX™ pretreatment, one of the important alterations occurring is the swelling and physical disruption of the lignocellulosic matrix structure (Dale, 1986; Balan *et al.,* 2009). This effect could have made the feedstocks more fragile and crumble contributing to the increased particle density after AFEX™ pretreatment.

2.4.2. Pellet unit density

Table 2.5 shows the analysis of variance (ANOVA) results for pellet unit density of both untreated and AFEX™ pretreated feedstocks. The analysis showed that all the selected variables (applied pressure, moisture content, hammer mill screen size, and feedstock) and their interactions had significant contribution in determining the pellet unit density ($p < 0.0001$). The diameter of pellets ranged from 6.36 to 6.55 mm designating the expansion of pellets after extruding from the die. Table 2.6 shows the pellet unit density of all untreated and AFEX™ pretreated samples. Pellet unit density of untreated and AFEX™ pretreated corn stover increased gradually with an increase in applied pressure and moisture content for all screen size samples. No increase in pellet unit density was observed when the moisture content was raised above 12% for untreated corn stover. Mani *et al* (2006) reported the significant role of moisture content in determining the bulk density of corn stover briquettes. Low moisture corn stover (5–10%) resulted in denser, more stable, and more durable briquettes than high moisture corn stover (15%). The study showed the occurrence of surface cracks when the moisture content of the feed was increased above 10 %. In this study, untreated corn stover produced maximum pellet unit densities of 1169.3 kg m^{-3} (2 mm hammer mill screen size) and 1153.6 kg m^{-3} (4 mm hammer mill screen size), when the moisture content was maintained at 12 %. AFEX™ pretreated corn stover (2 mm hammer mill screen size) produced pellets with unit density of 1419.4 kg m^{-3}. As the screen size was increased to 4 mm, pellets with unit density similar to the ones observed for 2 mm were produced at high loading and moisture content. A significant reduction in unit density of the pellets was observed at all moisture levels and loading conditions when the screen size was increased to 8 mm. The decrease in pellet unit density with increase in screen size can be attributed to smaller surface area available for binding. Increased surface area for smaller particle size aids in promoting better binding between the particles (Payne, 1978).

In the case of untreated prairie cord grass, a gradual increase in pellet unit density was observed as the moisture content was increased, and the maximum pellet unit density was obtained at the moisture content between 12 and 16 %. In all circumstances, AFEX™ pretreated prairie cord grass pellets unit density increased with increase in moisture content and applied pressure. At 20% moisture content, maximum pellet unit densities of 1430.7 kg m^{-3} and 1427.9 kg m^{-3} was produced at hammer mill screen size of 2 mm and 4 mm respectively. Untreated prairie cord grass produced relatively less unit density pellets in all the conditions. Pellets produced at 158.0 MPa applied pressure with 16% biomass moisture content (4 mm hammer mill screen size) had high unit density (1083.1 kg m^{-3}). Pellets with low unit density were produced with a screen size of 8 mm under all conditions. Increase in moisture content increased the pellet unit density of untreated and AFEX™ pretreated prairie cord grass.

AFEX™ pretreated switchgrass samples produced pellets with low unit density compared to AFEX™ pretreated corn stover and prairie cord grass pellets. In all cases, AFEX™ pretreated samples produced high density pellets. This might be due to the increased availability of lignin in the pretreated feedstocks for binding. AFEX™ pretreatment causes the biomass to swell and disrupt the lignocellulosic matrix structure, thus solubilizing and mobilizing the lignin to biomass surface (Dale, 1986; Chundawat *et al.,* 2011). This availability of lignin on the surface could have increased the binding property resulting in high density pellets. Shaw (2008) studied the effect of steam explosion pretreatment on the compression characteristics of poplar and wheat straw and had observed similar results. This increased density of the pellets can have significant reduction in cost associated with biomass transportation. Hoover *et al* (2014) stated the increase in bulk density of AFEX™ pellets in comparison with untreated corn stover pellets leads to benefits in transportation, as only fewer trips are necessary to transport the same quantity of material.

2.4.3. Compaction model results

Density data of the samples and the pressure applied to compress the biomass were fitted with Walker, Jones and Kawakitta Ludde models. Table 2.7 shows the model constants obtained after the pressure and density data were fitted to the Walker model (1). Constant 'm_1' in the equation represents the compressibility of the material. Compressibility is the change in density due to applied pressure (Peleg, 1973) and a higher extent indicates high compressibility of the material. Compressibility values of the samples ranged from 0.010 (AFEX™ pretreated corn stover, 4 mm, 20% wb) to 0.372 (untreated switchgrass, 4 mm, 8% wb). R^2 values for the fitting ranged from 0.64 (AFEX™ prairie cord grass, 8 mm, 20% wb) to 0.99 (corn stover 8 mm, 12% wb and prairie cord grass, 2 mm, 8% wb). It was found that an increase in moisture content decreased the compressibility values of all untreated and AFEX™ pretreated biomass samples. Minor increase in compressibility was noted for all three AFEX™ pretreated feedstocks when the hammer mill screen size was increased from 2 mm to 4 mm. The effect of hammer mill screen size for the untreated feedstocks was unclear. Untreated switchgrass was more compressible than untreated corn stover and prairie cord grass. Among AFEX™ pretreated samples, corn stover had high compressible value than all three biomass. AFEX™ pretreated samples showed decreased compressibility values signifying the impact of pretreatment. Shaw (2008) showed reduction in the compressibility, when poplar and wheat straw were subjected to steam expansion pretreatment.

Constant values of the Jones model were obtained when the logarithm of pellet unit density and applied pressure were fitted into the equation (2). Table 2.8 shows the constant values obtained from the Jones model. Similar to Walker model, the term ‘m_2’ in the Jones model represents the compressibility. Decrease in compressibility value was observed after the biomass were subjected to AFEX™ pretreatment. Besides, increment in moisture content decreased the compressibility representing the increased packing density of the biomass with increase in moisture. R^2 values for this model ranged from 0.53 (AFEX™ corn stover, 2 mm, 20% wb) to 0.99 (untreated corn stover 8 mm, 12% wb and untreated prairie cord grass, 2 mm, 8% wb). Hammer mill screen size showed no considerable effect on compressibility of AFEX™ pretreated feedstocks, whereas the increase in compressibility values were observed for untreated feedstocks with increase in hammer mill screen size.

One of the ideal requirements of a compaction equation is to have a sufficient accuracy, which can be defined in terms of the goodness of fit (Sonnergard, 2001). A higher degree of accuracy was obtained (R^2 values - 0.99 &1.00) when the data were fitted to Kawakita and Ludde model, representing the best fit conditions for all samples. Constant values obtained from the Kawakita and Ludde model are shown in Table 2.9. The term‘a’ in the model designates initial porosity of the sample and the value increased with an increase in hammer mill screen size. Among all untreated samples, corn stover (8 mm, 8% wb) had high initial porosity (0.938) and prairie cord grass (2 mm, 20% wb) had low porosity (0.817). In the case of AFEX™ pretreated samples, high initial porosity (0.909) was observed for corn stover and low porosity (0.827) for prairie cord grass. In the case of AFEX™ pretreated samples ‘a’ values ranged from 0.827 to 0.909, whereas untreated biomass samples ranged from 0.817 to 0.938. Denny (2002) identified that the constant ‘a’ does not represent initial porosity in all cases due to the non-linearity of the plots. Decrease in the initial porosity of the all the samples after AFEX™ pretreatment can be witnessed from Table 2.9 and Shaw (2008) observed similar decrease in initial porosity of poplar wood and wheat straw during steam explosion pretreatment. The author observed a weak relationship between the constant ‘a’ and the theoretical initial porosity. The other term ‘1/b’ in the model designates the yield strength or failure stress of the compacts, which in other words indicate the compressibility of the material (Kawakita and Ludde, 1971). Higher 1/b value was witnessed for untreated samples and the value ranged from 1.075 to 7.209. Relatively lower 1/b value was observed for pretreated samples, which signifies the impact of AFEX™ pretreatment and the requirement of less pressure to produce compacted biomass products. Adapa *et al* (2009) reported the impact of steam explosion pretreatment on barley, canola, oat and wheat straw grinds. AFEX™ pretreated corn stover (2 mm, 20% wb) produced low (0.033) and untreated prairie cord grass (4 mm, 8% wb) produced high yield strength value (7.209). Increase in the moisture content decreased the 1/b value implying the significance of moisture content in compacting. Mani *et al* (2003) stated the significance of moisture content, which plays a vital role in determining the density and strength of the densified products. In this study, lower values of yield strength were observed at high moisture content (16 and 20% wb) representing AFEX™ pretreated biomass at high moisture content leads to an onset of deformation at relatively low pressure. Moisture content had a mixed effect on the yield strength in the case of untreated biomass samples.

2.5. Conclusions

This study was intended to understand the compression mechanisms of untreated and AFEX™ pretreated corn stover, prairie cord grass and switchgrass. Single pelleting unit was employed for production of pellets and moisture content of the feedstocks, hammer mill screen size, and applied pressure were varied. The results of statistical analysis showed the moisture content, screen size, and applied pressure had significant effect on pellet unit density of both AFEX™ pretreated and untreated biomass samples ($p < 0.0001$). Pellets produced from 8 mm hammer mill screen size feedstocks exhibited lowest pellet unit density. Compression data obtained from different conditions were fitted with different compaction models. Kawakita and Ludde model provided the best fit for all biomass (R^2- 0.99 & 1.00) among the three models selected. Constant value '1/b' represents the yield strength, and lower value for AFEX™ pretreated biomass signifies the impact of pretreatment making the biomass to compress with less pressure. Lower values of yield strength were observed at high moisture content (16 and 20% wb) indicating AFEX™ pretreated biomass at high moisture content leads to an onset of deformation at relatively low pressure. Moisture content plays a vital role in compacting AFEX™ pretreated biomass samples and also, increase in the moisture content reduced the application of load to obtain highly compacted pellets.

Table 2.1. AFEX™ pretreatment conditions employed for different biomass*

Feedstock	NH_3 loading NH_3 to dry biomass loading (w/w)	Moisture content (db %)	Pretreatment soaking time (min)
Corn stover	1:1	60	15
Prairie cordgrass	1:2	40	30
Switchgrass	1:2	50	30

**Pretreatment was carried out at 100°C*

Table 2.2. Experimental variables

Feedstock	Corn stover, Prairie cordgrass, Switchgrass, AFEX™ Corn stover, AFEX™ Prairie cordgrass, and AFEX™ Switchgrass
Moisture content (% wet basis)	8,12,16, and 20
Load (N)	1000, 2000, 3000, 4000, and 5000
Hammer mill screen size (mm)	2, 4, and 8

Table 2.3. Bulk and particle density of untreated and AFEX™ pretreated corn stover, prairie cord grass, and switchgrass*

Hammer mill Screen size (mm)	Moisture content (%) w.b	Bulk density (kg/m^3)		Particle density (kg/m^3)	
		Untreated CS	**AFEX™ CS**	**Untreated CS**	**AFEX™ CS**
2	8	111.33 ± 0.9[31]	199.41 ± 2.6[8]	970.94 ±4.4[21]	1345.80 ± 9.2[9-11]
	12	118.90 ±1.3[30]	202.00 ± 3.7[7,8]	960.02 ± 8.2[22,23]	1336.12 ± 9.6[11,12]
	16	124.79± 2.6[29]	209.54 ± 2.8[6]	947.06 ± 7.3[24-26]	1325.56 ± 6.7[12-14]
	20	127.12 ± 0.6[29]	216.06 ± 2.9[5]	941.26 ± 8.8[26,27]	1321.36 ± 6.0[13,14]
4	8	97.30 ± 1.1[35-37]	179.77 ± 2.6[10,11]	954.85 ± 8.2[23,24]	1325.47 ± 10.5[12-14]
	12	100.04 ± 2.4[33,34]	192.33 ± 3.7[9]	939.66 ± 9.1[26,27]	1317.06 ± 10.0[13-15]
	16	104.42 ± 1.3[32]	199.83 ± 2.8[8]	919.50 ± 8.0[28]	1308.47 ± 9.0[15-17]
	20	108.82 ±1.4[31]	206.01 ± 2.9[6]	895.06 ± 6.8[29,30]	1302.10 ± 9.1[17]
8	8	79.21 ± 5.9[41,42]	134.12 ± 1.1[27]	842.32 ± 9.0[31,32]	1322.82 ± 9.2[13,14]
	12	82.47 ± 2.4[40]	138.08 ± 2.1[25,26]	834.47 ± 7.7[32-34]	1320.76 ± 11.7[13,14]
	16	88.47 ± 2.3[39]	142.46 ± 2.0[23]	830.90 ± 4.7[33,34]	1305.39 ± 5.7[16,17]
	20	91.35 ± 3.0[38]	150.18 ± 1.9[21,22]	824.37 ± 10.1[34]	1301.38 ± 13.8[17]
		Untreated PCG	**AFEX™ PCG**	**Untreated PCG**	**AFEX™ PCG**
2	8	199.54 ± 1.0[8]	232.09 ± 2.3[4]	1069.38 ± 7.6[18]	1435.17 ± 8.1[1,2]
	12	203.53 ± 2.3[7]	235.90 ± 1.3[3]	1062.68 ± 5.6[18]	1427.07 ± 3.9[2,3]
	16	207.86 ± 2.8[6]	243.68 ± 2.2[2]	1051.11 ± 3.2[19]	1419.86 ± 3.9[3,4]
	20	217.36 ± 1.7[5]	250.90 ± 1.7[1]	1043.70 ± 7.8[19]	1408.68 ± 8.3[5,6]
4	8	155.98 ± 1.3[19]	163.33 ± 1.3[16,17]	988.88 ± 8.0[20]	1441.38 ± 9.5[1]
	12	159.92 ± 2.5[18]	169.16 ± 1.7[13,14]	960.80 ± 5.8[21-23]	1438.36 ± 9.4[1]
	16	164.90 ± 2.4[15,16]	172.27 ± 2.4[12]	942.12 ± 4.7[25-27]	1418.76 ± 5.8[3-5]
	20	167.53 ± 2.2[14,15]	177.60 ± 2.2[11]	935.05 ± 9.2[27]	1415.63 ± 6.9[4,5]

8	8	95.41 ± 3.9[37]	134.42 ± 1.3[27]	966.87 ± 9.9[21,22]	1399.05 ± 8.6[6]
	12	98.57 ± 2.6[34-36]	139.23 ± 2.5[24,25]	960.68 ± 7.0[21-23]	1387.62 ± 14.8[7]
	16	101.54 ± 4.0[33,34]	135.81 ± 3.8[26,27]	952.88 ± 6.3[23-25]	1380.46 ± 2.8[7]
	20	103.47 ± 2.8[32,33]	141.38 ±2.7[23]	942.63 ± 10.0[25-27]	1363.24 ± 14.0[8]
		Untreated SG	**AFEX™ SG**	**Untreated SG**	**AFEX™ SG**
2	8	142.95 ± 0.9[23]	179.96 ± 1.8[10,11]	915.10 ± 6.5[28]	1363.78 ± 9.9[8]
	12	148.55 ± 1.7[22]	181.96 ± 1.3[10]	912.41 ± 8.4[28]	1355.64 ± 3.4[8,9]
	16	152.37 ± 1.7[20,21]	187.93 ± 2.3[9]	901.89 ± 4.6[29]	1347.34 ± 3.4[9,10]
	20	154.75 ± 1.3[19,20]	190.45 ± 2.9[9]	891.41 ± 8.9[30]	1339.30 ± 8.9[10,11]
4	8	96.07 ± 2.2[36,37]	160.75 ± 2.1[17,18]	892.53 ± 5.0[29,30]	1350.65 ± 9.8[9]
	12	99.42 ± 1.9[34,35]	168.91 ± 1.7[14]	852.44 ± 9.9[31]	1339.45 ± 10.2[10,11]
	16	104.89 ± 1.3[32]	171.74 ± 2.0[12,13]	836.51 ± 8.8[32,33]	1326.84 ± 6.2[12,13]
	20	109.84 ± 1.8[31]	177.88 ± 1.3[11]	830.27 ± 9.9[33,34]	1315.65 ± 10.5[14-16]
8	8	76.24 ± 1.8[43]	130.48 ± 2.4[28]	779.94 ± 8.9[35]	1338.77 ± 8.5[10,11]
	12	77.65 ± 3.8[42,43]	136.12 ± 1.1[26,27]	774.01 ± 12.2[35,36]	1327.22 ± 9.9[12,13]
	16	80.74 ± 2.0[40,41]	140.03 ± 2.1[23,24]	771.45 ± 9.0[35,36]	1321.90 ± 5.9[13,14]
	20	82.46± 2.3[40]	147.19 ± 2.4[22]	769.29 ± 6.9[36]	1320.48 ± 9.7[13,14]

*CS-Corn stover; PCG-Prairie cord grass; SG-Switchgrass. *Means sharing the same superscript numbers for a given property between the two columns are not significantly different ($p < 0.05$).*

Table 2.4. ANOVA for factors affecting bulk density and particle density

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Bulk density					
FS	5	457285.73	91457.14	16341.9	<.0001
SS	2	75050.97	37525.48	6705.19	<.0001
FS*SS	10	157162.89	15716.28	2808.24	<.0001
MC	3	5548.82	1849.60	330.49	<.0001
FS*MC	15	2002.91	133.52	23.86	<.0001
SS*MC	6	91140.40	15190.06	2714.22	<.0001
FS*SS*MC	30	125611.73	4187.05	748.16	<.0001
Particle density					
FS	5	18594599.42	3718919.88	53062.9	<.0001
SS	2	225245.03	112622.51	1606.94	<.0001
FS*SS	10	249540.68	24954.07	356.05	<.0001
MC	3	61448.57	20482.86	292.26	<.0001
FS*MC	15	12157.42	810.49	11.56	<.0001
SS*MC	6	6165.52	1027.59	14.66	<.0001
FS*SS*MC	30	13268.49	442.28	6.31	<.0001

**FS – Feedstock; SS – Screen size; MC – Moisture content;*

Table 2.5. ANOVA for factors affecting pellet unit density of untreated and AFEX™ pretreated feedstocks

Source	DF	Type I SS	Mean Square	F Value	Pr > F
FS	5	45847370.64	9169474.13	169563	<.0001
SS	2	2428375.94	1214187.97	22452.9	<.0001
FS*SS	10	607678.30	60767.83	1123.72	<.0001
MC	3	853307.99	284436.00	5259.82	<.0001
FS*MC	15	499873.63	33324.91	616.25	<.0001
SS*MC	6	30198.51	5033.09	93.07	<.0001
FS*SS*MC	30	256999.91	8566.66	158.42	<.0001
PR	4	4954803.05	1238700.76	22906.2	<.0001
FS*PR	20	735717.04	36785.85	680.25	<.0001
SS*PR	8	41681.44	5210.18	96.35	<.0001
FS*SS*PR	40	340287.45	8507.19	157.32	<.0001
MC*PR	12	192285.39	16023.78	296.31	<.0001
FS*MC*PR	60	162720.21	2712.00	50.15	<.0001
SS*MC*PR	24	32408.32	1350.35	24.97	<.0001
FS*SS*MC*PR	120	164514.19	1370.95	25.35	<.0001

**FS – Feedstock; SS – Screen size; MC – Moisture content; PR – Applied pressure*

Table 2.6. Pellet unit density of untreated and AFEX™ pretreated samples

Moisture (%) wb	Applied pressure (MPa)	Pellet unit density (kg/m^3)					
		Untreated CS	Untreated PCG	Untreated SG	AFEX™ CS	AFEX™ PCG	AFEX™ SG
		2 mm hammer mill screen size					
	31.6	1044.6 ± 4.1$^{108-110}$	770.9 ± 8.6^{155,156}	702.9 ± 11.1^{168}	1065.3 ± 8.4^{103,104}	1158.5 ± 4.6$^{82-86}$	1135.8 ± 9.7$^{89-91}$
	63.2	1108.4 ± 6.7$^{95-97}$	910.6 ± 6.8^{132,133}	737.8 ± 8.5$^{159-161}$	1216.5 ± 3.03$^{70-73}$	1191.3 ± 4.0^{76,77}	1216.3 ± 3.7$^{70-73}$
8	94.8	1159.5 ± 4.6$^{82-86}$	983.2 ± 2.5$^{118-121}$	811.1 ± 4.9$^{149-151}$	1283.7 ± 2.5$^{52-59}$	1223.2 ± 4.9$^{69-71}$	1260.3 ± 3.3$^{62-65}$
	126.4	1159.6 ± 7.4$^{82-86}$	1026.2 ± 7.3$^{113-115}$	951.3 ± 5.6$^{125-127}$	1313.1 ± 6.2$^{37-42}$	1266.0 ± 8.8$^{60-64}$	1274.6 ± 2.3$^{58-60}$
	158.0	1153.1 ± 3.8$^{84-87}$	1064.5 ± 5.4$^{103-105}$	1039.1 ± 7.9$^{109-111}$	1358.5 ± 3.7$^{25-29}$	1294.8 ± 7.6$^{47-53}$	1318.7 ± 5.0$^{35-40}$
	31.6	1086.0 ± 10.4^{100,101}	876.6 ± 6.9^{136,137}	723.9 ± 7.9$^{162-165}$	1297.3 ± 5.2$^{46-49}$	1179.3 ± 8.9$^{78-80}$	1101.1 ± 10.1$^{97-99}$
	63.2	1132.5 ± 3.4$^{90-92}$	929.0 ± 9.1$^{128-130}$	767.2 ± 6.4^{156,157}	1325.3 ± 8.6$^{34-36}$	1212.9 ± 12.3$^{71-73}$	1276.1 ± 6.5$^{55-60}$
12	94.8	1165.7 ± 1.9$^{81-83}$	1010.0 ± 8.0^{117}	835.9 ± 4.3$^{143-145}$	1392.4 ± 11.1$^{13-17}$	1254.6 ± 6.6^{64,65}	1322.3 ± 9.2$^{35-39}$
	126.4	1148.9 ± 12.0$^{86-88}$	1026.6 ± 5.8$^{112-115}$	976.5 ± 8.4$^{119-121}$	1409.2 ± 0.5$^{5-11}$	1323.5 ± 6.4$^{35-37}$	1353.6 ± 6.7$^{27-30}$
	158.0	1169.3 ± 9.2$^{80-82}$	1062.5 ± 3.1$^{103-105}$	1058.2 ± 7.6$^{104-107}$	1410.8 ± 8.2$^{5-9}$	1345.0 ± 9.6$^{30-32}$	1363.3 ± 7.2$^{24-27}$
	31.6	1083.7 ± 7.9^{100,101}	833.4 ± 8.5$^{144-146}$	714.9 ± 8.1$^{165-167}$	1388.0 ± 5.4$^{15-19}$	1325.9 ± 5.1$^{34-36}$	1300.1 ± 6.0$^{43-47}$
	63.2	1113.1 ± 8.6$^{94-96}$	903.1 ± 4.7^{133,134}	739.8 ± 8.2^{159,160}	1397.6 ± 5.5$^{11-16}$	1393.8 ± 3.6$^{12-17}$	1345.3 ± 6.6$^{30-32}$
16	94.8	1130.4 ± 7.8$^{91-93}$	957.6 ± 5.1$^{124-126}$	869.7 ± 6.6^{137,138}	1405.1 ± 3.3$^{7-12}$	1397.7 ± 6.7$^{12-16}$	1348.0 ± 2.2$^{29-32}$
	126.4	1169.6 ± 5.6$^{80-82}$	1013.5 ± 2.9^{116,117}	990.5 ± 4.5^{118}	1417.7 ± 4.3$^{2-5}$	1400.8 ± 8.1$^{9-13}$	1369.1 ± 4.2$^{21-25}$
	158.0	1155.5 ± 7.7$^{83-87}$	1054.3 ± 2.7$^{104-108}$	1083.1 ± 5.4$^{100-102}$	1419.4 ± 12.1$^{1-5}$	1402.2 ± 6.1$^{7-13}$	1372.4 ± 7.1$^{20-23}$
	31.6	1053.7 ± 10.9$^{105-108}$	840.3 ± 9.4$^{142-145}$	712.8 ± 5.6$^{165-168}$	1400.5 ± 13.5$^{9-13}$	1371.1 ± 9.8$^{20-23}$	1302.9 ± 14.2$^{42-47}$
	63.2	1113.6 ± 7.5$^{94-96}$	912.2 ± 7.2$^{131-133}$	742.6 ± 6.5^{159}	1415.2 ± 5.4$^{4-6}$	1415.7 ± 7.5$^{4-6}$	1376.4 ± 7.2$^{19-23}$
20	94.8	1115.6 ± 6.8^{94,95}	967.9 ± 9.7$^{122-124}$	822.9 ± 7.4$^{146-148}$	1420.0 ± 9.9$^{1-5}$	1416.1 ± 9.6$^{3-6}$	1378.5 ± 4.5$^{18-22}$
	126.4	1172.5 ± 10.6$^{79-81}$	1033.7 ± 8.2$^{110-113}$	971.7 ± 8.8$^{121-123}$	1413.3 ± 5.0$^{5-7}$	1427.9 ± 7.2^{1,2}	1382.8 ± 8.5$^{17-20}$
	158.0	1157.1 ± 2.1$^{83-86}$	1065.4 ± 5.9^{103,104}	1078.2 ± 2.8^{101,102}	1414.5 ± 8.0^{5,6}	1430.7 ± 7.6^{1}	1388.5 ± 10.4$^{14-18}$
		4 mm hammer mill screen size					
	31.6	954.6 ± 7.8^{125,126}	671.4 ± 9.6^{170}	615.9 ± 10.2^{173}	1065.1 ± 8.1^{103,104}	1195.1 ± 9.7^{75,76}	1155.2 ± 13.1$^{83-87}$
	63.2	1061.8 ± 6.4$^{103-105}$	733.5 ± 6.0$^{159-162}$	705.2 ± 7.6^{167,168}	1230.0 ± 7.8^{68,69}	1205.9 ± 12.3$^{73-75}$	1182.2 ± 7.3$^{77-79}$
8	94.8	1102.1 ± 7.3$^{96-98}$	853.4 ± 5.4^{140,141}	797.9 ± 7.6^{152,153}	1294.8 ± 7.6$^{47-53}$	1221.2 ± 14.1$^{69-72}$	1224.8 ± 10.8^{69,70}
	126.4	1135.0 ± 6.9$^{89-91}$	1028.0 ± 12.1$^{111-114}$	925.6 ± 8.4^{129,130}	1339.4 ± 2.5$^{31-33}$	1258.1 ± 7.8$^{64-66}$	1253.3 ± 4.5^{65,66}
	158.0	1142.5 ± 10.7$^{88-90}$	1056.0 ± 5.7$^{104-108}$	947.5 ± 3.2^{126,127}	1364.6 ± 8.6$^{24-27}$	1295.8 ± 12.3$^{47-52}$	1299.5 ± 6.3$^{44-48}$
	31.6	971.4 ± 5.2$^{121-123}$	720.3 ± 7.9$^{163-165}$	645.9 ± 7.7^{171,172}	1164.0 ± 6.3$^{81-84}$	1253.0 ± 7.5^{65,66}	1089.3 ± 10.5$^{99-101}$
	63.2	1083.5 ± 4.8$^{100-102}$	803.7 ± 6.9$^{149-152}$	727.0 ± 8.6$^{161-164}$	1253.8 ± 1.3^{65,66}	1361.5 ± 9.4$^{24-27}$	1242.2 ± 5.1^{66,67}
12	94.8	1104.3 ± 5.2$^{95-98}$	892.2 ± 4.3^{134,135}	812.3 ± 9.1$^{147-150}$	1366.6 ± 12.2$^{24-26}$	1400.1 ± 3.3$^{9-14}$	1284.3 ± 11.1$^{51-58}$
	126.4	1123.2 ± 7.4$^{92-94}$	1030.2 ± 3.1$^{111-114}$	903.1 ± 1.4^{134}	1382.6 ± 4.4$^{17-20}$	1411.7 ± 8.7$^{5-9}$	1299.3 ± 6.1$^{44-48}$
	158.0	1153.6 ± 6.9$^{84-87}$	1079.0 ± 8.8^{101,102}	952.6 ± 7.1^{125,126}	1401.2 ± 8.8$^{9-13}$	1415.8 ± 4.3$^{4-6}$	1303.4 ± 9.1$^{42-47}$

16	31.6	962.8 ± 9.9$^{123-125}$	801.8 ± 0.5$^{150-152}$	689.0 ± 8.7^{169}	1282.7 ± 4.9$^{54-59}$	1268.2 ± 10.9$^{60-63}$	1142.9 ± 11.2$^{88-90}$
	63.2	1032.5 ± 6.1$^{111-113}$	844.8 ± 3.9$^{141-143}$	729.2 ± 4.4$^{160-164}$	1391.8 ± 14.6$^{13-17}$	1362.0 ± 9.5$^{24-27}$	1262.8 ± 6.5$^{61-64}$
	94.8	1059.3 ± 5.8$^{104-106}$	918.5 ± 7.9$^{130-132}$	808.8 ± 8.7$^{149-152}$	1393.4 ± 6.8$^{12-17}$	1379.6 ± 7.6$^{18-21}$	1303.2 ± 13.4$^{42-47}$
	126.4	1131.5 ± 7.9$^{90-93}$	1062.8 ± 3.9$^{103-105}$	871.0 ± 5.1^{137,138}	1395.3 ± 4.2$^{12-16}$	1412.8 ± 8.9$^{5-8}$	1322.8 ± 9.3$^{35-38}$
	158.0	1144.4 ± 6.1$^{87-89}$	1088.4 ± 5.7^{100,101}	923.1 ± 8.0^{130,131}	1397.9 ± 8.8$^{10-15}$	1419.2 ± 5.4$^{1-5}$	1350.2 ± 8.7$^{28-31}$
20	31.6	935.5 ± 3.2^{128,129}	808.0 ± 11.5$^{149-152}$	680.9 ± 5.8^{169,170}	1386.0 ± 7.0$^{16-19}$	1345.8 ± 3.2$^{30-32}$	1274.5 ± 9.9$^{58-61}$
	63.2	1044.5 ± 6.2$^{108-110}$	866.1 ± 4.2$^{137-139}$	740.1 ± 6.9^{159,160}	1409.6 ± 4.7$^{5-10}$	1396.4 ± 10.1$^{12-16}$	1336.4 ± 2.9$^{32-34}$
	94.8	1046.5 ± 4.8$^{107-109}$	940.5 ± 9.1^{127,128}	829.5 ± 8.8^{145,146}	1410.4 ± 8.5$^{5-9}$	1396.9 ± 9.9$^{12-16}$	1355.0 ± 2.2$^{26-30}$
	126.4	1120.4 ± 6.8^{93,94}	1032.7 ± 7.2$^{111-113}$	854.4 ± 4.0$^{139-141}$	1410.6 ± 13.6$^{5-9}$	1426.5 ± 4.0$^{1-4}$	1359.1 ± 7.6$^{25-28}$
	158.0	1145.0 ± 3.0$^{87-89}$	1059.7 ± 3.0$^{104-106}$	909.4 ± 6.3^{132,133}	1411.3 ± 2.1$^{5-9}$	1427.6 ± 3.8$^{1-3}$	1367.2 ± 3.4$^{22-25}$
				8 mm hammer mill screen size			
8	31.6	682.7 ± 8.3^{169,170}	656.7 ± 7.1^{171}	589.5 ± 5.6^{174}	1052.9 ± 4.3$^{105-108}$	1071.9 ± 7.3^{102,103}	1087.2 ± 8.02^{100,101}
	63.2	849.5 ± 5.3$^{140-142}$	706.4 ± 7.9$^{166-168}$	657.0 ± 4.9^{171}	1206.0 ± 7.6$^{73-75}$	1211.2 ± 9.1$^{72-74}$	1206.3 ± 1.9$^{73-75}$
	94.8	977.0 ± 1.4$^{119-121}$	757.7 ± 4.6^{157,158}	731.0 ± 8.2$^{159-162}$	1259.3 ± 3.4$^{63-65}$	1225.7 ± 7.1^{69,70}	1225.7 ± 7.0^{69,70}
	126.4	1020.5 ± 8.8$^{114-117}$	823.6 ± 8.2^{146,147}	799.5 ± 4.3$^{151-153}$	1275.6 ± 9.9$^{56-60}$	1277.4 ± 10.7$^{54-60}$	1276.1 ± 8.9$^{55-60}$
	158.0	1063.4 ± 1.7$^{103-105}$	890.7 ± 6.5^{135}	828.8 ± 6.9^{145,146}	1300.3 ± 7.6$^{43-47}$	1283.9 ± 5.3$^{52-58}$	1284.7 ± 5.3$^{50-58}$
12	31.6	775.1 ± 6.8^{155,156}	723.9 ± 7.9$^{162-165}$	642.5 ± 3.2^{172}	1092.8 ± 8.5$^{98-100}$	1163.7 ± 2.1$^{81-85}$	1152.0 ± 5.0$^{85-88}$
	63.2	877.1 ± 5.5^{136,137}	767.2 ± 6.4^{156,157}	726.8 ± 8.2$^{161-164}$	1232.3 ± 8.9$^{67-69}$	1260.6 ± 10.8$^{62-65}$	1251.8 ± 9.9^{65,66}
	94.8	985.7 ± 9.7$^{118-120}$	812.3 ± 9.2$^{147-150}$	755.3 ± 2.7^{158}	1270.8 ± 1.8$^{60-62}$	1269.1 ± 15.6$^{60-63}$	1276.7 ± 8.3$^{54-60}$
	126.4	1023.1 ± 4.4$^{113-116}$	903.6 ± 9.4^{133,134}	814.1 ± 12.0$^{147-149}$	1288.5 ± 7.3$^{48-54}$	1287.4 ± 2.9$^{50-56}$	1287.2 ± 7.7$^{49-56}$
	158.0	1038.3 ± 8.9$^{109-112}$	918.1 ± 3.4$^{130-132}$	876.8 ± 3.3^{136,137}	1295.8 ± 6.5$^{47-51}$	1296.4 ± 5.6$^{46-49}$	1297.3 ± 4.5$^{46-49}$
16	31.6	832.2 ± 4.9^{145,146}	690.5 ± 7.6^{169}	643.4 ± 2.7^{172}	1194.8 ± 6.5$^{75.76}$	1237.6 ± 9.8^{67,68}	1188.9 ± 1.1$^{76-78}$
	63.2	887.0 ± 9.5^{135,136}	704.8 ± 3.8^{167,168}	741.6 ± 1.2^{159}	1251.6 ± 6.5^{65,66}	1283.2 ± 6.2$^{53-59}$	1284.7 ± 3.8$^{50-58}$
	94.8	975.4 ± 5.8$^{120-122}$	782.2 ± 8.9^{154,155}	776.1 ± 4.8^{155,156}	1294.8 ± 7.6$^{47-53}$	1306.4 ± 3.1$^{41-46}$	1298.5 ± 7.8$^{46-49}$
	126.4	1022.4 ± 2.4$^{113-116}$	847.8 ± 4.9^{141,142}	811.7 ± 1.8$^{148-150}$	1269.5 ± 8.1$^{60-63}$	1311.6 ± 10.2$^{38-44}$	1310.7 ± 3.1$^{39-45}$
	158.0	1049.7 ± 5.4$^{106-109}$	893.3 ± 7.9^{134,135}	859.8 ± 8.8^{139,140}	1302.9 ± 11.3$^{43-47}$	1311.8 ± 5.1$^{37-43}$	1322.5 ± 0.5$^{35-38}$
20	31.6	846.7 ± 2.6$^{141-143}$	685.8 ± 6.6^{169}	644.6 ± 6.8^{172}	1252.4 ± 6.5^{65,66}	1272.4 ± 5.5$^{59-61}$	1200.7 ± 8.7$^{74-76}$
	63.2	891.3 ± 5.1^{135}	717.6 ± 9.9$^{164-166}$	723.4 ± 3.9$^{162-165}$	1295.4 ± 10.1$^{47-52}$	1300.0 ± 6.1$^{44-48}$	1275.3 ± 4.2$^{57-60}$
	94.8	987.5 ± 3.4^{118,119}	823.8 ± 5.3^{146,147}	789.5 ± 11.8^{153,154}	1315.6 ± 0.6$^{36-41}$	1304.2 ± 2.5$^{41-47}$	1286.9 ± 7.7$^{49-56}$
	126.4	1016.0 ± 9.1$^{115-117}$	865.4 ± 7.4$^{137-139}$	801.5 ± 2.2$^{150-152}$	1299.8 ± 8.5$^{44-48}$	1305.8 ± 0.9$^{41-47}$	1308.0 ± 1.5$^{40-46}$
	158.0	1047.1 ± 8.6$^{107-109}$	897.2 ± 7.2^{133,134}	867.6 ± 7.5^{137,138}	1329.9 ± 5.6$^{33-35}$	1326.4 ± 0.5$^{34-36}$	1348.4 ± 1.8$^{29-31}$

**CS – Corn stover; PCG – Prairie cord grass; SG – Switchgrass; Means sharing the same superscript numbers between the columns are not significantly different from each other ($p < 0.05$).*

Table 2.7. Model values obtained from Walker model (1923)

Screen size (mm)	Moisture content (%)	m_1	z_1	R^2	SSE*	m_1	z_1	R^2	SSE*
	Untreated Corn stover					**AFEX™ Corn stover**			
2	8	-0.237	5.522	0.91	0.053	-0.097	2.872	0.98	0.008
	12	-0.199	4.805	0.94	0.036	-0.144	3.686	0.91	0.032
	16	-0.192	4.696	0.89	0.049	-0.032	1.583	0.94	0.005
	20	-0.181	4.481	0.93	0.035	-0.037	1.655	0.80	0.013
4	8	-0.103	2.779	0.96	0.015	-0.169	4.156	0.96	0.024
	12	-0.090	2.510	0.93	0.017	-0.126	3.307	0.96	0.017
	16	-0.096	2.616	0.97	0.011	-0.049	1.862	0.74	0.021
	20	-0.105	2.765	0.95	0.017	-0.010	1.108	0.75	0.004
8	8	-0.271	5.864	0.97	0.033	-0.158	3.971	0.95	0.023
	12	-0.185	4.288	0.99	0.008	-0.113	3.138	0.91	0.025
	16	0.134	3.332	0.98	0.010	-0.062	2.179	0.97	0.007
	20	-0.136	3.341	0.97	0.016	-0.034	1.624	0.97	0.003
	Untreated Prairie cord grass					**AFEX™ Prairie cord grass**			
2	8	-0.257	5.808	0.99	0.014	-0.080	2.640	0.94	0.013
	12	-0.233	5.360	0.96	0.034	-0.096	2.883	0.92	0.019
	16	-0.230	5.308	0.96	0.033	-0.034	1.660	0.79	0.012
	20	-0.173	4.241	0.93	0.033	-0.026	1.470	0.89	0.006
4	8	-0.359	7.725	0.94	0.065	-0.055	2.176	0.86	0.016
	12	-0.285	6.284	0.97	0.035	-0.083	2.568	0.91	0.018
	16	-0.191	4.501	0.89	0.047	-0.074	2.386	0.95	0.012
	20	-0.179	4.276	0.96	0.024	-0.037	1.695	0.94	0.006
8	8	-0.235	5.567	0.95	0.037	-0.129	3.511	0.95	0.020
	12	-0.183	4.521	0.93	0.035	-0.077	2.517	0.90	0.018
	16	-0.203	4.941	0.89	0.052	-0.041	1.817	0.92	0.008
	20	-0.216	5.140	0.93	0.041	-0.010	1.233	0.64	0.005
	Untreated Switchgrass					**AFEX™ Switchgrass**			
2	8	-0.223	5.204	0.91	0.050	-0.099	2.907	0.98	0.008
	12	-0.188	4.549	0.92	0.038	-0.146	3.740	0.91	0.033
	16	-0.183	4.472	0.89	0.047	-0.044	1.809	0.78	0.033
	20	-0.171	4.244	0.93	0.033	-0.024	1.398	0.89	0.006
4	8	-0.372	7.918	0.97	0.045	-0.078	2.530	0.93	0.015
	12	-0.328	7.020	0.97	0.041	-0.125	3.373	0.88	0.033
	16	-0.284	6.175	0.94	0.052	-0.108	3.016	0.95	0.017
	20	-0.279	6.096	0.93	0.055	-0.042	1.764	0.91	0.009
8	8	-0.248	5.633	0.98	0.018	-0.117	3.248	0.96	0.015
	12	-0.191	4.523	0.97	0.020	-0.078	2.497	0.90	0.018
	16	-0.180	4.311	0.98	0.016	-0.068	2.285	0.90	0.016
	20	-0.184	4.371	0.98	0.016	-0.068	2.278	0.96	0.009

**SSE - Sum of squared errors*

Table 2.8. Model values obtained from Jones model (1960)

Screen size (mm)	Moisture content (%)	m_2	z_2	R^2	SSE*	m_2	z_2	R^2	SSE*
		Untreated Corn stover				**AFEX™ Corn stover**			
2	8	0.067	5.802	0.89	0.017	0.148	4.416	0.98	0.014
	12	0.044	6.234	0.87	0.012	0.058	0.928	0.92	0.011
	16	0.045	6.198	0.91	0.010	0.014	0.954	0.95	0.002
	20	0.062	5.891	0.89	0.015	0.005	7.144	0.53	0.004
4	8	0.133	4.911	0.96	0.015	0.154	4.322	0.97	0.018
	12	0.101	5.144	0.94	0.017	0.122	4.947	0.96	0.017
	16	0.109	4.973	0.96	0.014	0.050	6.295	0.74	0.021
	20	0.121	4.753	0.95	0.020	0.010	7.052	0.75	0.004
8	8	0.277	1.764	0.98	0.022	0.140	4.541	0.97	0.018
	12	0.196	3.238	0.99	0.007	0.102	5.249	0.92	0.021
	16	0.151	4.096	0.98	0.014	0.059	6.051	0.97	0.006
	20	0.154	4.055	0.97	0.019	0.033	6.552	0.97	0.003
		Untreated Prairie cord grass				**AFEX™ Prairie cord grass**			
2	8	0.220	2.838	0.99	0.008	0.068	5.862	0.94	0.012
	12	0.200	3.213	0.97	0.024	0.084	5.599	0.92	0.018
	16	0.155	4.057	0.94	0.027	0.033	6.623	0.79	0.012
	20	0.198	3.232	0.97	0.022	0.025	6.782	0.89	0.006
4	8	0.302	1.236	0.92	0.064	0.047	6.251	0.85	0.014
	12	0.258	2.079	0.95	0.041	0.077	5.815	0.91	0.016
	16	0.185	3.444	0.87	0.051	0.070	5.945	0.95	0.010
	20	0.176	3.621	0.95	0.027	0.036	6.574	0.94	0.006
8	8	0.183	3.290	0.93	0.035	0.108	5.124	0.96	0.015
	12	0.155	3.880	0.92	0.032	0.068	5.888	0.91	0.015
	16	0.145	4.004	0.83	0.044	0.038	6.471	0.92	0.007
	20	0.174	3.500	0.89	0.035	0.010	6.992	0.64	0.005
		Untreated Switchgrass				**AFEX™ Switchgrass**			
2	8	0.198	3.097	0.89	0.040	0.088	5.505	0.98	0.007
	12	0.171	3.603	0.92	0.035	0.132	4.732	0.92	0.020
	16	0.163	3.717	0.88	0.044	0.033	6.601	0.94	0.005
	20	0.153	3.894	0.92	0.032	0.038	6.520	0.80	0.013
4	8	0.326	0.734	0.94	0.056	0.070	5.823	0.92	0.014
	12	0.312	1.038	0.94	0.052	0.112	5.081	0.89	0.014
	16	0.287	1.516	0.92	0.061	0.101	5.305	0.96	0.014
	20	0.282	1.598	0.90	0.068	0.043	6.415	0.92	0.007
8	8	0.219	2.573	0.98	0.021	0.103	5.207	0.97	0.012
	12	0.182	3.309	0.96	0.024	0.072	5.806	0.91	0.016
	16	0.171	3.505	0.98	0.013	0.071	5.857	0.91	0.014
	20	0.176	3.416	0.98	0.018	0.065	5.958	0.96	0.008

**SSE - Sum of squared errors*

Table 2.9. Kawakita and Ludde (1971) model constant values

Screen size (mm)	Moisture content (%)	1/b (1/MPa)	a	R^2	SSE	1/b (1/MPa)	a	R^2	SSE
	Untreated Corn stover					**AFEX™ Corn stover**			
2	8	3.251	0.897	0.99	0.94	2.371	0.863	1.00	0.19
	12	3.089	0.887	0.99	0.94	0.887	0.861	1.00	0.20
	16	3.341	0.878	0.99	0.99	0.253	0.853	1.00	0.06
	20	2.996	0.871	0.99	0.79	0.032	0.847	1.00	0.05
4	8	0.825	0.919	1.00	0.04	1.407	0.873	1.00	0.03
	12	0.769	0.917	1.00	0.11	1.136	0.859	1.00	0.17
	16	1.075	0.914	1.00	0.26	0.312	0.851	1.00	0.11
	20	1.207	0.910	1.00	0.30	0.067	0.847	1.00	0.02
8	8	2.035	0.938	1.00	0.07	1.918	0.909	1.00	0.04
	12	1.614	0.929	1.00	0.18	1.377	0.907	1.00	0.11
	16	1.383	0.923	1.00	0.25	0.934	0.900	1.00	0.09
	20	1.388	0.921	1.00	0.23	0.541	0.894	1.00	0.07
	Untreated Prairie cord grass					**AFEX™ Prairie cord grass**			
2	8	5.659	0.842	0.99	0.72	1.786	0.827	0.99	0.51
	12	4.904	0.832	0.99	0.58	2.161	0.833	0.99	0.63
	16	3.962	0.822	0.99	0.94	0.448	0.828	1.00	0.11
	20	5.370	0.817	1.00	0.19	0.398	0.826	1.00	0.04
4	8	7.209	0.885	0.99	1.28	0.841	0.877	1.00	0.32
	12	5.892	0.877	0.99	1.33	0.738	0.884	1.00	0.08
	16	4.268	0.862	0.99	1.39	0.760	0.882	1.00	0.06
	20	3.971	0.858	0.99	0.89	0.425	0.878	1.00	0.08
8	8	2.728	0.903	0.99	0.78	1.024	0.900	1.00	0.10
	12	2.115	0.902	0.99	0.60	0.584	0.896	1.00	0.05
	16	2.684	0.897	0.99	0.79	0.298	0.898	1.00	0.03
	20	2.587	0.896	0.99	0.58	0.238	0.894	1.00	0.08
	Untreated Switchgrass					**AFEX™ Switchgrass**			
2	8	4.572	0.868	0.99	1.31	1.341	0.869	1.00	0.27
	12	4.199	0.859	0.99	1.27	1.589	0.875	1.00	0.13
	16	4.428	0.851	0.99	1.31	0.436	0.865	1.00	0.08
	20	3.962	0.844	0.99	1.04	0.384	0.865	1.00	0.09
4	8	4.399	0.927	0.99	1.04	1.144	0.880	1.00	0.37
	12	4.184	0.925	0.99	0.95	1.186	0.877	1.00	0.17
	16	4.092	0.921	0.99	1.03	1.227	0.878	1.00	0.09
	20	4.494	0.916	0.99	1.33	0.462	0.872	1.00	0.03
8	8	2.379	0.920	1.00	0.42	0.965	0.903	1.00	0.08
	12	1.957	0.919	0.99	0.51	0.602	0.898	1.00	0.04
	16	1.745	0.913	1.00	0.31	0.554	0.897	1.00	0.06
	20	1.901	0.913	1.00	0.43	0.743	0.893	1.00	0.19

**SSE - Sum of squared errors*

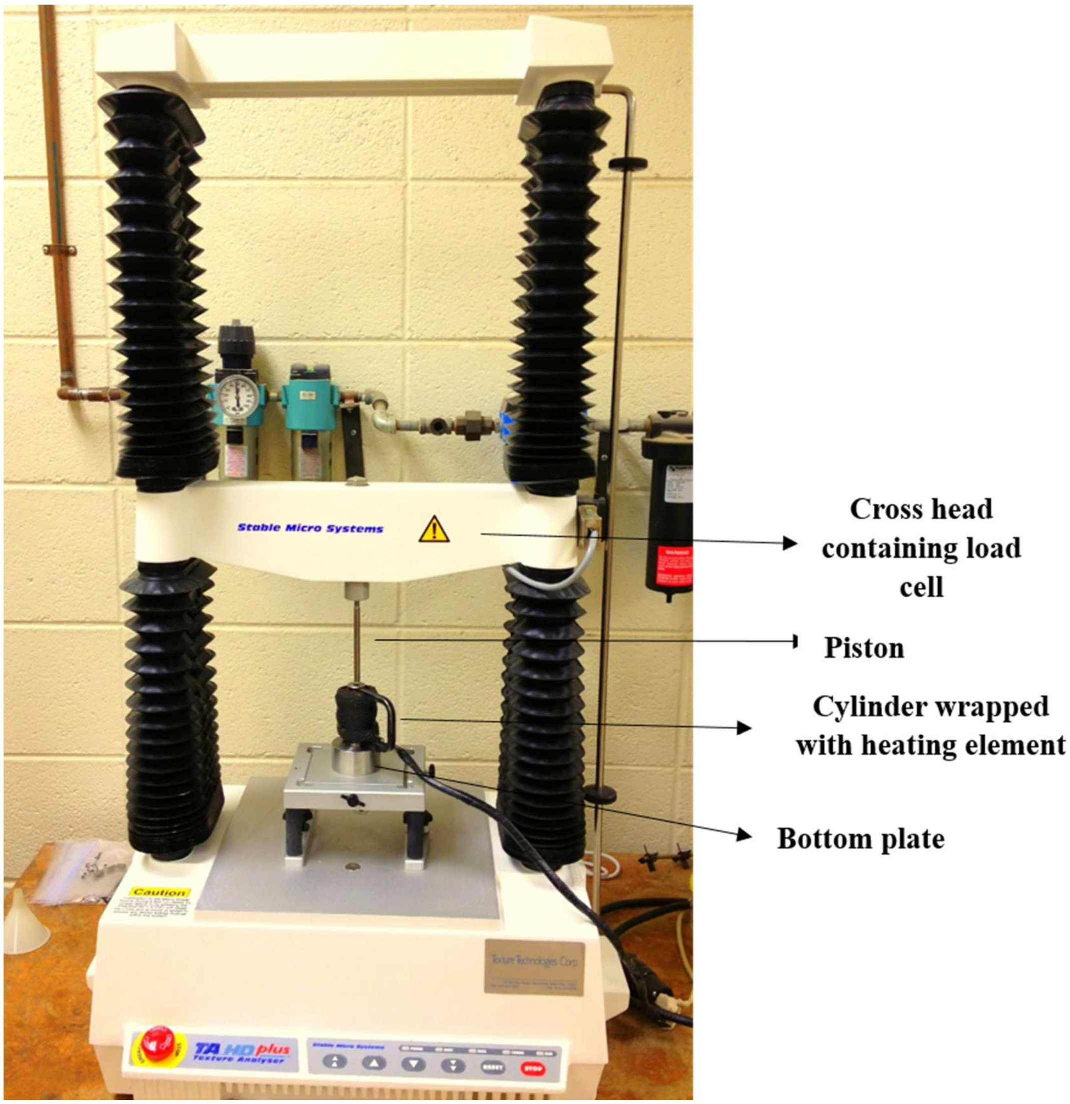


Fig. 2.1. Single pelleting unit positioned in the texture analyzer

3. EFFECT OF AFEX™ PRETREATMENT, COMPRESSIVE LOAD, SCREEN SIZE, AND MOISTURE CONTENT ON THE SUGAR YIELDS OF CORN STOVER, PRAIRIE CORD GRASS, AND SWITCHGRASS.

3.1. Abstract

Densified feedstocks should have positive influence on the biomass logistics, however the densification should not have any negative influence during downstream processing. Understanding the impacts of densification is important to control the factors affecting the yields of the end product. This study was intended to study the effects of AFEX™ pretreatment, feedstock moisture content (8, 12, 16, and 20% wb), hammer mill screen size (2, 4, and 8 mm), compressive load (1000, 2000, 3000, 4000, and 5000 N) on sugar recovery from corn stover, prairie cord grass, and switchgrass. Pellets were produced from untreated and AFEX™ pretreated corn stover, prairie cord grass, and switchgrass produced using a single pelleting unit. Untreated and AFEX™ pretreated feedstock pellets were subjected to enzymatic hydrolysis and the glucose and xylose yields were investigated. A significant increase in the glucose and the xylose recoveries was noted in all the feedstocks after AFEX™ pretreatment. Statistical analysis showed that only hammer mill screen size was significant ($p<0.05$) in controlling the sugar yields whereas compressive load and feedstocks moisture content were not ($p>0.05$). These results indicate that the larger screen size AFEX™ pretreated samples can be densified to increase the bulk density of the feedstocks without affecting the sugar yields.

3.2. Introduction

The United States energy independence and security act of 2007 mandates the production of 36 billion gallons of renewable fuels by the year 2022. The allocations include 16 BGY (billion gallons per year) of cellulosic biofuels, 14 BGY of advanced biofuels, 1 BGY of biomass-based biodiesel, and 15 BGY of conventional biofuels (corn, starch-based ethanol). To achieve the target of 36 billion gallons by 2022, the United States should increase the current biofuels production up to three times (USEIA, 2013). To meet this ambitious target, biorefineries should overcome the challenges associated with lignocellulosic feedstocks logistics and conversion process.

Biofuels production using food based feedstocks (corn, sugarcane, soybeans, etc.) could not be an attractive option to reach the ambitious goal set by the energy independence and security act. Besides, the diversion of food crops for biofuels production will escalate the food price. Lignocellulosic feedstocks appear to be an alternate energy resources for biofuels production also providing an alternative and effective way of waste disposal. Lignocellulosic feedstocks which include agricultural residues, forest residues, organic portion of municipal and industrial wastes, and perennial grass. These lignocellulosic feedstocks can be employed to produce biofuels and this option is an attractive due to the plentiful availability, renewable nature, and carbon neutral characteristics. This will also help to deviate production of biofuels from food crops thus avoiding food vs fuel disputes. Different lignocellulosic biomass (agricultural residues, forest residues, wood residues, and energy crops) were considered by the U.S. Department of energy as a potential resource to replace 30% of the current petroleum consumption (Perlack *et al.,* 2011). These lignocellulosic feedstocks can be transformed into different biofuels using biochemical and thermochemical pathways. In the thermochemical conversion process, the biomass will be subjected to pyrolysis or gasification process to yield syngas which turn can be converted into liquid biofuels via Fisher-Tropsch or biological conversion process (Balan, 2014). In biochemical conversion pathway, the carbohydrate components of the biomass (cellulose and hemicellulose) will be hydrolyzed to yield simple sugars (glucose, xylose, arabinose, etc.), which in turn will be converted into bioethanol via fermentation process using microorganisms. Bioethanol is currently the most widely produced and utilized biofuel (Rabinovitch-Deere *et al.,* 2013).

The conversion of biomass to bioethanol via biochemical conversion poses significant challenges. Lignocellulosic biomass possesses complex chemical structure comprising cellulose, hemicellulose, and lignin. Among the components, cellulose and hemicellulose are the polysaccharides enclosed by lignin. Due to this complexion, the polysaccharide components will not have an access to the enzymes during the hydrolysis step. To overcome this hurdle, an effective pretreatment step is mandatory. An effective pretreatment involves altering the chemical structure of the lignocellulosic biomass, thus exposing the cellulose and hemicellulose components accessible to the enzyme attack. An effective pretreatment also requires less or no toxic compound formation, which will affect the enzymatic hydrolysis and subsequent fermentation process. Several pretreatment techniques have been extensively studied on different lignocellulosic biomass and different conditions are being optimized to define the best pretreatment method. It is difficult to conclude the best pretreatment, as the method depends on the type of lignocellulosic biomass and desired products (Harmsen *et al.,* 2010).

Ammonia Fiber Expansion (AFEX™) is a promising physiochemical pretreatment process, which involves treating the biomass with liquid ammonia at a moderate temperature and pressure (Balan *et al.,* 2009). The process involves treating biomass with liquid ammonia under moderate pressure (100–400 psi) and temperature (70–200 °C) in a stainless steel reactor for a short residence period of 5–30 min (Bals *et al.,* 2010). The selection of optimum parameters like pressure, temperature, and residence time depends on the recalcitrant nature of lignocellulosic biomass (Balan *et al.,* 2009). Release of rapid pressure after the residence period marks the end of pretreatment process. This rapid release of pressure results in breaking of complex chemical structure of biomass, thus exposing cellulose and hemicellulose fibers for enzymes to attack (Chundawat *et al.,* 2011; Kumar *et al.,* 2009). AFEX™ pretreated corn stover (Teymouri *et al.,* 2005), switchgrass (Alizadeh *et al.,* 2005), and rice straw (Sulbarán-de-Ferrer *et al.,* 2003) exhibited an increase in sugar yields when subjected to enzymatic hydrolysis.

Handling, transporting, and storing of low bulk density lignocellulosic feedstocks are another major hurdles for economic biofuels production. Densification is one of the preprocessing operations, which involve compression of lignocellulosic biomass to form as a compacted product. This helps in improving the handling, transporting, and storage obstacles associated with the lignocellulosic biomass logistics. Tumuluru *et al* (2012) specified that integrating densification with pretreatment helps to overcome the hurdles connected with biomass logistics. It is also imperative that densification process should not create any adverse effects on the biomass conversion to biofuels. Kaliyan and Morey (2010) indicated that the heat generated during the densification process softens the lignin, which acts as a binding agent in sticking the fibers together**.** Considering the changes in the lignocellulosic biomass structure during the AFEX™ pretreatment and densification, it is imperative to determine the sugar yields to understand that the alterations during pretreatment and densification are productive or destructive. Hence, the objective of this chapter is to study the impacts of AFEX™ pretreatment and densification using a single pelleting unit on the sugar yields from corn stover, prairie cord grass, and switchgrass. The specific objectives are to study the impacts of feedstock moisture content (5, 10, 15% wb), hammer mill screen size (2, 4, and 8 mm), and applied load (1000, 2000, 3000, 4000, and 5000 N) on the glucose and xylose yields from the untreated and AFEX™ pretreated corn stover, prairie cord grass, and switchgrass.

3.3. Materials and Methods

3.3.1. Feedstock preparation

The feedstocks corn stover (2008), prairie cord grass, and switchgrass (2009) obtained from local farms in Brookings, South Dakota were ground with three different screen opening sizes viz. 2, 4 (Hammer Mill, Thomas Wiley Laboratory Mill, Swedesboro, NJ) and 8 mm (Speed King, Winona Attrition Mill Co., Winona, MN). The ground materials were sealed in plastic bags and sent to the biomass conversion research laboratory (BCRL, Michigan State University, MI) for AFEX™ pretreatment. The pretreatment conditions were optimized individually for each feedstock based on the recalcitrant nature of lignocellulosic biomass (Balan *et al.,* 2009) by BCRL. The key variables employed during the AFEX™ process were pretreatment time, ammonia–biomass ratio, temperature, and feedstock moisture content. The AFEX™ pretreatment conditions used for different feedstocks are given in Table 3.1. The pretreated materials were sealed in plastic bags and stored in a refrigerator at 4 °C until further use.

3.3.2. Moisture conditioning

The moisture content of the samples was determined using ASABE Standards (2006) standard and was reported in percent wet basis. The initial moisture content of the stored untreated feedstocks varied from 4% to 8%, and for the AFEX™ pretreated feedstocks the moisture content varied from 5% to 8% on a wet basis. Moisture content was varied at four different levels (8, 12, 16, and 20% on wet basis) and the selection of moisture content range was based on Kaliyan and Morey (2009) study. In their study, the authors optimized the conditions to produce durable briquettes from corn stover and switchgrass by varying the moisture content from 8% to 20%. To achieve the desired moisture levels, a calculated quantity of water was added to the samples in a plastic container, and the contents were tumbled manually. Moisture adjusted samples were stored in sealed plastic bags at 4 °C overnight, and the samples were brought to room temperature prior to the beginning of experiments.

3.3.3. Compression test using single pelleting unit

Compression tests were performance on the AFEX™ pretreated and untreated biomass grinds, using single pelleting unit (Mani et al., 2002, Tabil and Sokhansanj, 1996a and Tabil and Sokhansanj, 1996b). The unit consists of a piston and cylinder assembly with a base plate resting on the platform. The piston was connected to the crosshead of the texture analyzer (TA HD plus, Texture Technologies Corp., NY). Internal diameter and height of the cylinder were 6.35–76.2 mm, respectively. The cylinder was wrapped with a heating element to heat the contents of the cylinder during the compression. Thermocouples were attached to the cylinder, and the temperature was regulated by a temperature controller (SDC 120KC-A, Brisk Heat Corp., OH). The cylinder section was rested on the base plate, which had an internal diameter matching the diameter of the cylinder. Feedstocks with different combinations of moisture contents (8, 14, 16 and 20% w.b) and hammer mill sizes (2, 4, and 8 mm) were pelleted at different loading conditions (1000, 2000, 3000, 4000, and 5000 N) with corresponding pressure (31.6, 63.2, 94.8, 126.4 and 158.0 MPa) using the single pelleting unit. Samples of a quantity of 0.5–0.7 g were loaded into the cylinder, and the piston was allowed to compress in a single stroke. The temperature of the cylinder was maintained at 100 ± 2 °C to mimic the commercial pelleting process (Mani *et al.,* 2004). The crosshead speed of the texture analyzer was set at 50 mm min^{-1}. After reaching the preset load, the piston was allowed to detain at an indicated preset load for a period of 30 s to avoid the spring back effect. The piston was raised, and bottom plate was attached to the cylinder to eject the pellet produced by lowering the piston. Five replications were produced for each combination.

3.3.4. Enzymatic hydrolysis

Untreated, AFEX™ pretreated, untreated pelleted, AFEX™ pretreated pelleted samples were subjected to enzymatic hydrolysis following NREL protocol (Selig *et al.,* 2008). The enzymatic hydrolysis was carried out using 10 ml hungate glass tubes. Samples with the equivalent of 0.1 g of cellulose along with sodium citrate buffer (0.1 M, pH 4.8) was taken in the glass tubes. 100 µl of 2% sodium azide was added to inhibit the growth of organisms during the digestion. Enzyme loadings added were 15 FPU/g of glucan, 30CBU/g of glucan, and 250 XU/g of glucan. All the enzymes were provided by Novozymes (Krogshoejvej, Denmark). The sample tubes were incubated at 50 °C for 72 h in an incubated orbital shaker (MaxQ™ HP 420, Thermo scientific, MA) at an RPM of 150. After 72 h, the sample tubes were kept in boiling water for a period of 10 min to inactivate the enzymes. Supernatants from each tube were collected from hydrolyzed samples and were subjected to centrifugation at 13,000 × g for 15 min in a centrifuge (Fisher scientific, Accuspin™ 400). The centrifuged samples were frozen and thawed twice to settle the impurities and the supernatant was taken in HPLC vials. The supernatants were injected into sugar analysis in an HPLC (Agilent Technologies, Santa Clara, CA; Bio-rad Aminex 87H column, Hercules, CA) to quantify the sugars present in the samples. A sample volume of 20 µl was injected into the column at a flow rate of 0.6 ml/min at a 65 °C column temperature. Sugar yields were calculated using Selig *et al.* (2008) procedure by considering the chemical composition of the samples and the concentration of sugars obtained from HPLC analysis.

3.3.5. Statistical analysis

In this study, the effects of moisture content, screen size, and applied force were tested on the glucose and xylose yields of corn stover, prairie cord grass, and switchgrass. Analysis of variance (ANOVA) was used to determine the significant difference among the means of the samples. Design-Expert software (Version 8.0.7.1, Stat-Ease, Minneapolis, MN) was used to develop the model equations using full-factorial design.

3.4. Results and discussion

The results of the chemical composition analysis of untreated corn stover, prairie cord grass, and switchgrass are provided Table 3.1. Glucose and xylose yields were recorded for the untreated, untreated pelleted, AFEX™ pretreated, AFEX™ pretreated pelleted corn stover, prairie cord grass, and switchgrass. Table 2 and 3 shows the glucose and xylose yields of the pellets produced from AFEX™ pretreated corn stover, prairie cord grass, and switchgrass. Glucose yield for the pellets produced from AFEX™ corn stover, prairie cord grass, and switchgrass varied from 87.7 % to 94.9 %, 89.3 % to 95.0%, and 89.8 % to 95.0%, respectively. Xylose yield for the AFEX™ corn stover, prairie cord grass, and switchgrass varied from 39.0 % to 51.9 %, 37.5 % to 49.8%, and 37.5% to 50.8%, respectively. Xylose yields from the AFEX™ pretreated feedstocks were lower compared to the glucose yields and the reason could be due to the usage of multi-enzyme for xylose conversion. The multi-enzyme (NS50012) is a mixture of xylanase, pectinase, arabinose, cellulose, and β-glucanase and this cocktail of enzymes could have reduced the xylose yields. Glucose yield for the pellets made from untreated corn stover, prairie cord grass, and switchgrass varied from 87.7 % to 94.9 %, 89.3 % to 95.0%, and 89.8 % to 95.0%, respectively. Xylose yield for the pellets produced from untreated corn stover, prairie cord grass, and switchgrass varied from 39.0 % to 51.9 %, 37.5 % to 49.8%, and 37.5% to 50.8%, respectively. Increase in the glucose and xylose yields were observed for all the biomass subjected to AFEX™ pretreatment and this shows the impact of AFEX™ pretreatment on the selected lignocellulosic biomass. AFEX™ pretreatment impacts physical and chemical structure changes in the ultra and macro structure of lignocellulosic biomass (Dale, 1986) and some of the alterations include cellulose decrystallization, partial depolymerization of hemicellulose, cleavage of lignin-carbohydrate complex (LCC), and surface area increase (Balan, 2009). The breaking of lignin - carbohydrate complex is vital which could be the reason for the increased sugar yields in all the three biomass.

Fig 3.1 and 3.2 shows the glucose and xylose yields from the pellets produced from untreated corn stover, prairie cord grass, and switchgrass under different conditions. Reduction in the hammer mill screen size increased the sugar yields of all the untreated feedstocks. Particle size reduction leads to increase in the surface area to volume ratio thus improving the accessibility for the enzymes to reach the active substrate sites (Mansfield *et al.,* 1999). Biomass particle size had considerable amount of impact on the enzymatic hydrolysis yields for AFEX™ corn stover (Chundawat *et al.,* 2006). Elshafei *et al* (1991) observed a slight increase in the hydrolysis yields with decrease in the particle size of the untreated corn stover and the authors attributed the increase to the increased surface area of the feedstock accessible to the enzyme. The other selected factor, compressive load did not influence the glucose and xylose yields for both untreated and AFEX™ pretreated biomass ($p<0.05$). This results indicate that AFEX™ pretreated biomass can be densified to increase the bulk density for efficient handling and transportation, while maintaining the sugar yields similar to the loose biomass. Rijal *et al* (2014) observed that the low temperature, low-pressure novel densification method had no effects on the ethanol yields from AFEX™ pretreated corn stover and switchgrass. Sundaram *et al* (2016) observed the similar glucose and xylose yields when AFEX™ pretreated corn stover, prairie cord grass, and switchgrass and the extruded pellets from the AFEX™ biomass were subjected to enzymatic hydrolysis. Moisture content did not affect the glucose and xylose yields from untreated and AFEX™ pretreated feedstocks ($p>0.05$). Karunanithy and Muthukumarappan (2010) reported that the increase in the glucose recovery when prairie cord grass and switchgrass were subjected to extrusion at low moisture content (15%). The authors observed the biomass softening when the moisture content was increased leading to less friction developed inside the extruder barrel.

Table 3.4 shows the model equations developed for the sugar yields from the pellets produced from untreated corn stover, prairie cord grass, and switchgrass under different conditions. The *p* value for the AFEX™ pretreated feedstocks was higher than 0.05, indicating the insignificance of screen size, moisture content and loading interactions on the glucose and xylose yields from enzymatic hydrolysis. The quality of the regression equation was determined by the R^2 value and the influences of the independent variables on dependent variable was determined by the *p* values. The model equations developed for the pellets made from AFEX™ pretreated feedstocks were not significant ($p>0.05$) and for the untreated feedstocks the equations were significant ($p<0.05$) as shown in Table 3.4. For the pellets produced from untreated feedstocks the model equation was significant, indicating the variables affecting the sugar yields. The independent variables X_1, X_2, and X_3 represent hammer mill screen size (mm), moisture content (%), and compressive load (N). The dependent variables Y_g and Y_x represent glucose and xylose recovery. Among all the independent variables, only hammer mill screen size had significant impact on glucose and xylose recovery ($p<0.05$). The ANOVA results for the pelleted produced from untreated corn stover, prairie cord grass, and switchgrass under different conditions are provided in Table 3.5, 3.6, and 3.7 respectively. Based on the ANOVA, it was clear that glucose and xylose recovery increased with decrease in the hammer mill screen size whereas moisture content and loading was not significant in deciding the sugar yields from untreated feedstocks. Biomass densification involves only mechanical compression and no changes in the biomass chemical structure was cited in the literature of biomass. Mani *et al* (2002) hypothesized the three different stages involved in the densification process namely particle rearrangement, plastic and elastic deformation, and mechanical interlocking of the particles. The inability of the densification to break the complex chemical structure could be the reason for similar sugar yields, regardless of the increase in the compressive load. No influences on glucose and xylose yields after densification indicates that AFEX™ pretreated biomass can be densified to improve the handling characteristics without affecting the sugar yields during downstream processing.

3.5. Conclusions

The impacts of AFEX™ pretreatment and densification on the enzymatic hydrolysis yields were investigated for corn stover, prairie cord grass, and switchgrass. The feedstocks were subjected to AFEX™ pretreatment followed by densification using a single pelleting unit. The pelleted feedstocks were subjected to enzymatic hydrolysis and glucose and xylose yields were calculated. Glucose yields for the AFEX™ corn stover, prairie cord grass, and switchgrass varied from 73.1 % to 94.0 %, 69.3 % to 93.2% and 69.7 % to 95.5%, respectively. Xylose yields for the pellets produced from untreated corn stover, prairie cord grass, and switchgrass varied from 39.0 % to 51.9 %, 37.5 % to 49.8%, and 37.5% to 50.8%, respectively. Glucose and xylose yields for the loose AFEX™ pretreated feedstocks were statistically similar to the pellets produced from the AFEX™ pretreated feedstocks. Moisture content and compressive load was not significant ($p>0.05$) in affecting the glucose and xylose yields, whereas hammer mill screen size was significant ($p<0.05$) for untreated feedstocks. It can be concluded from the results that the AFEX™ pretreated corn stover, prairie cord grass, and switchgrass can be densified for efficient transportation, while maintaining the sugar yields similar to that of loose biomass.

Table 3.1. Chemical composition of untreated corn stover, prairie cord grass, and switchgrass

Feedstock	Corn stover	Prairie cord grass	Switchgrass
Glucan (%)	34.3	37.8	32.2
Xylan (%)	18.5	22.6	14.8
Arabinan (%)	2.5	2.9	2.3
Lignin (%)	15.7	15.3	13.3

Table 3.2. Glucose yields of the pellets produced from AFEX™ pretreated corn stover, prairie cord grass, and switchgrass

SS (mm)	Moisture (%)	Load (N)	AFEX™ CS	AFEX™ PCG	AFEX™ SG
2	8	1000	94.9	90.6	94.6
		2000	93.4	91.0	91.9
		3000	91.3	91.6	91.6
		4000	93.4	93.6	94.7
		5000	93.6	93.8	90.8
	12	1000	92.5	91.5	93.9
		2000	92.7	95.0	92.9
		3000	90.7	92.7	91.1
		4000	93.4	92.6	94.4
		5000	91.5	92.0	93.8
	16	1000	94.0	90.5	92.3
		2000	93.5	94.6	94.6
		3000	92.7	90.6	91.0
		4000	92.6	90.3	91.4
		5000	91.3	89.8	92.0
	20	1000	93.2	93.8	91.0
		2000	92.0	90.3	94.4
		3000	93.6	91.2	94.6
		4000	92.9	93.5	91.0
		5000	91.6	94.2	91.4
4	8	1000	93.9	95.0	92.8
		2000	93.3	90.9	92.1
		3000	90.1	92.8	90.6
		4000	93.1	90.3	91.5
		5000	92.8	89.3	93.5
	12	1000	93.7	94.4	91.3
		2000	94.4	90.3	91.6
		3000	90.1	91.2	93.9
		4000	91.4	94.4	92.8
		5000	93.6	94.3	94.9

	16	1000	92.3	92.2	93.4
		2000	93.3	91.4	93.4
		3000	91.3	94.1	89.8
		4000	93.2	93.7	90.6
		5000	92.6	90.3	91.0
	20	1000	92.1	91.4	91.6
		2000	94.1	92.5	91.5
		3000	91.4	92.5	92.7
		4000	93.6	89.9	94.5
		5000	92.3	90.2	92.6
8	8	1000	93.5	92.2	90.5
		2000	90.9	90.8	94.6
		3000	93.5	90.0	90.3
		4000	94.2	90.9	91.2
		5000	88.9	90.1	95.0
	12	1000	94.8	93.6	92.8
		2000	89.5	92.3	90.3
		3000	91.0	91.3	90.3
		4000	92.9	92.1	91.2
		5000	92.4	91.4	92.2
	16	1000	91.4	92.3	91.4
		2000	91.4	93.5	93.7
		3000	90.7	94.8	90.8
		4000	89.9	93.3	90.2
		5000	92.2	92.4	91.0
	20	1000	87.7	94.9	91.0
		2000	90.9	89.7	92.9
		3000	92.3	93.6	91.4
		4000	93.3	93.3	92.2
		5000	91.3	92.3	90.9

Table 3.3. Xylose yields of the pellets produced from AFEX™ pretreated corn stover, prairie cord grass, and switchgrass

SS (mm)	Moisture (%)	Load (N)	AFEX™ CS	AFEX™ PCG	AFEX™ SG
2	8	1000	44.5	44.0	49.5
		2000	43.2	48.7	44.1
		3000	45.6	44.5	49.0
		4000	48.8	40.7	40.6
		5000	46.6	49.5	44.4
	12	1000	50.4	43.0	46.3
		2000	50.0	45.6	44.3
		3000	49.9	45.0	43.0
		4000	50.2	40.4	43.2
		5000	43.2	44.1	50.2
	16	1000	44.2	43.0	44.7
		2000	44.7	48.0	50.8
		3000	47.6	48.6	41.5
		4000	47.0	49.0	47.6
		5000	47.2	46.2	44.9
	20	1000	51.9	42.7	49.1
		2000	50.8	43.6	46.4
		3000	49.9	44.9	45.9
		4000	43.5	43.1	44.7
		5000	41.5	46.1	44.4
4	8	1000	45.3	40.6	46.9
		2000	47.6	44.8	43.0
		3000	45.1	42.4	42.7
		4000	46.3	40.8	40.6
		5000	47.7	42.6	44.7
	12	1000	50.4	45.5	37.5
		2000	50.0	42.9	43.9
		3000	42.6	45.7	43.4
		4000	44.8	44.4	45.4
		5000	42.4	41.2	45.0

	16	1000	43.5	44.7	46.6
		2000	44.9	42.0	45.6
		3000	47.4	37.5	44.5
		4000	47.0	41.8	39.9
		5000	49.1	45.6	50.0
	20	1000	48.9	49.8	43.5
		2000	46.4	43.9	48.9
		3000	53.6	47.7	45.9
		4000	48.1	45.7	47.0
		5000	47.8	46.3	40.6
8	8	1000	44.1	47.8	45.9
		2000	41.0	46.4	47.4
		3000	42.9	43.4	46.9
		4000	45.9	47.4	41.6
		5000	43.8	44.1	44.7
	12	1000	47.4	45.4	44.4
		2000	47.0	46.3	47.8
		3000	46.9	41.0	46.9
		4000	47.2	45.0	39.0
		5000	40.6	43.4	45.0
	16	1000	41.6	39.7	44.1
		2000	42.0	44.3	48.0
		3000	44.7	43.5	42.7
		4000	44.2	43.0	42.4
		5000	44.4	46.6	42.6
	20	1000	48.8	46.0	42.9
		2000	47.8	45.6	44.4
		3000	46.9	42.7	37.5
		4000	40.9	42.9	39.8
		5000	39.0	43.0	42.8

Table 3.4. *p* value and model equations for the glucose yield from the pellets produced from untreated corn stover, prairie cord grass, and switchgrass

Feedstocks	Model equations	*p*-value	R^2
Untreated corn stover	$Yg = 1.703 + 0.057X_1 - 0.035X_2 - 0.003X_3$	$p<0.05$	0.84
Untreated switchgrass	$Yg = 25.41 + 1.300X_1 - 0.08X_2 - 0.0002X_3$	$p<0.05$	0.88
Untreated switchgrass	$Yg = 25.32 - 1.87X_1 - 0.005X_2 - 0.0001X_3$	$p<0.05$	0.87

Table 3.5. ANOVA results for the factors affecting the glucose yields from untreated corn stover pellets

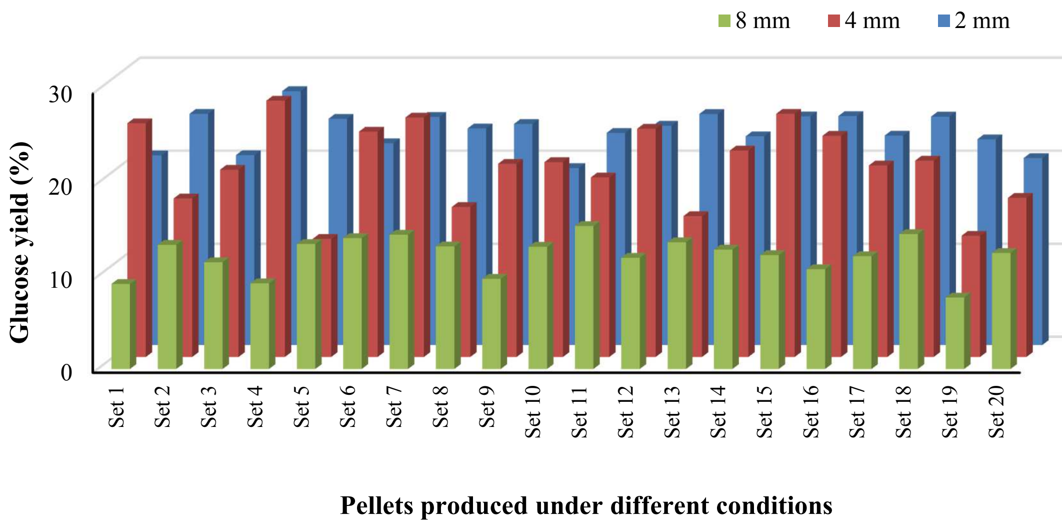
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	1569.106	35	44.83159	4.453847	0.0001
A-SS	1290.943	2	645.4715	64.12513	< 0.0001
B-Moisture	22.40198	3	7.467326	0.74185	0.5376
C-Load	24.99014	4	6.247535	0.620669	0.6521
AB	15.23801	6	2.539669	0.252306	0.9535
AC	81.68245	8	10.21031	1.014355	0.4517
BC	133.8498	12	11.15415	1.108122	0.3976
Residual	241.5795	24	10.06581		
Cor Total	1810.685	59			

Table 3.6. ANOVA results for the factors affecting the glucose yields from untreated prairie cord grass

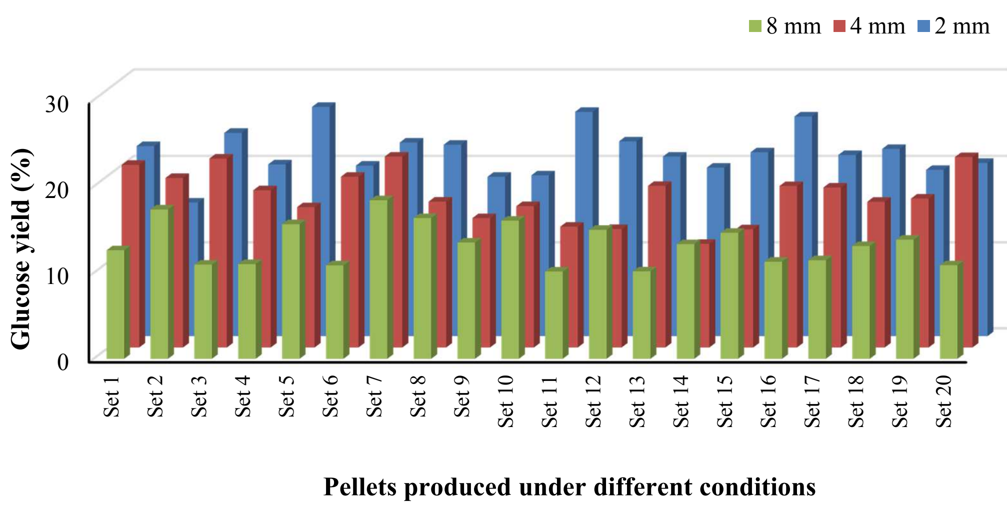
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	905.5571	35	25.87306	3.734835	0.0006
A-SS	644.2078	2	322.1039	46.49643	< 0.0001
B-Moisture	26.3772	3	8.7924	1.269203	0.3073
C-Load	35.17635	4	8.794088	1.269447	0.3094
AB	79.87404	6	13.31234	1.921667	0.1183
AC	73.2398	8	9.154975	1.321541	0.2802
BC	46.68188	12	3.890157	0.561553	0.8509
Residual	166.2599	24	6.927497		
Cor Total	1071.817	59			

Table 3.7. ANOVA results for the factors affecting the glucose yields from untreated switchgrass

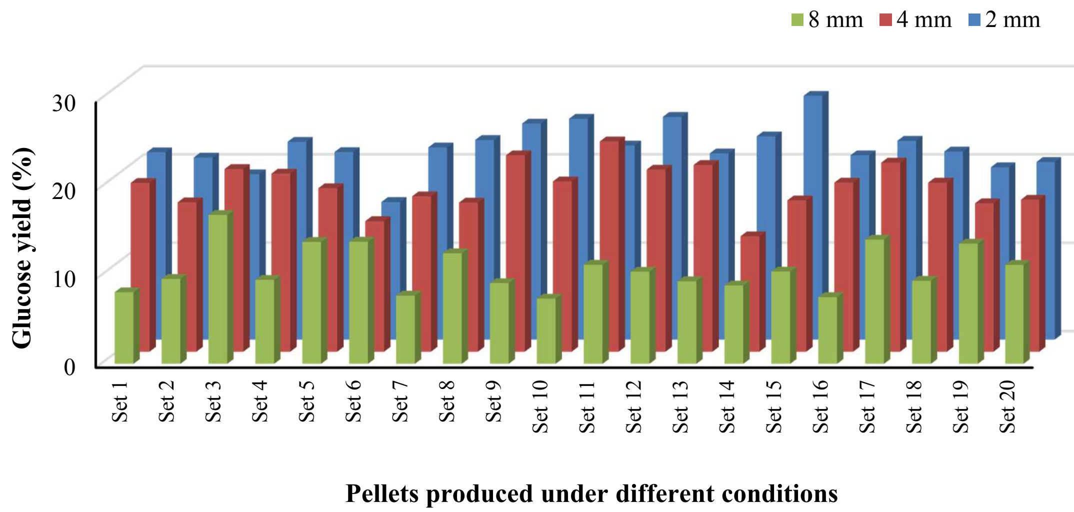
Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F
Model	1508.097	35	43.0885	5.053072	< 0.0001
A-SS	907.0375	2	453.5188	53.18503	< 0.0001
B-Moisture	14.27523	3	4.758408	0.558028	0.6478
C-Load	30.6544	4	7.663601	0.898725	0.4802
AB	43.41082	6	7.235137	0.848479	0.5457
AC	391.0799	8	48.88499	5.732838	0.0004
BC	121.6395	12	10.13663	1.188742	0.3446
Residual	204.6525	24	8.527188		
Cor Total	1712.75	59			



(a) Corn stover



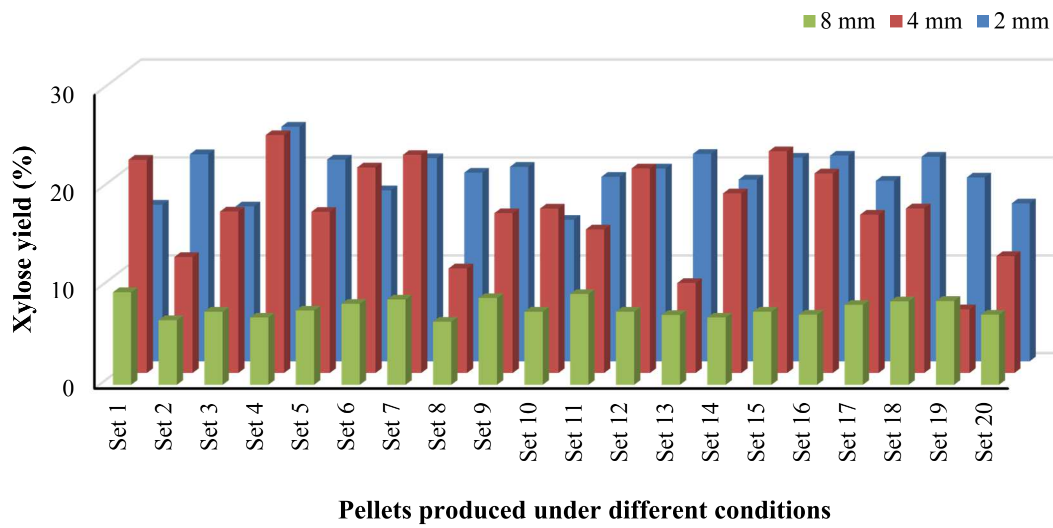
(b) Prairie cord grass



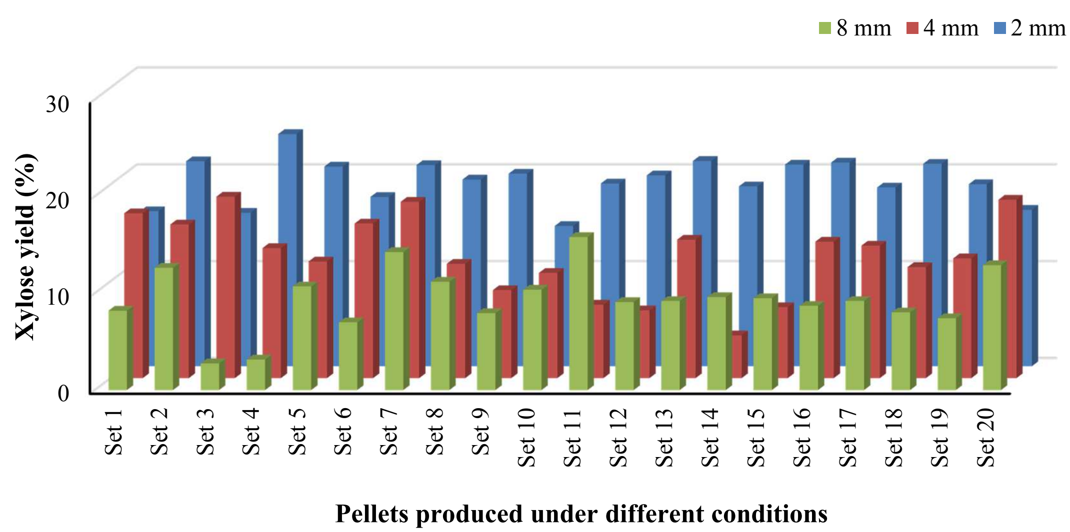
(c) switchgrass

Set 1:8% moisture at 1000 N; **Set 2**: 8% moisture at 2000 N; **Set 3**: 8% moisture at 3000 N; **Set 4**: 8% moisture at 4000 N; **Set 5**: 8% moisture at 5000 N; **Set 6**: 12% moisture at 1000 N; **Set 7**: 12% moisture at 2000 N; **Set 8**: 12% moisture at 3000 N; **Set 9**: 12% moisture at 4000 N; **Set 10**: 12% moisture at 5000 N; **Set 11**: 16% moisture at 1000 N; **Set 12**: 16% moisture at 2000 N; **Set 13**: 16% moisture at 3000 N; **Set 14**: 16% moisture at 4000 N; **Set 15**: 16% moisture at 5000 N; **Set 16**: 20% moisture at 1000 N; **Set 17**: 20% moisture at 2000 N; **Set 18**: 20% moisture at 3000 N; **Set 19**: 20% moisture at 4000 N; **Set 20**: 20% moisture at 5000 N;

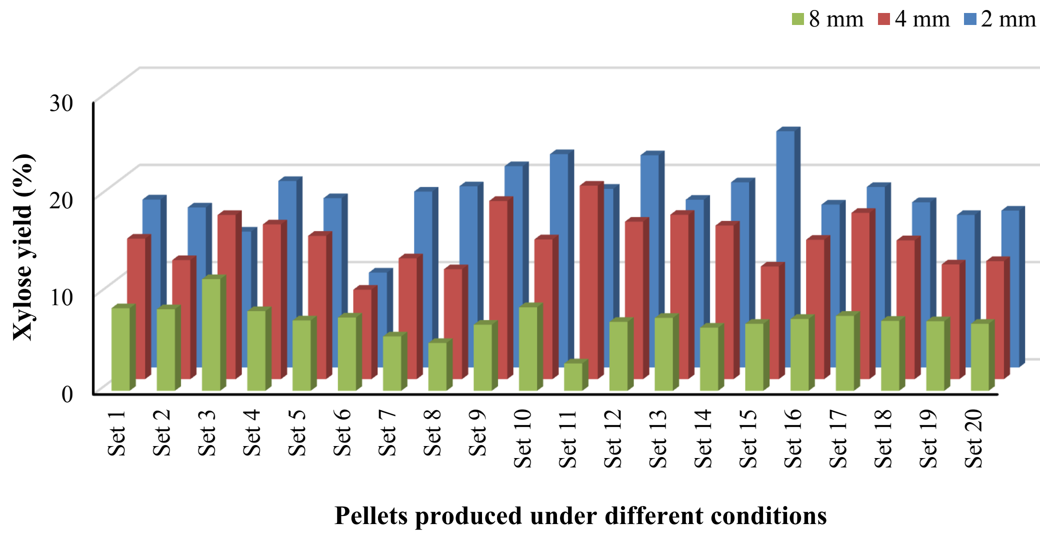
Fig. 3.1. Glucose yields from pellets produced under different conditions (a) untreated corn stover; (b) untreated prairie cord grass; (c) untreated switchgrass.



(a) corn stover



(b) prairie cord grass



(c) switchgrass

Set 1:8% moisture at 1000 N; **Set 2**: 8% moisture at 2000 N; **Set 3**: 8% moisture at 3000 N; **Set 4**: 8% moisture at 4000 N; **Set 5**: 8% moisture at 5000 N; **Set 6**: 12% moisture at 1000 N; **Set 7**: 12% moisture at 2000 N; **Set 8**: 12% moisture at 3000 N; **Set 9**: 12% moisture at 4000 N; **Set 10**: 12% moisture at 5000 N; **Set 11**: 16% moisture at 1000 N; **Set 12**: 16% moisture at 2000 N; **Set 13**: 16% moisture at 3000 N; **Set 14**: 16% moisture at 4000 N; **Set 15**: 16% moisture at 5000 N; **Set 16**: 20% moisture at 1000 N; **Set 17**: 20% moisture at 2000 N; **Set 18**: 20% moisture at 3000 N; **Set 19**: 20% moisture at 4000 N; **Set 20**: 20% moisture at 5000 N;

Fig. 3.2. Xylose yields from pellets produced under different conditions (a) untreated corn stover; (b) untreated prairie cord grass; (c) untreated switchgrass.

4. INFLUENCE OF AFEX™ PRETREATED CORN STOVER AND SWITCH GRASS BLENDING ON THE COMPACTION CHARACTERISTICS AND SUGAR YIELDS OF THE PELLETS

4.1. Abstract

The objective of this research was to investigate the impacts of Ammonia Fiber Expansion (AFEX™) pretreated corn stover and switchgrass blending ratio (25:75, 50:50 and 75:25 percent on dry weight), compressive pressure (31.6, 94.8, and 158.0 MPa), and screen size (2 and 4 mm) on pellet unit density, pellet hardness, specific energy consumption for pellets production, and the sugar yields. A single pelleting unit was employed in the study, and the untreated, AFEX™ pretreated, and AFEX™ pretreated blended samples were pelleted. The pellets produced from AFEX™ pretreated samples reached their maximum pellet unit densities at an applied pressure of 94.8 MPa. Pellet hardness was tested by applying the force to the pellets and recording the maximum force required to break. Results showed that the pellets produced from the small screen size sample at a higher applied pressure required more force to break. Besides, blend with higher proportion of AFEX™ pretreated corn stover produced harder pellets (711 N). Specific energy consumption for the pellets production varied from 11.4 to 57.9 kW h t^{-1}, and due to low bulk density of switchgrass, blends with a higher proportion of switchgrass consumed more energy for pellet production. Glucose yields of the AFEX™ pretreated samples were enhanced by 4–4.5 times and the xylose yields by 2–2.5 times compared to the untreated samples. Pelleting and biomass blending had no significant effects on sugar yields of the AFEX™ pretreated corn stover and switchgrass samples.

4.2. Introduction

The Energy Independence and Security Act of 2007 mandates the United States to produce 36 billion gallons of renewable biofuels annually by the year 2022 (Sissine, 2007). Considering the sustainable and environmental friendly characteristics, lignocellulosic biomass appears to be an alternative source to the fossil fuel usage. Greene and Mugica (2005) suggested the research focus towards demonstration and development of effective lignocellulosic biomass pretreatment, production of diverse bioproducts, and cost effective biofuels production from high yielding feedstocks. Preprocessing is a crucial phase in the biomass supply chain, which involves different operations to convert the harvested biomass appropriate for the end use in biorefineries. Conventional biorefinery adopts centralized processing approach, however, by shifting the preprocessing operations to the storage sites, the risks associated with handling diverse formats of biomass can be eliminated at the processing site (Hess *et al.,* 2007). Wright *et al* (2006) showed the improvement in transportation, handling, and merchandising potential of the biomass processed through distributed processing. A network of distributed processing facilities termed as 'Regional Biomass Processing Depot' (RBPD) involves different operations such as feedstock procurement, pretreatment, densification, and delivery of single product to the biorefineries (Eranki and Dale, 2011). The authors showed that RBPDs produce similar net energy yield and reduce greenhouse gas emissions by 3.7 percent than the centralized conventional system.

Overcoming the biomass recalcitrant nature is one of the key challenges in biofuel production from lignocellulosic feedstocks (Brodeur *et al.,* 2011). Biomass pretreatment is a vital preprocessing operation in breaking the complex chemical structure, thus separating the cellulose and hemicellulose components from lignin matrix and making them available for enzymatic hydrolysis. Developing an effective and economical pretreatment process is imperative in producing biofuels at a competitive price. Ammonia Fiber Expansion (AFEX™) is a promising physiochemical pretreatment process, which involves treating the biomass with liquid ammonia at a moderate temperature and pressure (Balan *et al.,* 2009). The process involves treating biomass with liquid ammonia under moderate pressure (100–400 psi) and temperature (70–200 °C) in a stainless steel reactor for a short residence period of 5–30 min (Bals *et al.,* 2010). The selection of optimum parameters like pressure, temperature, and residence time depends on the recalcitrant nature of lignocellulosic biomass (Balan *et al.,* 2009). Release of rapid pressure after the residence period marks the end of pretreatment process. This rapid release of pressure results in breaking of complex chemical structure of biomass, thus exposing cellulose and hemicellulose fibers for enzymes to attack (Chundawat *et al.,* 2011 and Kumar *et al.,* 2009). AFEX™ pretreated corn stover (Teymouri *et al.,* 2005), switchgrass (Alizadeh *et al.,* 2005), and rice straw (Sulbarán-de-Ferrer *et al.,* 2003) exhibited an increase in sugar yields when subjected to enzymatic hydrolysis.

One of the important physical limitations in handling, transporting, and storing lignocellulosic biomass is its low bulk density, (Eranki and Dale, 2011) which directly influences the production cost of biofuels. Densification involves application of mechanical and thermal energy to the bulky biomass to produce uniform densified products for efficient handling, transport, and storage. Mani *et al* (2002) elucidated the basic mechanisms involved in densification process. During the first stage, the biomass particles rearrange to form a closely packed mass. In the second stage, plastic and elastic deformation of particles occur with the increase in the applied pressure. Biomass undergo reduction in the volume with an increase in the applied pressure, till attaining its true density during the third stage. Lignin, one of the components of lignocellulosic biomass becomes soft and acts as a natural binder when subjected to high temperature and pressure (van Dam *et al.,* 2004). The softened lignin acts as a glue in sticking the fibers together. Different densification methods like baling, pelleting, briquetting, and compaction have been tested on different feedstocks (Tumuluru *et al.,* 2011). However, literature on the impacts of pretreatment and densification on physical quality of the pellets (durability, pellet density, bulk density, hardness, etc.) and sugar yields are limited. Hoover *et al* (2014) studied the impacts of AFEX™ pretreatment and pelleting of corn stover on physical quality of pellets and sugar yields from enzymatic hydrolysis. Rijal *et al* (2014) investigated the impacts of AFEX™ pretreatment and ComPAKco densification method of corn stover, prairie cord grass, and switchgrass on the sugar yields from simultaneous saccharification and fermentation (SSF) and simultaneous hydrolysis and fermentation (SHF). Sundaram *et al* (2015) studied the effects of AFEX™ pretreatment on the compression characteristics of corn stover, prairie cord grass, and switchgrass. To reduce the overall biofuel production costs and to enhance the energy balance of biomass supply and conversion chain, Shi *et al* (2013) proposed that the pretreatment and densification of mixed biomass feedstocks could be an effective method. Considering the potential of mixed biomass pellets and AFEX™ pretreatment as a promising pretreatment technology, this research was intended to study the impacts of AFEX™ pretreatment, blending, and densification on the physical qualities of the pellets and the sugar yields from corn stover and switchgrass.

4.3. Materials and methods

4.3.1. Feedstock preparation

The feedstocks corn stover and switchgrass obtained from the local farms in Brookings, South Dakota were milled using a hammer mill (Thomas Wiley laboratory mill, USA) attached with screen sizes of 2 and 4 mm. The milled materials were sealed in plastic bags and sent to the Biomass Conversion Research Laboratory (BCRL, Michigan State University, MI,) for AFEX™ pretreatment. The optimum conditions used for AFEX™ pretreatment are provided in Table 4.1. The samples received after the pretreatment were sealed in plastic bags and stored in the refrigerator at 4 °C until further use. Initial moisture content of the samples was determined using oven drying method ASABE standard S358.2 (ASABE Standards, 2006). Dry weight of untreated corn stover (UCS), untreated switchgrass (USG), AFEX™ pretreated corn stover (ACS), and AFEX™ pretreated switchgrass (ASG) were determined and the blends were prepared based on the dry weight of individual biomass. Three different blends were produced viz. B_1 (25% ACS and 75% ASG), B_2 (50% ACS and 50% ASG), B_3 (75% ACS and 25% ASG). Moisture content of the samples and the blends was adjusted to 15 percent on a wet basis, considering the requirement of less pressure at higher moisture content to produce highly compacted pellets (Sundaram *et al.,* 2015). Moisture content was adjusted by addition of calculated quantity of distilled water and the contents were mixed using a kitchen aid mixer (Kitchen aid professional plus 5, St. Joseph, MI). Moisture adjusted samples were stored at 4 °C in refrigerator and were thawed to the room temperature before beginning the experiments. The chemical composition of untreated corn stover and switchgrass was determined using National Renewable Energy Laboratory—laboratory analytical procedure (Sluiter *et al.,* 2007). The retention of the components cellulose, hemicellulose, and lignin after pretreatment is the unique feature of AFEX™ pretreatment. Hence, for the calculations of enzymatic yields, the compositions of untreated samples were used (Campbell *et al.,* 2013).

4.3.2. Bulk and particle density determination

Bulk density of untreated and AFEX™ pretreated samples was determined by measuring the mass of the sample occupying a known container volume. A hopper and stand apparatus (Seedburo equipment Co., Des Plaines, IL) was used to determine the bulk density of the samples. Samples were fed through the hopper and the cylindrical container with a volume of 0.5 l was placed underneath the hopper to collect the samples. Surplus samples collected were removed by passing a thin wire across the top of the cylindrical container. Mass of samples collected in the container was weighed and was divided by the volume of the container to determine the bulk density. Particle density of untreated and AFEX™ pretreated samples was measured using a multivolume gas pycnometer (Micrometritics multivolume pycnometer 1305, Norcross, GA). The measurement was based on the pressure difference between the volume of reference cell and the sample cell. Helium gas was used as a displacement medium and three replications were carried out for each sample.

4.3.3. Single pelleting unit

Pellets were produced by compressing the biomass in a single pelleting unit shown in fig. 2.1. The unit comprised of a piston and cylinder assembly with a base plate. The cylinder had an internal diameter of 6.35 mm and height of were 6.35 and 76.2 mm.

A mass of 0.5–0.7 g of sample was fed into the cylinder and the piston attached to the texture analyzer (TA HD plus, Texture Technologies Corp, NY) cross head was allowed to compress the sample at a speed of 50 mm min−1. The contents inside the cylinder were heated by the heating element wrapped around it. The cylinder was heated to a temperature of 100 ± 2 °C to simulate the commercial pelleting operation (Mani *et al.,* 2004). Thermocouple attached to the cylinder was regulated by a controller (SDC 120KC-A, Brisk heat corporation, OH) to control the temperature. The diameter of base plate was same as the cylinder diameter and bottom of the cylinder was rested on base plate during compression. To avoid the spring back effect, after attaining the preset load piston was allowed to maintain at same preset load for 30 s (Tabil and Sokhansanj, 1996a). Ejection of pellets produced was carried out by attaching the bottom plate above base plate and the piston was lowered. Pellets were produced under three different applied loads viz. 1000, 3000, and 5000 N with corresponding applied pressures of 31.6, 94.8, and 158.0 MPa respectively. Three replications of each sample were compressed.

4.3.4. Pellet unit density and hardness

Dimensions (height and diameter) of the pellets were measured using a digital vernier caliper (Digimatic, Mitutoyo Corp., Japan) and the mass of sample using digital weighing balance (Mettler PM 2500 Delta range, Columbus, OH). The ratio of mass of a pellet to its volume provided the unit density of a pellet. Compressive resistance or hardness test mimics the environment where pellets underneath are subject to stress by the weight of pellets placed over it during transportation and storage conditions. Hardness of pellets was tested by crushing the pellets using a cylindrical probe (TA-4, Texture Technologies Corp, NY) attached to the crosshead of texture analyzer. A single pellet was positioned in its natural position and a vertical force was applied at a speed of 50 mm min−1 to the pellet. The force applied vs deformation was recorded by the exponent software (Stable Micro Systems Ltd., UK) and the maximum force recorded in the curve was taken as the pellet hardness.

4.3.5. Specific energy consumption

During the compression tests, force applied vs. displacement curve was recorded by exponent software (Stable Micro Systems Ltd., UK) and the energy spent for compression of biomass and ejection of pellets were calculated by integrating the area under the curve. The ratio of energy spent (for compression and ejection) and the mass of the sample were used to calculate the specific energy consumption and is given in kW h t^{-1}. Three replications of each sample compressed were used to calculate the specific energy consumption.

4.3.6. Enzymatic hydrolysis

Untreated, AFEX™ pretreated, untreated pelleted, AFEX™ pretreated pelleted, and blended samples were subjected to enzymatic hydrolysis following NREL protocol (Selig *et al.,* 2008). The enzymatic hydrolysis was carried out using 10 ml hungate glass tubes. Samples with the equivalent of 0.1 g of cellulose along with sodium citrate buffer (0.1 M, pH 4.8) was taken in the glass tubes. 100 µl of 2% sodium azide was added to inhibit the growth of organisms during the digestion. The enzyme cellulase (NS50013 activity 70 FPU g^{-1}) was maintained at 15 FPU g^{-1} DM, β-glucosidase (NS50010 activity 250 CBU g^{-1}) at 30 CBUg^{-1} DM, and multienzyme (NS50012 activity 100 FBG g^{-1}) at 30 FBG g^{-1}. All the enzymes were provided by Novozymes (Krogshoejvej, Denmark). The sample tubes were incubated at 50 °C for 72 h in an incubated orbital shaker (MaxQ™ HP 420, Thermo scientific, MA) at an RPM of 150. After 72 h, the sample tubes were kept in boiling water for a period of 10 min to inactivate the enzymes. Supernatants from each tube were collected from hydrolyzed samples and were subjected to centrifugation at 13,000 × g for 15 min in a centrifuge (Fisher scientific, Accuspin™ 400). The centrifuged samples were frozen and thawed twice to settle the impurities and the supernatant was taken in HPLC vials. The supernatants were injected into sugar analysis in an HPLC (Agilent Technologies, Santa Clara, CA; Bio-rad Aminex 87H column, Hercules, CA) to quantify the sugars present in the samples. A sample volume of 20 µl was injected into the column at a flow rate of 0.6 ml/min at a 65 °C column temperature. Sugar yields were calculated using Selig *et al* (2008) procedure by considering the chemical composition of the samples and the concentration of sugars obtained from HPLC analysis.

4.3.7. Statistical analysis

Least significant difference test was carried out using PROC GLM method in the SAS web editor (SAS 9.3, Cary, NC) to determine the significant effects of selected parameters on the pellet properties and the sugar yields. Level of confidence was set at 95%.

4.4. Results and discussion

4.4.1. Bulk and particle density

Bulk and particle densities of untreated, AFEX™ pretreated, and blended samples are reported in Table 4.2. Mani *et al* (2006) reported the bulk density of corn stover as

156 kg m^{-3} (1.6 mm screen size) and 131 kg m^{-3} (3.2 mm screen size). Similarly, for the switchgrass, bulk densities were reported as 156 kg m^{-3} (1.6 mm screen size) and 115 kg m^{-3} (3.2 mm screen size). In this study, the bulk density of untreated stover (UCS) was 120.9 kg m^{-3} (2 mm screen size) and 107.3 kg m^{-3} (4 mm screen size). Untreated switchgrass bulk density was 115.5 kg m^{-3} (2 mm screen size) and 100.8 kg m^{-3} (4 mm screen size). Compared to the control samples, AFEX™ pretreated samples exhibited higher bulk and particle densities. This could be due to the conversion of fibrous biomass into brittle material during AFEX™ pretreatment. Hoover *et al* (2014) noticed the brittle and friable nature of corn stover when subjected to AFEX™ pretreatment.

The mean bulk and particle densities of the sample ACS (2 mm screen size) was highest (237.8 kg m^{-3} and 1423.1 kg m^{-3}, respectively) among all the samples taken and among the blended samples, blend with a high proportion of corn stover (B_3) at 2 mm and 4 mm screen size produced high bulk and particle density. AFEX™ pretreated corn stover sample had the higher bulk and particle densities than AFEX™ pretreated switchgrass and the presence of a higher proportion of corn stover could have increased the bulk and particle densities in the B_3 sample. Bulk densities of all the samples were statistically significant and the blending ratio and screen size had a significant effect ($p < 0.0001$). However, the mean particle densities of the blends B_1, B_2, B_3 for 2 mm screen size and blends B_2 and B_3 for 4 mm screen size were statistically similar. The factors blending ratio and screen size were not significant in deciding the particle densities of the blends. In all the conditions, bulk and particle densities of the samples increased with a decrease in the screen size.

4.4.2. Pellet unit density

Fig.4.1 shows the pellet unit density of 2 mm and 4 mm screen size samples compressed at different applied pressures. It can be inferred from the figure that, unit density of the pellets increased with an increase in the applied pressure for both screen size samples. The factors screen size, blending ratio, and applied pressure had significant effect on the pellet unit density ($p < 0.0001$), but their interactions were not significant. It was observed that the increase of pellet unit density was minor when the applied pressure was increased from 94.8 to 158.0 MPa. Stelte *et al* (2011) observed the minor increase in the pellet unit density of wheat straw, Norway spruce and European beech, when the pelleting pressure was increased between 250 and 600 MPa and major change in the pellet density was observed when the pressure was below 50 MPa. Similarly, Adapa *et al* (2009) reported the significant increase ($p < 0.05$) in the compact density of canola and oat straw when the pressure applied was increased from 31.6 to 94.7 MPa. When the pressure applied was increased above 94.7 MPa, there was no significant increase in the compact density as the compacts reached their corresponding particle densities. Similar fashion was observed in this study as the pellet unit densities approached their respective particle densities.

Particle density values reported were in the range of 900–1200 kg m^{-3} for corn stover and 600–1000 kg m^{-3} for switchgrass samples (Mani *et al.,* 2006). In this study, AFEX™ pretreated samples produced pellets with higher unit density than the untreated samples, representing the impact of AFEX™ pretreatment. During AFEX™ pretreatment the lignin—carbohydrate matrix structure is broken down and the components are free from the complex matrix, thus solubilizing and mobilizing the lignin to biomass surface

(Dale, 1986, Bals *et al.,* 2010 and Chundawat *et al.,* 2011). This increased availability of lignin could have contributed to better binding of AFEX™ pretreated samples compared to the untreated samples. Sundaram *et al* (2015) studied the impacts of AFEX™ pretreatment on the compression characteristics of corn stover, prairie cord grass, and switchgrass. The study showed the requirement of less pressure to produce highly compacted products after the feedstocks were subjected to AFEX™ pretreatment. In this study, blend comprising higher proportion of corn stover (B_3, 2 mm screen size) at a maximum compressive pressure (158 MPa) produced pellets with maximum unit density (1416.25 kg m^{-3}). Higher density of AFEX™ pellets can have benefits in transportation with fewer trucks or railcars necessary to transport the same weight of material (Hoover *et al.,* 2014).

4.4.3. Pellet hardness

Table 4.3 shows the hardness of pellets produced from untreated, AFEX™ pretreated, and AFEX™ pretreated blended samples at different applied pressures. Maximum pellet hardness (923 N) was recorded for AFEX™ pretreated corn stover pellets (2 mm screen size) produced at 158.0 MPa. AFEX™ pretreated corn stover pellets were strongest among the samples, and the sample with a high proportion of corn stover at 2 mm screen size (B_3) produced pellets with maximum hardness (711 N). Increased hardness of the corn stover pellets can be attributed to the higher lignin content present in the corn stover than the switchgrass samples. Lignin becomes soft and acts as a natural binder when subjected to high temperature and pressure (van Dam *et al.,* 2004). It was observed that the pellets produced from smaller screen size samples under maximum load can withstand maximum force before breaking. The hardness values of the pellets produced from 2 mm screen size particles were higher compared to the pellets produced from 4 mm screen size particles. This could be due to the increased surface area available for binding during the pelleting process. Tabil and Sokhansanj (1996b) observed that the screen size was not significant in determining the durability of the pellets, but smaller screen size particles produced more durable pellets. Jannasch *et al* (2001) reported the increase in pellet hardness of switchgrass when the particle size was decreased from 1/8 (3.2 mm) to 7/64 (2.8 mm) inch. Table 4.4 shows the main and interaction effects of the selected variables on pellet hardness. The variables blending ratio, screen size, applied pressure and their interactions had a significant impact ($p < 0.001$) on pellet hardness. AFEX™ pretreatment impacts physical and chemical alterations to the structure of lignocellulosic biomass (Balan *et al.,* 2009 and Dale, 1986). Lignin melting, depolymerization and depositing on the biomass surface (Dale, 1986 and Chundawat *et al.,* 2011) are the significant alterations benefitting the biomass densification process. The increased availability of lignin in AFEX™ pretreated samples during the pelleting process could be the reason for increased pellet hardness compared to the untreated samples.

4.4.4. Specific energy consumption

Energy consumption comprises the energy required for biomass compression and ejection of pellets from the die. Energy spent for pellet production from different samples at different applied loads are shown in Fig.4.2. The energy required for compression was relatively higher than the energy required for pellet ejection in all the conditions. The energy consumption ranged from 11.4 to 57.9 kW h t^{-1}, and it can be observed that the energy consumption increased with an increase in the applied pressure. Energy consumption for AFEX™ pretreated switchgrass pellets production was relatively higher than that of AFEX™ corn stover pellets, and the reason could be due to the low bulk density nature of switchgrass compared to the corn stover samples. Adapa *et al* (2002) reported the similar result when fractionated alfalfa grinds exhibited higher displacement values during the compression and the authors credited the reason to low bulk density of the feedstock. Among the blended samples, blend with equal proportion of AFEX™ corn stover and AFEX™ switchgrass (B_2) consumed higher energy (57.9 kW h t^{-1}). However, the magnitude of energy consumption for the pellets produced from 2 mm and 4 mm screen size samples was less. In other words, AFEX™ pretreatment had reduced the energy consumption required for pellets production for large screen size samples. Statistical analysis showed the significant impact of selected variables and their interactions ($p < 0.0001$) on specific energy consumption. Table 4.4 shows the main and interaction effects of variables for specific energy consumption. In this study, the energy spent was relatively less when the pressure applied was increased above 94.8 MPa as the pellets approached their corresponding particle densities (Adapa *et al.,* 2009).

4.4.5. Enzymatic hydrolysis and the sugar yields

Table 4.5 shows the chemical composition of untreated corn stover and switchgrass samples. The glucose yields of 2 mm and 4 mm unpelleted AFEX™ pretreated corn stover (ACS) were 92.8% and 93.2% respectively. For unpelleted AFEX™ pretreated switchgrass (ASG), the glucose yields were 92.5% (2 mm) and 91.8% (4 mm). In the case of untreated corn stover (UCS), the glucose yields were 21.4% (2 mm) and 20.3% (4 mm), whereas for switchgrass samples (USG) the yields were 18.8% (2 mm) and 19.5% (4 mm). It was observed that the glucose yields from AFEX™

pretreated samples were 4–4.5 times higher than that of untreated samples. Xylose yields of unpelleted AFEX™ pretreated corn stover were 45.8% (2 mm) and 46.9% (4 mm) and for unpelleted AFEX™ pretreated switchgrass the yields were 45.3% (2 mm) and 47.4% (4 mm). Untreated samples xylose yields were 15.5% (2 mm) and 20.5% (4 mm) for corn stover and 13.1% (2 mm) and 19.4% (2 mm) for switchgrass samples. Increase in xylose yields of AFEX™ pretreated corn stover and switchgrass samples was 2–2.5 times higher than that of untreated samples. Increase in the glucose and xylose yields of AFEX™ pretreated samples compared to the untreated samples exhibited the influence of the pretreatment on the biomass. Lignocellulosic biomass has limited accessible surface area available for enzyme interaction with cellulose components (Fan *et al.,* 1980 and Hajny and Reese, 1969), due to the linkage of cellulose and hemicelluloses with lignin components acting as a physical barrier. AFEX™ pretreatment results in cellulose decrystallization, hemicellulose depolymerization, and cleaving of lignin-carbohydrate linkages (Balan *et al.,* 2009 and Dale, 1986). These physicochemical alterations in the structure of biomass have resulted in enhanced sugar yields from AFEX™ pretreated corn stover and switchgrass samples.

Glucose and xylose yields of the pellets produced from AFEX™ pretreated and AFEX™ pretreated blend samples compressed under different pressures are shown in Fig.4.3 and 4.4. Glucose yields varied from 92.3 to 93.5% for AFEX™ pretreated corn stover pellets and from 91.8 to 92.5% for AFEX™ pretreated switchgrass pellets. Xylose yields of pelleted AFEX™ pretreated corn stover ranged from 46.8% to 48.9% and for AFEX™ pretreated switchgrass pellets the yields ranged from 45.3% to 49.4%. From Fig.4.3 and 4.4, it can be observed that under different applied pressures, the yields of glucose and xylose from AFEX™ pretreated and AFEX™ pretreated blended pellets were not significant. In other words, pelleting pressure had a neutral effect on the glucose and xylose yields from the AFEX™ pretreated and AFEX™ pretreated blended pellets. Rijal *et al* (2014) also observed the densification of AFEX™ pretreated corn stover and switchgrass using ComPAKco technology had no significant effect on the sugar yields after 48 h of hydrolysis.

Reduction in biomass particle size increases the surface area to volume ratio, thus improving the enzymatic digestibility (Mansfield *et al.,* 1999). In this study, the screen size was not a significant factor in deciding the sugar yields from of AFEX™ pretreated corn stover and switchgrass samples. Hoover *et al* (2014) noted the decrease in the sugar yields of AFEX™ pretreated corn stover pellets when the grind size was increased from 4 mm to 6 mm. In this study, the screen sizes employed were 2 mm and 4 mm and no significant differences in the sugar yields were noted. This could be due to the increased surface area available for enzymes to interact with cellulose and hemicellulose components after the AFEX™ pretreatment. Glucose yields of the pellets produced from blended samples varied from 90.5% to 93.6% and the xylose yields varied from 45.3% to 49.5%. The statistical analysis showed that the sugar yields from the blended samples were statistically similar and blending of two different AFEX™ pretreated biomass had no significant effects. Shi *et al* (2013) also showed that the mixed biomass pellets produced from ionic liquid pretreated feedstocks had neutral effects on the sugar yield and it can be a viable and valuable resource considering the availability of biomass.

To summarize, pellets achieved their true densities at an applied pressure of 94.8 MPa and pelleting beyond this pressure did not produce denser pellets. Pelleting at different pressures had no significant effect on the sugar yields of AFEX™ pretreated and AFEX™ pretreated blended samples. Reducing the screen size from 4 mm to 2 mm had minor positive effect on the pellet physical qualities and no effects on the sugar yields. Use of the large screen size sample could decrease the energy required for raw material preparation for pretreatment and densification. Blending of two different lignocellulosic biomass had no significant effect on the sugar yields and the pellets produced from the AFEX™ pretreated mixed feedstocks could be a feasible resource considering the availability of biomass around the processing depots.

4.5. Conclusions

This study investigated the impacts of the blending of AFEX™ pretreated corn stover and switchgrass on the pellet compaction characteristics and sugar yields. Pellets were produced under different conditions using a single pelleting unit. Pellet unit density, pellet hardness, specific energy consumption for pellet production, and sugar yields were investigated. Following are the outcomes obtained from the study:

1. AFEX™ pretreatment increased the pellet unit density and pellet hardness of corn stover and switchgrass samples. Increase in pellet unit density was observed with increase in the applied load, and the AFEX™ pretreated samples achieved their maximum pellet unit density at 94.8 MPa applied pressure.

2. Pellets produced from the blend with a higher proportion of corn stover (B_3) (2 mm) produced strongest pellets with hardness of 711 N. Besides, the pellets produced from 2 mm screen size samples required more force to break than the 4 mm samples.

3. The variables blending ratio, screen size, and applied pressure had significant effect on energy consumption. The energy required for pellets production varied from

11.4 to 57.9 kW h t^{-1}, and the energy consumption increased with increase in the applied pressure. AFEX™ pretreated switchgrass required more energy for compaction because of its low bulk density compared to corn stover, and the blend with higher proportion of switchgrass consumed more energy.

4. Glucose and xylose yields of AFEX™ pretreated samples were 4–4.5 times and 2–2.5 times higher than that of the untreated samples. Biomass blending and pelleting had no significant effect on glucose and xylose yields of all the samples. These results indicate that blending and pelleting the feedstocks can be a potential and viable option to minimize the logistical issues without affecting the sugar yields.

Table 4.1. Optimum AFEX™ pretreatment conditions employed for corn stover and switchgrass

Feedstock	Ammonia loading (Ammonia: Dry biomass) (w/w)	Temperature (˚C)	Moisture content (db %)	Pretreatment soaking time (min)
Corn stover	1:1	100	60	15
Switchgrass	1:2	100	50	30

Table 4.2. Bulk and particle density of different samples

Samples	Bulk density (kg m^{-3})		Particle density (kg m^{-3})	
	2 mm	4 mm	2 mm	4 mm
ASG	150.5 ± 3.5^{f}	116.3 ± 5.4^{i}	1368.6 ± 17.8^{bc}	1332.1 ± 11.3^{d}
B_1	176.1 ± 2.8^{d}	135.9 ± 3.8^{g}	1369.1 ± 21.6^{bc}	1360.3 ± 25.0^{dc}
B_2	202.5 ± 6.8^{b}	162.5 ± 6.3^{e}	1377.1 ± 19.0^{bc}	1374.0 ± 20.0^{bc}
B_3	230.0 ± 8.1^{a}	190.3 ± 7.7^{c}	1385.4 ± 29.5^{bc}	1380.6 ± 20.5^{bc}
ACS	237.8 ± 6.9^{a}	197.3 ± 6.5^{bc}	1423.1 ± 11.2^{a}	1393.6 ± 13.8^{ab}
UCS	120.9 ± 4.7^{h}	107.6 ± 3.8^{j}	956.7 ± 7.8^{e}	923.5 ± 5.8^{f}
USG	$115. 5 \pm 3.4^{i}$	100.8 ± 2.7^{k}	905.2 ± 6.9^{g}	843.6 ± 9.7^{h}

Same letters in superscript within column for a given property are not significantly different ($p < 0.0001$)

Table 4.3. Pellet hardness of the samples compressed at different applied pressures

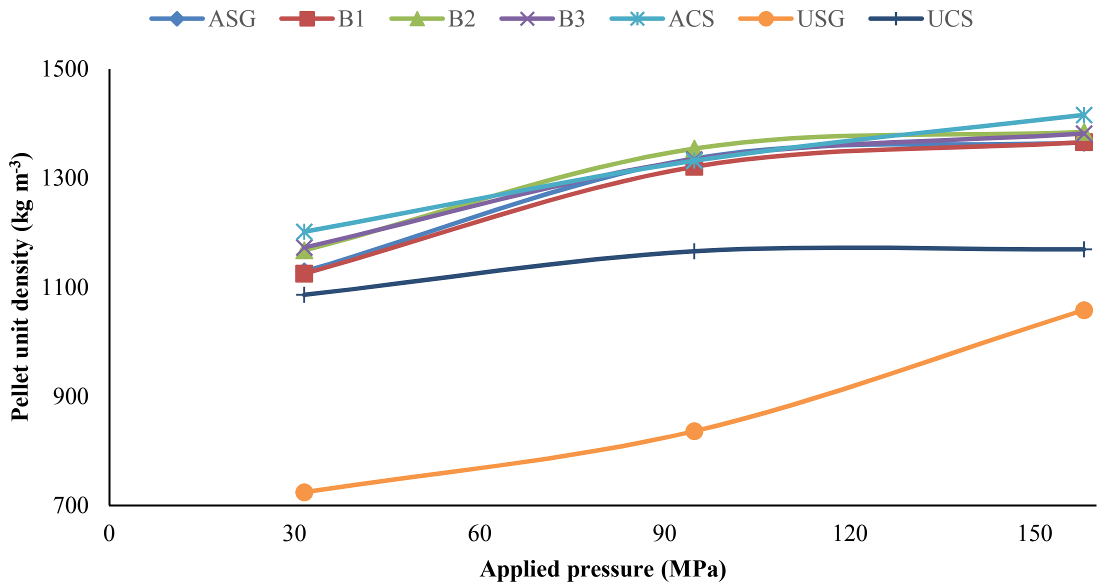
Feedstock	Pressure (MPa)	Pellet hardness (N)	
		2 mm	4 mm
ASG	31.6	132 ± 5.0	124 ± 16.9
	94.8	404 ± 79.6	361 ± 49.4
	158.0	564 ± 27.7	367 ± 63.3
B_1	31.6	138 ± 7.3	135 ± 52.1
	94.8	394 ± 39.4	334 ± 24.1
	158.0	587 ± 22.9	556 ± 58.6
B_2	31.6	120 ± 13.0	183 ± 33.7
	94.8	426 ± 17.2	355 ± 54.4
	158.0	626 ± 40.4	613 ± 32.8
B_3	31.6	334 ± 51.6	173 ± 66.1
	94.8	668 ± 43.7	418 ± 51.6
	158.0	711 ± 94.1	633 ± 34.1
ACS	31.6	192 ± 81.8	410 ± 54.5
	94.8	771 ± 47.9	483 ± 89.8
	158.0	923 ± 72.2	805 ± 90.1
USG	31.6	107 ± 18.6	105 ± 35.7
	94.8	138 ± 27.5	129 ± 64.8
	158.0	272 ± 38.7	248 ± 28.4
UCS	31.6	128 ± 15.8	132 ± 34.8
	94.8	176 ± 40.0	186 ± 51.9
	158.0	307 ± 32.4	296 ± 19.9

Table 4.4. Main and interaction effects of variables on pellet hardness and specific energy consumption

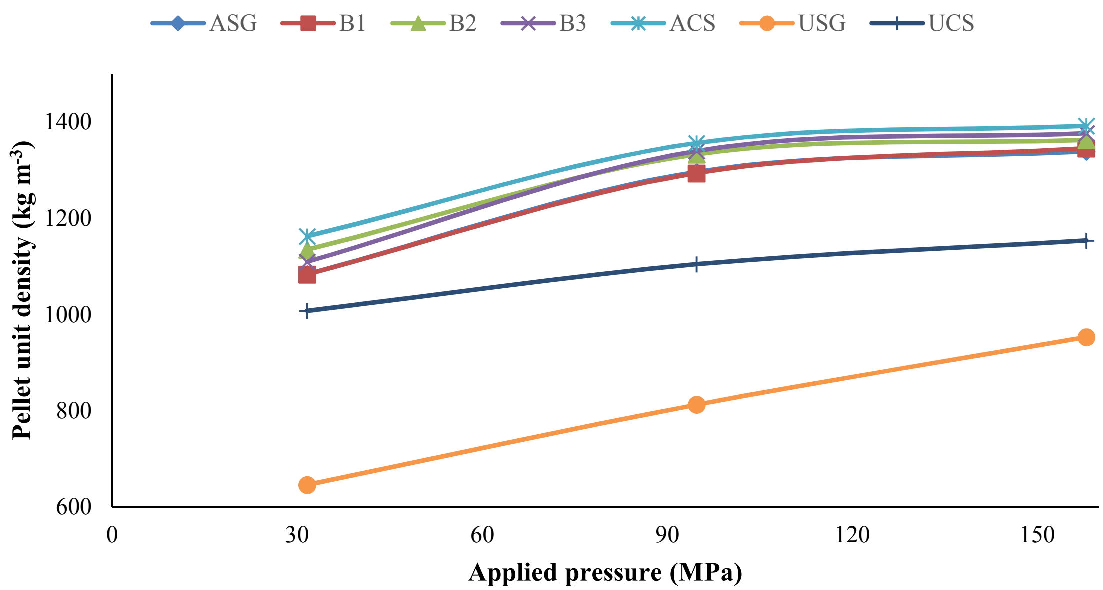
Source	DF	Type III SS	Mean Square	F Value	Pr > F
Pellet hardness					
Blend ratio	4	893904	223476	49	<.0001
Screen size	1	108736	108736	23	<.0001
Blending ratio* Screen size	4	64485	16121	3	0.0114
Applied pressure	2	3005969	1502984	331	<.0001
Blend ratio*Applied pressure	8	103422	12927	2	0.0094
Screen size*Applied pressure	2	104458	52229	11	<.0001
Blend ratio* Screen size*Applied pressure	8	162220	20277	4	0.0003
Specific energy consumption					
Blend ratio	4	395	99	63	<.0001
Screen size	1	2	2	2	0.2208
Blending ratio* Screen size	4	442	110	71	<.0001
Applied pressure	2	42448	21224	13607	<.0001
Blend ratio*Applied pressure	8	38	5	3	0.0033
Screen size*Applied pressure	2	186	93	60	<.0001
Blend ratio* Screen size*Applied pressure	8	160	20	13	<.0001

Table 4.5. Chemical composition of untreated corn stover and switchgrass

Feedstock	Glucan (%)	Xylan (%)	Arabinan (%)	Ash (%)	Lignin (%)
Corn stover	34.3	18.5	2.5	5.5	15.7
Switchgrass	32.2	14.8	2.3	3.7	13.3



a) 2 mm



b) 4 mm

Fig. 4.1. Pellet unit density of the samples at different applied pressures

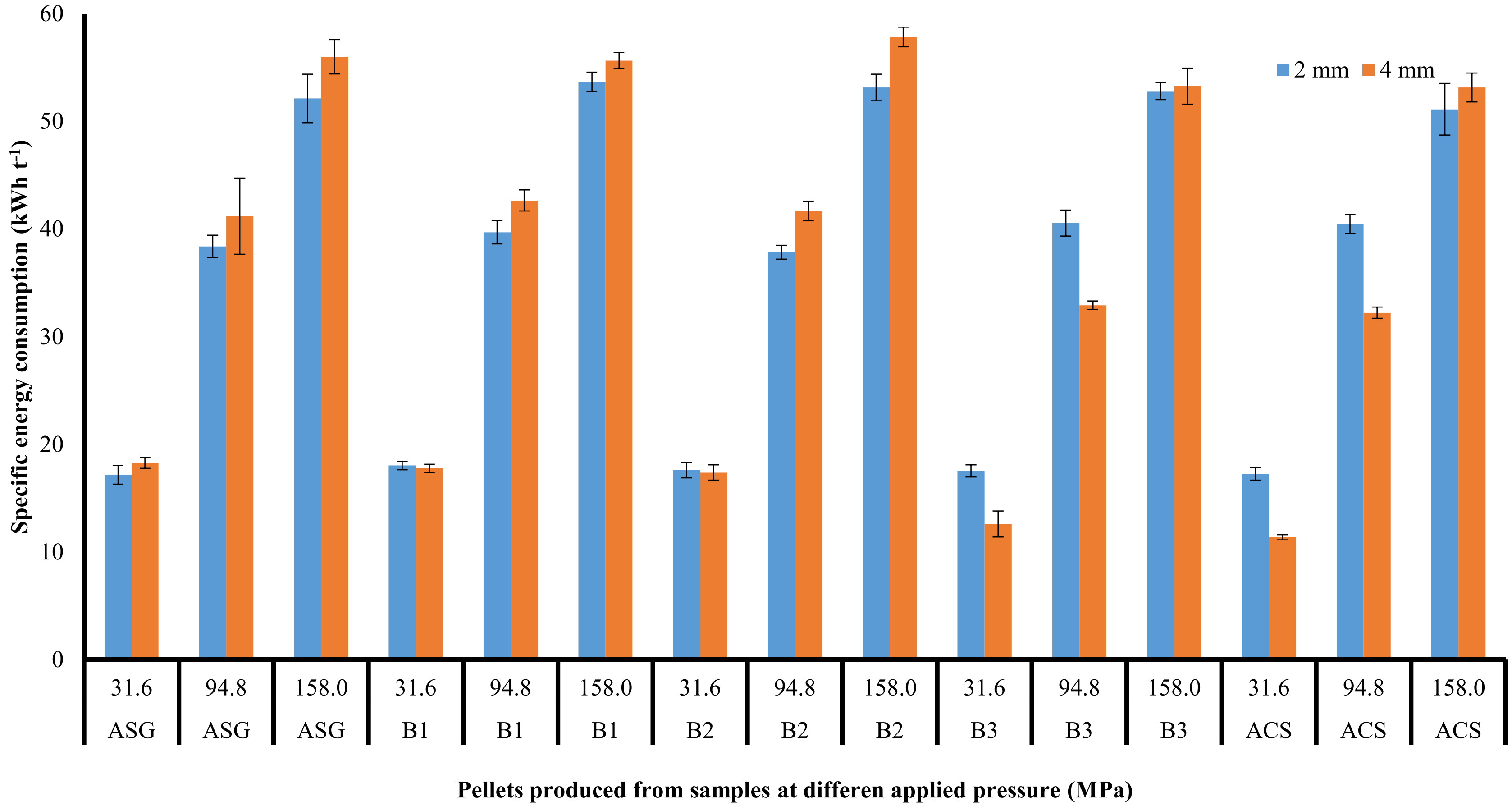


Fig. 4.2. Specific energy consumption of different samples at different applied pressures

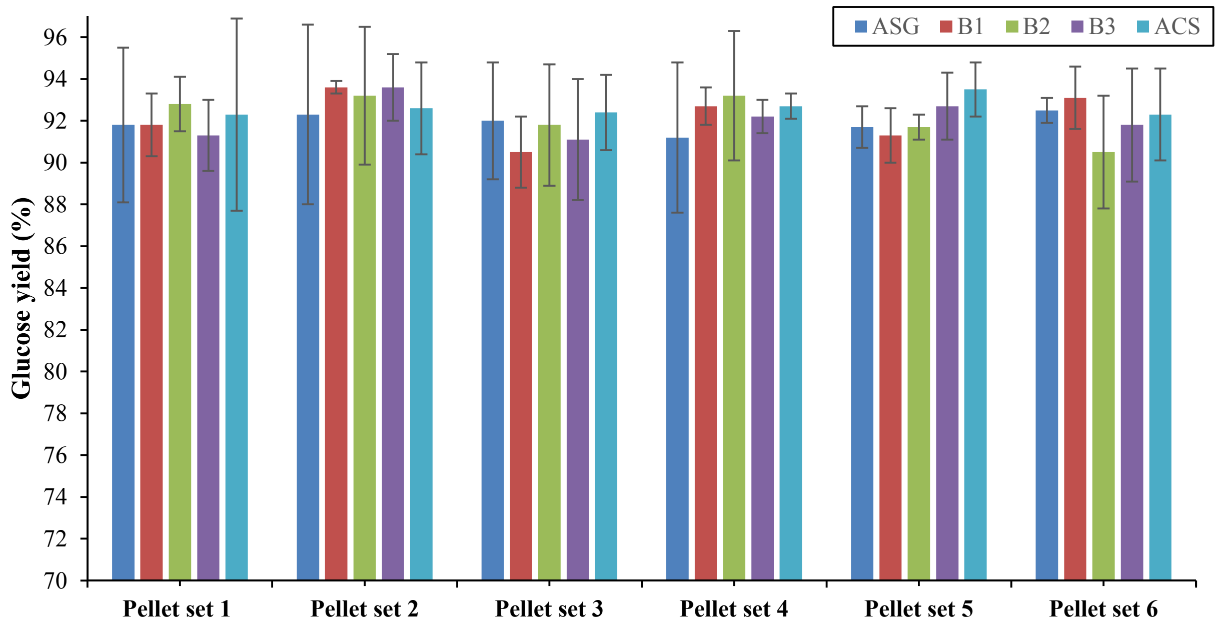


Fig. 4.3. Glucose yield of pelleted produced under different conditions

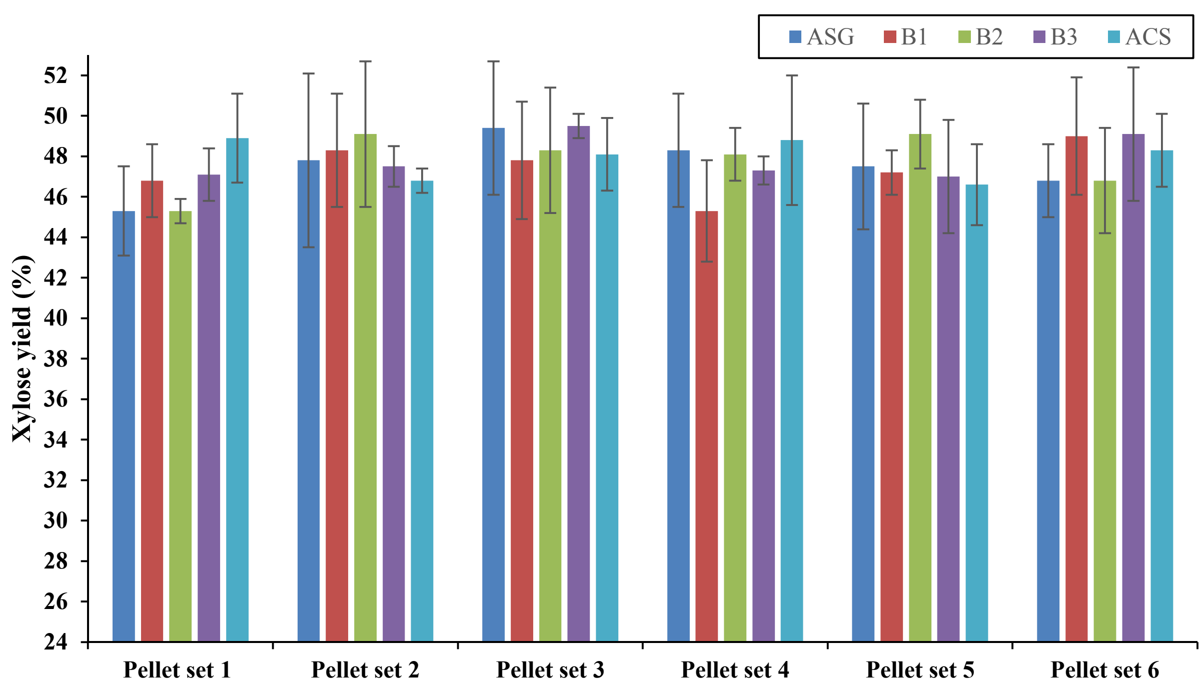


Fig. 4.4. Xylose yields of pellets produced under different conditions

Pellet set 1 = 2 mm screen size samples compressed at 31.6 MPa; Pellet set 2 = 2 mm screen size samples compressed at 94.8 MPa; Pellet set 3 = 2 mm screen size samples compressed at 158.0 MPa; Pellet set 4 = 4 mm screen size samples compressed at 31.6 MPa; Pellet set 5 = 4 mm screen size samples compressed at 94.8 MPa; Pellet set 6 = 4 mm screen size samples compressed at 158.0 MPa.

5. IMPACT OF AFEX™ PRETREATMENT AND EXTRUSION PELLETING ON PELLET PHYSICAL PROPERTIES AND SUGAR RECOVERY FROM CORN STOVER, PRAIRIE CORD GRASS, AND SWITCHGRASS

5.1. Abstract

The effects of AFEX™ pretreatment, feedstock moisture content (5,10, and 15% wb), particle size (screen sizes of 2, 4, and 8 mm), and extrusion temperature (75, 100, and 125°C) on pellet bulk density, pellet hardness, and sugar recovery from corn stover, prairie cord grass, and switchgrass were investigated. Pellets were produced from untreated and AFEX™ pretreated feedstocks using a laboratory scale extruder. AFEX™ pretreatment increased subsequent pellet bulk density from 453.0 kg m^{-3} to 650.6 kg m^{-3} for corn stover from 463.2 kg m^{-3} to 680.1 kg m^{-3} for prairie cord grass, and from 433.9 kg m^{-3} to 627.7 kg m^{-3} for switchgrass. Maximum pellet hardness of 2342.8 N, 2424.3 N, and 1298.6 N was recorded for AFEX™ pretreated corn stover, prairie cord grass, and switchgrass respectively. Glucose yields of AFEX™ corn stover pellets, prairie cord grass, and switchgrass pellets varied from 88.9% to 94.9%, 90.1% to 94.9%, and 87.0% to 92.9% respectively. Glucose and xylose yields of AFEX™ pellets were not affected by the extruder barrel temperature and the hammer mill screen size. The results obtained showed that low temperature and large particle size during the extrusion pelleting process can be employed for AFEX™ treated biomass without compromising sugar yields.

5.2. Introduction

Lignocellulosic biomass can be envisaged as an alternative to limited availability, environmentally polluting, and import reliant fossil fuels. However, challenges associated with the conversion of lignocellulosic biomass into biofuels are significant. Biofuels production are not economically competitive with fossil fuels due to technological limitations, low demand, and logistical constraints (Caputo *et al.,* 2005). Among the technical issues, the recalcitrant nature of lignocellulosic biomass and its low bulk density are two of the most significant challenge that need to be addressed before biofuels production can be competitive with fossil fuels.

5.2.1. Biomass densification

Physical limitations of lignocellulosic feedstocks include low bulk density, irregular shape, and high moisture content. Due to these difficulties, biomass poses significant challenges in the feedstock supply chain (Tumuluru *et al.,* 2010). To overcome these challenges, Kaliyan and Morey (2009) suggested that biomass can be densified into different densified products such as pellets, briquettes, or cubes. Densification involves the application of mechanical compression to the biomass particles, thus increasing the biomass density (Mani *et al.,* 2006). During the densification process, biomass particles undergo three different stages (Mani *et al.,* 2003). In the first stage, biomass particles rearrange to form a closely packed mass. During the second stage, biomass particles undergo elastic and plastic deformation as the applied force increases the inter-particle contact. With this increase in the applied pressure and temperature, lignin, one of the basic structural components of lignocellulosic biomass, becomes soft and acts a natural binding agent. In the third stage, the compression continues at high pressure till the grinds achieving the particle density. Biomass densification is affected by the following parameters: feedstock particle size, moisture content, chemical composition, preheating temperature, densification pressure and temperature, retention time, and die rotation (Tumuluru *et al.,* 2010). These factors can be optimized to produce high quality densified products.

5.2.2. Biomass pretreatment

Lignocellulosic biomass is made up of three basic structural components viz. cellulose, hemicelluloses, and lignin. Among these components, cellulose and hemicelluloses are sugar polymers and can be hydrolyzed to yield fermentable sugars. But the cellulose and hemicelluloses are surrounded by lignin, which acts as a barrier to protect the sugar polymers from degradation. Biomass pretreatment is a crucial preprocessing operation, which involves altering the cellulose-hemicellulose-lignin matrix, thus removing the barriers to degradation. Several biomass pretreatment technologies have been designed to improve feedstock characteristics, process conversion efficiency, energy density of bulky biomass, and to reduce the costs associated with handling, transportation, and storage (Eisentraut and Brown, 2012).

Ammonia Fiber Expansion (AFEX™) is a thirty-year-old pretreatment method that involves treating biomass with liquid ammonia under mild temperature (70-200°C) and pressure (100-400 psi) for a specific time (Bals *et al.,* 2010). This swell the cellulose fibers, which are allowed to explode when the pressure is rapidly released (Dale, 1986). The explosion effect results in several physical and chemical alterations in biomass structure. Some of the alterations include cellulose decrystallization, partial depolymerization of hemicellulose, cleavage of lignin-carbohydrate complex (LCC), and surface area increase due to structural disruption. Chundawat *et al* (2007) studied the effect of AFEX™ pretreatment on the enzymatic digestibility of corn stover. FTIR results confirmed the cleavage of lignin–carbohydrate complex (LCC) for AFEX™-treated fractions and spectroscopy results showed the extraction of cleaved-lignin phenolic fragments and other extractives to the biomass surface. AFEX™ pretreatment increased sugar yield of different lignocellulosic biomass. Biersbach *et al* (2015) showed the significant improvement in the ethanol yields from corn stover, prairie cord grass, and switchgrass pretreated through AFEX™. Alizadeh *et al* (2005) reported a 2.5 times increase in ethanol yield after the switchgrass was subjected to AFEX™ pretreatment. Similarly, Teymouri *et al* (2005) reported an increase in ethanol yield of 2.3 times after the corn stover was pretreated through AFEX™.

5.2.3. Regional biomass processing depots (RBPD)

For economical and successful operation of large scale biorefineries, developing a reliable feedstock supply chain is crucial. A biomass supply chain may comprise several processing steps including harvest/collection, storage, preprocessing, and transportation. Carolan *et al* (2007) proposed a network called “Regional biomass processing depots” (RBPD) to address the logistical issues for the large scale biorefineries. RBPDs involves procuring, pretreating, and densifying biomass on a distributed scale to minimize transport of bulk, low density feedstocks. RBPDs densifies the feedstock prior to shipment to a larger, centralized biofuel production facility (Eranki and Dale, 2011).

To make the RBPDs successful, it is imperative to understand the impacts of different preprocessing operations on the physical qualities and the sugar yields from the densified products. Rijal *et al* (2014) studied the impact of particle size and densification on AFEX™ pretreated corn stover, switchgrass, and prairie cord grass on ethanol yield. The results showed that densification had no adverse effects on ethanol yield for corn stover and switchgrass, but the yield was reduced for prairie cord grass. Hoover *et al*

(2014) studied the effect of pelleting variables on physical properties and sugar yields of corn stover pretreated through AFEX™. Improved durability and bulk density were noticed and die speed, heating, and particle size did not affect the sugar yield.

The objective of this study was to understand the effect of AFEX™ pretreatment and extrusion pelleting process on the pellet physical qualities and sugar yields from corn stover, prairie cord grass, and switchgrass. The impacts of selected variables viz. barrel temperature (75, 100, and 125°C), hammer mill screen size (2, 4, and 8 mm), and feedstock moisture content (5, 10, and 15% wet basis) on pellet physical qualities (pellet bulk density and pellet hardness) and sugar yields (glucose and xylose) were examined.

5.3. Materials and Methods

5.3.1. Samples preparation

The feedstocks corn stover, prairie cord grass, and switchgrass were harvested from local farms in Brookings, SD (2009), and were milled using three different screen sizes viz. 2, 4 mm (Hammer Mill, Thomas Wiley laboratory mill, Swedesboro, NJ), and 8 mm (Speed King, Winona Attriltion mill Co, Winona MN). Samples (2 kg) of milled samples were sealed in ziploc bags and sent to Michigan State University (Biomass conversion research laboratory) for AFEX™ pretreatment. The optimum conditions employed for AFEX™ pretreatment of the feedstocks are given in Table 5.1. AFEX™ pretreated samples were returned and stored in the refrigerator at 4°C until use. Before pelleting, the moisture content of the untreated and pretreated samples was adjusted to 5, 10, and 15% on a wet basis by adding a calculated quantity of water. To improve the quality of pellets and to attain the standards, additives can be added to the feedstocks in the range of 0.5-5% (by weight) to produce quality pellets (Tabil, 1996). In this study, 2% of corn starch (by weight) was added to the untreated samples before pelleting.

5.3.2. Extrusion pelleting

Pelleting was carried out using a single screw extruder (Brabender Plasti-corder Extruder model PL 2000, Hackensack, NJ). The barrel length to screw diameter (l/d) was 20:1 and the compression ratio used in the extruder was 3:1. The temperature of the barrel and the die section of the extruder were maintained at three different levels, viz. 75,100, and 125°C. The speed of the extruder screw was controlled by a 7.5 HP motor, which had the ability to vary the screw speed from 0 to 210 rpm. A constant screw speed of 50 rpm was maintained during the experiment and the sample feeding was done manually through the hopper. Compressed air was employed as a cooling agent and to maintain the required temperature whole through the barrel length. 200 g of moisture adjusted samples were fed into the hopper and pellets were collected in the die section. Fig.5.1 shows the single screw extruder, the pellets obtained from the untreated and AFEX™ pretreated prairie cord grass (b) and (c).

5.3.3. Analytical methods

Biomass bulk density is a key parameter in determining the economics and logical requirements for handling and transporting the biomass from field to the biorefineries (Lam *et al.,* 2007). Bulk density of the pelleted and unpelleted corn stover, prairie cord grass, and switchgrass samples were determined using a hopper and stand equipment (151, Seedburo equipment Co., Des Plaines, IL). The mass of samples collected was divided by the known cylinder volume to determine the bulk density of the samples. Gas pycnometer (Micrometritics multivolume 1305, Norcross, GA) was employed to determine the particle density of untreated and AFEX™ pretreated samples.

Texture analyzer (TA HD plus, Texture Technologies Corp, NY) shown in Fig.5.2 was used to determine the hardness of untreated and AFEX™ pretreated pellets. Force vs. displacement graph was depicted by the exponent software (Version 6.0, Stable Microsystems Ltd, UK) and the maximum force required to break the sample was taken from the graph. Untreated, AFEX™ pretreated, untreated pelleted, and AFEX™ pretreated pelleted samples were subjected to enzymatic hydrolysis using NREL LAP 009 procedure (Selig *et al.,* 2008). The amount of cellulase enzyme (NS50013 activity 70 FPU g^{-1}) was maintained at 15 FPU g^{-1} DM, β-glucosidase (NS50010 activity 250 CBU g^{-1}) at 30 CBUg^{-1} DM, and multienzyme (NS50012 activity 100 FBG g^{-1}) at 30 FBG g^{-1}. The contents were incubated at 50 ±1°C in an incubated bench top orbital shaker (Thermo forma scientific 420, Waltham, MA) at 150 rpm of for a period of 72 hours. A representative sample of 1 mL was subjected to sugar analysis in HPLC (Agilent Technologies, Santa Clara, CA; Bio-Rad Aminex 87H column, Hercules, CA) using a mobile phase of 0.005 M sulfuric acid at 0.6 ml min^{-1} flow rate at a column temperature of 65°C. Sugar yields were calculated based on Seling *et al* (2008) procedure, considering the chemical composition of untreated samples and the sugar concentrations from HPLC analysis.

5.3.4. Statistical analysis

Statistical analysis was executed using SAS statistical software (SAS 9.3, SAS Institute Inc. Cary, NC) at 5% level of significance. One-way analysis of variance (ANOVA) was performed to determine the significant difference between the means of different properties. PROC GLM procedure in SAS software was employed to determine the least significant difference (LSD) values at $p < 0.05$. Experimental design was made using Design-Expert software (Version 8.0.7.1, Stat-Ease, Minneapolis, MN). Second-order polynomial equation (Eq 5.1) was developed to evaluate the impacts of barrel temperature (X_1 - 75, 100, 125°C), screen size (X_2 - 2, 4, 8 mm), and moisture content (X_3 - 5, 10, 15% wb) on glucose and xylose yields.

$$Y=\alpha_0+\alpha_1X_1+\alpha_2X_2+\alpha_3X_3+\alpha_{11}X_1^2+\alpha_{22}X_2^2+\alpha_{33}X_3^2+\alpha_{12}X_1X_2+\alpha_{13}X_1X_3+\alpha_{23}X_2X_3 \quad \text{----- Eq (5.1)}$$

Where, Y – sugar yields (glucose and xylose); X_1, X_2, and X_3 are selected independent variables; α_0 to α_{33} – coefficients to be estimated and they represent the linear, quadratic and interaction terms.

5.4. Results and Discussion

5.4.1. Bulk and particle densities of feedstocks

Table 5.2 shows the bulk and particle density of untreated and AFEX™ pretreated corn stover, prairie cord grass, and switchgrass samples. The bulk density of the samples decreased as the particle size increased, since larger particles result more pore volume (Mani *et al.,* 2004). The highest bulk density of 234.3 kg m^{-3} (2 mm screen size, 15% moisture content) was observed in AFEX™ pretreated prairie cord grass, while untreated prairie cord grass (2 mm screen size, 15% moisture content) resulted in a density of 201.3 kg m^{-3}. Increasing the moisture content increased the bulk density of all the samples. Similar to the bulk density, the highest particle densities were 1447.9 kg m^{-3} (4 mm screen size, 5% moisture content) in AFEX™ pretreated prairie cord grass and 1070 kg m^{-3} in untreated prairie cord grass (2 mm screen size, 5% moisture content). Particle density is a good indicator of pelletability (Oginni, 2014) and higher values allow for production of high quality pellets at lower energy consumption (McBain, 1966). Smaller particle size results in reduced air pores and increased particle density. As moisture content of the untreated and AFEX™ pretreated samples was increased, the particle density decreased due to faster volumetric expansion of particles (McMullen *et al.,* 2005; Bernhart and Fasina, 2009). Sundaram *et al* (2015) observed a similar decrease in particle density, when moisture content of untreated and AFEX™ pretreated corn stover, prairie cord grass, and switchgrass samples was varied from 8% to 20%.

A significant increase in bulk and particle density of corn stover, prairie cord grass, and switchgrass samples was noted after the samples were pretreated through AFEX™. This increase highlights the impact of AFEX™ pretreatment on feedstocks properties. AFEX™ pretreatment impacts physico-chemical alterations in the ultra and macro structure of lignocellulosic biomass (Dale, 1986). Hoover *et al* (2014) studied the AFEX™ pretreatment of corn stover and concluded that the corn stover become more brittle and friable after pretreatment. This could be the reason for increased bulk and particle density of AFEX™ pretreated samples. ANOVA results for the factors (hammer mill screen size and feedstock moisture content) affecting the bulk and particle density of the samples are given in Table 5.3. The statistical analysis confirmed that moisture content and feedstock particle size (hammer mill screen size) had significant impact ($p < 0.05$) on the bulk and particle density of the untreated and AFEX™ pretreated samples.

5.4.2. Effect of barrel temperature, moisture content, and screen size on pellet bulk density

Pellet bulk density is one of the important properties which directly impacts costs involved in feedstock storage and transportation (Tarasov *et al.,* 2013). Pellet bulk density of untreated and AFEX™ pretreated corn stover, prairie cord grass, and switchgrass pellets produced under different conditions are provided in Table 5.4. Pellets produced from samples pretreated through AFEX™ technology had higher bulk density than the untreated samples. Pellet bulk density of untreated corn stover, prairie cord grass, and switchgrass were 453.0, 463.2, and 433.9 kg m^{-3}, respectively, while the densities were increased to 650.6, 680.1, and 627.7 kg m^{-3}, respectively when the feedstocks were first subjected to AFEX™ pretreatment. One of the important impacts of AFEX™ pretreatment is the extraction of cleaved lignin phenolic fragments and other extractives to the biomass surface (Chundawat *et al.,* 2007). This increased availability of lignin on the surface of biomass acts as a binding agent during the pelletization process, resulting in a highly compacted product. Sundaram *et al* (2015) studied the compaction behavior of AFEX™ pretreated corn stover, prairie cord grass, and switchgrass through compression experiments. Based on the yield strength from the Kawakita and Luddde model, the authors concluded that AFEX™ pretreatment made the biomass samples easier to compress compared to the untreated samples.

The effects of selected variables (barrel temperature, screen size, and moisture content) on pellet bulk density of untreated and AFEX™ samples were statistically analyzed, and Table 5.5 shows the ANOVA results. The moisture content of the feedstock had a significant effect on pellet bulk density. Higher moisture content increased the bulk density of pellets produced from AFEX™ pretreated and untreated samples. Mani et al (2006) found that water present in the feedstock acts as a binder and as a lubrication agent which aids in increasing the bonding between particles by promoting van der Waals forces and by increasing the true area of contact between the particles. Feedstock particle size had an inverse effect on the pellet bulk density of untreated samples ($p<0.05$), but was not a significant factor for the AFEX™ pretreated samples. During the extrusion process, the feedstock is subjected to heating, mixing, and shearing, resulting in physical and chemical alterations to the feedstock (Lin *et al.,* 2012). The brittle and friable AFEX™ pretreated feedstocks (Hoover *et al.,* 2014) when subjected to extrusion could have experienced high shear between the particles and between the particles and barrel. These actions could have further reduced the particle size of feedstock milled through larger screens thus making the screen size an insignificant factor.

Similar to screen size, extrusion temperature had a direct and significant effect on the pellet bulk density of untreated feedstocks. This outcome can be attributed to the effect of temperature on the binding agent. Lee *et al* (2000) observed that gelatinization of corn starch increased as barrel temperature was increased in a twin screw extruder. Kaliyan and Morey (2009) stated mechanical shearing of feedstocks during densification improves gelatinization of starch. In this study, corn starch added as a binding agent and was likely subjected to gelatinization, thus acting as a binding agent in sticking the particles together. Barrel temperature did not significant affect pellet bulk density of AFEX™ pretreated corn stover, prairie cord grass, and switchgrass pellets. Hoover *et al* (2014) also concluded that preheating had no significant effect on the density and durability of the pellets made from AFEX™ pretreated corn stover. The increased availability of lignin after the AFEX™ pretreatment, when subjected to thermal softening during the extrusion process could be the responsible for improved binding to produced compacted pellets. AFEX™ pellets with higher bulk density can have benefits during the logistics, since fewer trips are necessary to transport the same amount of untreated feedstocks (Hoover *et al.,* 2014).

5.4.3. Effect of barrel temperature, moisture content, and screen size on pellet hardness

The pellet hardness or compressive resistance test is useful in assessing the pellets ability to withstand crushing loads by the weight of pellets overhead, as would occur during storage, handling, and transportation. Table 5.6 shows the hardness values of pellets produced from untreated versus AFEX™ pretreated corn stover, prairie cord grass, and switchgrass under different conditions. Lignin is a natural binding agent that plays a vital role in densifying biomass (Kaliyan and Morey, 2010). In untreated feedstocks the presence of lignin, in its natural form, resulted in extruded pellets with maximum hardness of 238.5 N, 267.5 N, 162.8 N for corn stover, prairie cord grass, and switchgrass, respectively. In comparison, the hardness of the pellets produced from the AFEX™ pretreated samples were significantly higher. This increase in hardness can be attributed to the disintegration of lignocellulosic structure of biomass after AFEX™ pretreatment, especially in terms of modifications to lignin structure. Lignin modifications include cleaving of the lignin-carbohydrate complex and lignin C-O-C bonds, which results in solubilization of lignin and redepositing on the surface of the biomass (Dale, 1986). This increased surface availability of lignin after AFEX™

pretreatment contributed to the better binding of particles during the pelleting process, thus increasing pellet hardness by an order of magnitude.

Barrel temperature had a significant positive correlation to pellet hardness in untreated feedstocks. This can be attributed to the effects of temperature on the binding agent added to the feedstock, and to the thermal softening of lignin during the extrusion pelleting. Wood (1987) studied the effect of raw and pre-gelatinized starch on the pellet hardness and concluded that pellets produced from pre-gelatinized starch had higher hardness. Starch granules could have been subjected to gelatinization (Cavalcanti, 2004) when the untreated feedstocks were subjected to shear friction during the extrusion pelleting. Maximum hardness of 2424.3 N was recorded for AFEX™ pretreated prairie cord grass pellets (4 mm screen size, 15% moisture content, and 125°C barrel temperature). AFEX™ pretreated corn stover achieved a maximum hardness of 2342.8 N (2 mm screen size, 15% moisture content, and 125°C barrel temperature), while AFEX™ pretreated switchgrass produced a maximum hardness of 1298.6 N (4 mm screen size, 10% moisture content, and 75°C barrel temperature). Statistical analysis showed that extrusion barrel temperature was not a significant factor ($p>0.05$) in affecting pellet hardness of AFEX™ pretreated samples. This result indicates that good quality AFEX™ pellets can be produced at a low temperature of 75°C using extrusion pelleting. Karki *et al* (2015) reported the high quality pellets produced from AFEX™ pretreated corn stover, prairie cord grass, and switchgrass using an alternative, low temperature (ambient to 60°C) densification system. Producing quality pellets at low temperature will have significant impact in reducing the pellet production cost.

Feedstock moisture content was directly correlated with pellet hardness for both untreated and AFEX™ pretreated feedstock samples ($p < 0.0001$) as shown in Table 5.7. Water acts as a binding and lubricating agent during the pelleting process. Moisture content of the feedstocks is a crucial factor in extruder machines to produce harder pellets, since water acts a binding and lubricating agent (Grover and Mishra, 1996). Lehtikangas (2001) found that moisture reduce the lignin softening temperature by plasticizing the molecular chains. For the untreated feedstocks, the combination of starch gelatinization (Kaliyan and Morey, 2009) and lignin softening could have increased the pellet hardness when the moisture content was increased.

Screen size also had a significant influence on pellet hardness ($p < 0.0001$) of untreated and AFEX™ pretreated samples. For both untreated and AFEX™ pretreated samples, maximum pellet hardness was obtained using 2 mm and 4 mm screen size samples. A significant reduction in hardness was observed when the screen size was increased to 8 mm. Finely ground materials will produce highly compacted products due to filling of voids by the way of particle rearrangement when the applied pressure is increased (Jiang *et al.,* 2014). Moreover, smaller particles will have a better surface area available for binding during the densification process. Payne (1978) stated that medium or fine ground materials will have greater surface area for moisture addition, which increases the starch gelatinization promoting better binding of particles during the pelleting process.

5.4.4. Effect of barrel temperature, moisture content, and screen size on sugar recovery

The chemical composition of untreated corn stover, prairie cord grass, and switchgrass are given in Table 5.8. Glucose and xylose recovery from untreated corn stover, prairie cord grass, and switchgrass pelleted under different conditions are shown in Fig.5.3. For the untreated feedstocks, the glucose yields were 56.3 to 68.6% for corn stover pellets, 42.6% to 52.0% for prairie cord grass pellets, and 38.7% to 58.1% for the switchgrass pellets. The glucose yields varied from 88.9% to 94.9% for the pellets produced from AFEX™ pretreated corn stover and from 90.1% to 94.9% for the pellets produced from AFEX™ pretreated prairie cord grass. For pellets produced from AFEX™ pretreated switchgrass the variation ranged from 87.0% to 92.9%. Glucose yields from the pellets produced from AFEX™ corn stover, AFEX™ prairie cord grass, and AFEX™ switchgrass were 1.6 times, 2.1 times, and 2.3 times higher respectively, compared to pellets produced from untreated samples. Increases in xylose yields from the AFEX™ corn stover, prairie cord grass, switchgrass pellets were 1.6, 1.4, and 2.0 times compared to the pellets produced from untreated samples. The increase in glucose and xylose recovery can be credited to the influence of AFEX™ pretreatment. AFEX™ pretreatment produce physical and chemical structure alterations in the ultra and macro structure of lignocellulosic biomass (Dale, 1986). The alterations include cellulose decrystallization (Gollapalli *et al.,* 2002), hemicellulose depolymerization, cleaving of lignin-carbohydrate linkages, cleaving of lignin C-O-C bonds, and increased surface area due to structural disruption (Chundawat *et al.,* 2011). These alterations could have increased enzyme accessibility to cellulose and hemicellulose, thus increasing sugar yields.

Table 5.9 shows the p-value and model equations for the glucose and xylose yields from the pellets produced from untreated corn stover, prairie cord grass, and switchgrass. The model values (p-value) for the pellets produced from the untreated corn stover, prairie cord grass, and switchgrass were significant ($p<0.05$). For the AFEX™ pretreated pellets the selected variables did not affect the sugar yields ($p>0.05$). Feedstock particle size (hammer mill screen size) did not significantly ($p > 0.05$) affect glucose and xylose yields of the pellets produced from AFEX™ pretreated corn stover, prairie cord grass, and switchgrass. This could be due to the friable and brittle nature of AFEX™ pretreated biomass (Hoover *et al.,* 2014) undergoing further size reduction during the extrusion pelleting process. This outcome suggests that the large screen size AFEX™ pretreated samples can be employed, without compromising the sugar yields. This will reduce biofuel production costs (Kaliyan and Morey, 2009). For the pellets produced from untreated samples, hammer mill screen size did not significantly affect the glucose and xylose yields ($p < 0.05$). Maximum glucose recovery of 68.6 % (4 mm screen size, 15% moisture content, 125°C barrel temperature) was obtained from the untreated corn stover pellets, whereas for untreated prairie cord grass pellets the maximum recovery was 52.9 % (4 mm screen size, 125°C). Glucose recovery was much lower when the screen size was increased 8 mm for untreated corn stover and prairie cord grass pellets. For the untreated switchgrass pellets, the maximum sugar recovery of 58.1% was obtained from the pellets produced from 2 mm screen size particle with 10% moisture content extruded at 125°C.

Moisture content (5% and 15%) did not affect the glucose and xylose yields of pellets produced from untreated and AFEX™ pretreated samples ($p>0.05$). Karunanithy and Muthukumarappan (2010) observed that glucose recovery from prairie cord grass and switchgrass decreased, when the moisture content was increased beyond 15%. The authors attributed this decrease in glucose recovery to the less resistance offered by the high moisture samples during the extrusion.

Barrel temperature did not have a significant effect on glucose and xylose recoveries of untreated samples. Maximum glucose recovery of untreated corn stover (68.6%), prairie cord grass (52.9%), and switchgrass (58.1%) was obtained at 125°C barrel temperature. Glucose recovery dropped when these samples were pelleted at lower temperatures. Maximum glucose recovery at higher temperature suggests the cell wall disruption during extrusion pelleting. Karunanithy and Muthukumarappan (2009, 2010) studied the potential of extrusion as a pretreatment method to enhance the enzymatic digestibility of corn stover, prairie cord grass, and switchgrass. The studies showed maximum sugar recoveries were obtained at a barrel temperature of 150°C for corn stover and switchgrass. Barrel temperature had no significant effect on the sugar recovery of the pellets produced from AFEX™ pretreated samples. This results indicate that pellets can be produced from AFEX™ pretreated samples at very low temperature of 75° with maximum sugar yields.

Extrusion pelleting had no significant impact on the sugar recovery of pellets produced from the AFEX™ samples compared to the unpelletized AFEX™ pretreated samples. Bals *et al* (2014) studied the downstream processing of pellets produced from AFEX™ pretreated corn stover and noted that AFEX™ pellets were easily mixable, and that glucose and xylose yields for pelletized and non-pelletized AFEX™ corn stover were equal. Rijal *et al* (2014) also suggested that the subsequent grinding of densified products was not necessary, as ethanol yields were statistically similar for the AFEX™ PAKs and milled AFEX™ PAKs produced from AFEX™ pretreated corn stover, prairie cord grass, and switchgrass.

5.5. Conclusions

The current work examined the impacts of feedstock moisture content, hammer mill screen size, and extruder barrel temperature on pellet bulk density, pellet hardness, and sugar yields from untreated and AFEX™ pretreated corn stover, prairie cord grass, and switchgrass. Following are the conclusions obtained from the results:

- AFEX™ pretreatment increased the bulk and particle densities of the corn stover, prairie cord grass, and switchgrass. Moisture content and screen size had significant impacts on the bulk and particle density of the AFEX™ pretreated samples.
- Pellet bulk density of the corn stover, prairie cord grass, and switchgrass increased to 650.6 kg m^{-3}, 680.1 kg m^{-3}, and 627.7 kg m^{-3} after pretreatment by the AFEX™ technique. Barrel temperature and screen size were not significant factors, whereas moisture content was significantly affecting bulk density of the compacted AFEX™ pellets.
- Pellets produced from the AFEX™ pretreated samples were more than 10 times harder than pellets produced from the untreated samples. Moisture content was a significant factor in producing the harder pellets from all AFEX™ pretreated samples. Harder pellets were produced from the AFEX™ pretreated samples at a selected low barrel temperature of 75°C.

- Reducing the hammer mill screen size from 8 mm to 2 mm and increasing the temperature from 75°C to 125°C did not increase the sugar yields from AFEX™ pretreated pellets. Hence, producing AFEX™ pellets using low barrel temperature (75°C) and large screen size (8 mm) could effectively reduce the cost of pellets production without compromising sugar yields.

Table 5.1. AFEX™ pretreatment conditions employed for different biomass*

Conditions	Corn stover	Prairie cord grass	Switchgrass
Ammonia loading, NH3 to dry biomass loading (w/w)	1:1	1:2	1:2
Moisture content (db %)	60	40	50
Pretreatment soaking time (min)	15	30	30

**Pretreatment was carried out at 100°C*

Table 5.2. Bulk and particle densities of untreated and AFEX™ pretreated corn stover, prairie cord grass, and switchgrass

Hammer mill screen size (mm)	Moisture content (%) wb	Bulk density (kg m^{-3})*					
		Untreated corn stover	AFEX™ corn stover	Untreated prairie cord grass	AFEX™ prairie cord grass	Untreated switchgrass	AFEX™ switchgrass
2	5	104.5 ± 1.5^{24}	196.8 ± 2.9^{6}	186.8 ± 4.7^{7}	222.6 ± 4.1^{3}	131.6 ± 3.6^{20,21}	169.8 ± 4.0^{9}
	10	116.8 ± 2.6^{23}	199.9 ± 5.0^{5,6}	190.4 ± 2.6^{7}	229.0 ± 3.7^{2}	147.5 ± 1.8^{15}	176.2 ± 3.4^{8}
	15	121.1 ± 2.6^{22}	207.3 ± 2.9^{4}	201.3 ± 3.2^{5}	234.3 ± 2.9^{1}	149.8 ± 3.0^{15}	179.9 ± 3.9^{8}
4	5	95.4 ± 2.5^{25,26}	165.0 ± 5.9^{10}	154.4 ± 3.7^{14}	156.7 ± 2.8^{13,14}	88.1 ± 2.5^{27,28}	155.5 ± 2.5^{13,14}
	10	98.1 ± 2.3^{25,26}	179.9 ± 4.4^{8}	158.2 ± 4.5^{12,13}	162.1 ± 2.7^{10,11}	95.6 ± 3.2^{25,26}	160.9 ± 3.2^{11,12}
	15	103.5 ± 2.6^{24}	189.9 ± 5.2^{7}	164.1 ± 1.3^{10}	169.2 ± 4.7^{9}	103.5 ± 2.6^{24}	170.4 ± 3.9^{9}
8	5	76.6 ± 6.7^{30,31}	132.2 ± 2.1^{20,21}	90.1 ± 1.5^{27}	129.4 ± 0.7^{21}	74.2 ± 2.6^{31}	122.0 ± 3.6^{22}
	10	81.7 ± 3.2^{29}	136.4 ± 1.5^{18,19}	95.2 ± 3.2^{26}	138.2 ± 3.3^{17,18}	75.7 ± 2.0^{31}	133.3 ± 2.7^{19,20}
	15	85.5 ± 3.5^{28}	141.0 ± 3.7$^{16-18}$	99.1 ± 2.8^{25}	143.3 ± 2.8^{16}	80.3 ± 1.9^{29,30}	140.1 ± 1.3^{16,17}
Hammer mill screen size (mm)	**Moisture content (%) wb**	**Particle density (kg m^{-3})***					
		Untreated corn stover	**AFEX™ corn stover**	**Untreated prairie cord grass**	**AFEX™ prairie cord grass**	**Untreated switchgrass**	**AFEX™ switchgrass**
2	5	981.6 ± 13.0^{18,19}	1348.3 ± 12.9$^{6-9}$	1086.5 ± 9.8^{16}	1438.3 ± 5.6^{1,2}	922.0 ± 7.3^{24,25}	1367.6 ± 9.5^{5}
	10	965.6 ± 6.8$^{20-22}$	1340.0 ± 8.7$^{8-12}$	1075.4 ± 4.2^{16,17}	1430.3 ± 10.8^{2}	913.2 ± 10.0^{25}	1356.1 ± 5.3^{5,6}
	15	948.6 ± 2.6^{23}	1328.1 ± 16.9$^{12-15}$	1070.0 ± 4.4^{17}	1426.9 ± 11.7^{2}	910.8 ± 4.5^{25}	1355.1 ± 4.2^{6,7}
4	5	957.5 ± 10.3$^{21-23}$	1340.2 ± 12.8$^{8-12}$	988.2 ± 3.3^{18}	1447.9 ± 6.8^{1}	894.8 ± 14.3^{26}	1353.1 ± 12.7^{6,7}
	10	949.4 ± 9.1^{23}	1330.3 ± 6.6$^{11-14}$	973.6 ± 8.9^{19,20}	1446.5 ± 11.4^{1}	888.2 ± 12.9^{26,27}	1349.7 ± 5.5$^{6-8}$
	15	930.2 ± 8.6^{24}	1317.28 ± 9.7^{15}	981.1 ± 9.1^{18,19}	1430.0 ± 8.4^{2}	877.5 ± 5.2^{27}	1343.6 ± 6.9$^{7-10.}$
8	5	853.4 ± 13.5^{28}	1325.1 ± 14.9$^{13-15}$	975.8 ± 11.9^{19,20}	1402.3 ± 6.3^{3}	779.4 ± 12.2^{29}	1340.8 ± 13.2$^{8-11}$
	10	846.7 ± 11.5^{28}	1319.9 ± 11.9^{14,15}	968.0 ± 6.5^{20,21}	1389.3 ± 5.2^{4}	770.3 ± 11.2$^{29-30}$	1332.8 ± 12.2$^{10-13}$
	15	844.6 ± 7.0^{28}	1316.7 ± 15.1^{15}	954.1 ± 9.8^{22,23}	1390.7 ± 4.3^{3,4}	765.0 ± 12.6^{30}	1336.7 ± 4.5$^{9-13}$

**Means with same superscripts between columns for different properties are not significantly different ($p<0.05$)*

Table 5.3. ANOVA results for the factors affecting bulk and particle density of untreated and AFEX™ pretreated corn stover, prairie cord grass, and switchgrass

Source	DF	Type III SS	Mean Square	F Value	Pr > F
		Bulk density			
Feedstock (FS)	5	301906.1	60381.2	5305.8	<.0001
Screen size (SS)	2	196886.8	98443.4	8650.4	<.0001
FS*SS	10	81254.2	8125.4	714.0	<.0001
Moisture content (MC)	2	9008.6	4504.3	395.8	<.0001
FS*MC	10	164.4	16.4	1.4	0.1604
SS*MC	4	108.9	27.2	2.3	0.0509
FS*SS*MC	20	1254.8	62.7	5.5	<.0001
		Particle density			
Feedstock (FS)	5	8979311.7	1795862.3	122.5	<.0001
Screen size (SS)	2	814977.9	407488.9	27.8	<.0001
FS*SS	10	112924.3	11292.4	0.7	0.6570
Moisture content (MC)	2	22224.8	11112.4	0.7	0.0497
FS*MC	10	721297.1	72129.7	4.9	<.0001
SS*MC	4	155690.8	38922.7	2.6	0.0339
FS*SS*MC	20	180538.9	9026.9	0.6	0.8988

Table 5.4. Pellet bulk density untreated and AFEX™ pretreated corn stover, prairie cord grass, and switchgrass

Screen size (mm)	Barrel temperature (°C)	Moisture content (% wb)	Corn stover		Prairie cord grass		Switchgrass	
			AFEX™	Untreated	AFEX™	Untreated	AFEX™	Untreated
2	75	5	$622.0 \pm 2.7^{26-33}$	$454.7 \pm 10.0^{53-67}$	$641.3 \pm 9.4^{13-21}$	$466.0 \pm 5.4^{47-54}$	$614.0 \pm 7.5^{31-33}$	$442.2 \pm 3.6^{67-70}$
	75	10	$629.7 \pm 5.2^{21-29}$	$453.0 \pm 7.1^{55-67}$	$668.5 \pm 16.8^{1-6}$	$475.0 \pm 9.9^{46-48}$	$618.7 \pm 10.3^{28-33}$	$449.0 \pm 5.6^{60-69}$
	75	15	631.2 ± 12.3	$460.8 \pm 11.9^{50-60}$	680.1 ± 7.8^{1}	$463.2 \pm 3.9^{47-57}$	$620.2 \pm 4.2^{27-33}$	$450.9 \pm 5.0^{57-68}$
	100	5	$627.8 \pm 11.8^{22-30}$	$460.7 \pm 3.9^{50-60}$	$656.2 \pm 10.1^{6-11}$	$490.7 \pm 10.0^{43-45}$	$619.4 \pm 4.2^{27-33}$	$448.3 \pm 4.9^{61-69}$
	100	10	$638.1 \pm 3.8^{15-23}$	$461.5 \pm 4.4^{49-58}$	$663.0 \pm 14.6^{2-6}$	$482.8 \pm 7.6^{45,46}$	$621.4 \pm 2.0^{26-33}$	$464.5 \pm 6.2^{47-56}$
	100	15	$643.9 \pm 8.4^{12-20}$	$460.4 \pm 2.2^{50-60}$	$676.0 \pm 7.3^{1,2}$	$497.2 \pm 3.6^{41-44}$	$625.2 \pm 5.4^{24-31}$	$473.7 \pm 2.8^{46-49}$
	125	5	$625.3 \pm 7.6^{23-31}$	$463.8 \pm 3.7^{47-57}$	$653.0 \pm 6.9^{7-13}$	$513.6 \pm 8.2^{37-40}$	$618.1 \pm 4.7^{29-33}$	$459.1 \pm 9.7^{51-62}$
	125	10	$643.2 \pm 5.2^{13-20}$	$467.2 \pm 8.4^{47-53}$	$659.9 \pm 9.9^{4-9}$	$503.0 \pm 5.7^{39-43}$	$622.0 \pm 1.1^{26-33}$	$472.7 \pm 3.9^{46-50}$
	125	15	$646.0 \pm 11.7^{10-18}$	$469.5 \pm 7.1^{47-51}$	$642.6 \pm 4.6^{13-20}$	$497.9 \pm 4.6^{41-43}$	$627.7 \pm 5.9^{22-30}$	$475.1 \pm 1.2^{46,47}$
4	75	5	$633.9 \pm 13.5^{18-26}$	$455.2 \pm 5.8^{52-66}$	$640.1 \pm 3.9^{14-22}$	$482.8 \pm 12.6^{45,46}$	$615.2 \pm 0.3^{30-33}$	$458.2 \pm 6.0^{51-63}$
	75	10	$636.5 \pm 4.6^{17-25}$	$458.4 \pm 4.6^{51-62}$	677.7 ± 3.7^{1}	$493.2 \pm 8.6^{42-45}$	$612.7 \pm 4.8^{31-33}$	$466.5 \pm 4.5^{47-54}$
	75	15	$638.0 \pm 6.0^{15-24}$	$458.6 \pm 3.0^{51-62}$	$673.4 \pm 6.3^{1-3}$	$484.4 \pm 4.4^{44-46}$	$619.3 \pm 1.7^{27-33}$	$456.5 \pm 4.8^{52-64}$
	100	5	$636.9 \pm 4.8^{16-24}$	$459.6 \pm 2.7^{51-61}$	$651.1 \pm 7.1^{7-14}$	$504.4 \pm 9.5^{39-42}$	$610.5 \pm 4.8^{32,33}$	$454.8 \pm 7.1^{52-67}$
	100	10	$644.6 \pm 12.7^{12-19}$	$465.9 \pm 5.7^{47-54}$	$669.5 \pm 9.5^{1-5}$	$512.7 \pm 5.7^{37-40}$	$615.6 \pm 8.7^{30-33}$	$466.9 \pm 4.5^{47-54}$
	100	15	$650.6 \pm 16.9^{7-15}$	$462.2 \pm 4.6^{48-58}$	$671.1 \pm 6.5^{1-5}$	$482.8 \pm 8.5^{45,46}$	$624.3 \pm 9.2^{25-31}$	$467.7 \pm 3.1^{47-52}$
	125	5	$641.6 \pm 8.0^{13-21}$	$465.0 \pm 2.9^{47-56}$	$659.1 \pm 8.6^{4-10}$	$520.3 \pm 7.5^{35-38}$	610.3 ± 3.7^{33}	$452.6 \pm 1.9^{56-67}$
	125	10	$649.7 \pm 14.3^{8-15}$	$465.6 \pm 4.3^{47-55}$	678.7 ± 5.9^{1}	$508.3 \pm 6.4^{38-41}$	$618.2 \pm 9.9^{29-33}$	$458.1 \pm 8.9^{51-64}$
	125	15	$645.5 \pm 9.8^{11-18}$	$464.8 \pm 2.8^{47-56}$	$662.3 \pm 12.7^{3-8}$	$515.6 \pm 9.8^{36-39}$	$619.1 \pm 3.8^{26-33}$	$464.4 \pm 5.5^{47-56}$
8	75	5	$633.9 \pm 8.0^{18-26}$	$449.3 \pm 3.8^{58-69}$	$631.9 \pm 13.2^{20-28}$	$502.5 \pm 9.9^{40-43}$	$612.7 \pm 4.3^{31-33}$	$436.9 \pm 1.4^{69,70}$
	75	10	$647.3 \pm 10.4^{9-17}$	$455.7 \pm 9.3^{52-65}$	$661.3 \pm 9.8^{3-8}$	$497.2 \pm 11.2^{41-44}$	$620.9 \pm 10.4^{27-33}$	$445.3 \pm 9.8^{63-70}$
	75	15	$649.7 \pm 15.2^{8-16}$	$454.4 \pm 1.2^{53-67}$	677.5 ± 10.0^{1}	$498.1 \pm 4.9^{41-43}$	$623.3 \pm 15.2^{26-32}$	$447.1 \pm 3.6^{61-69}$
	100	5	$636.3 \pm 9.0^{17-24}$	$448.0 \pm 0.3^{61-69}$	$645.0 \pm 12.4^{12-18}$	$524.0 \pm 8.5^{34-37}$	$612.4 \pm 5.4^{31-33}$	$438.1 \pm 0.3^{68-70}$
	100	10	$646.4 \pm 8.2^{10-17}$	$452.4 \pm 1.4^{56-67}$	678.9 ± 5.8^{1}	$532.3 \pm 12.2^{34,35}$	$617.4 \pm 5.6^{29-33}$	$447.5 \pm 7.8^{61-69}$
	100	15	$650.6 \pm 16.9^{7-15}$	$454.1 \pm 5.5^{54-67}$	$672.5 \pm 4.1^{1-4}$	$522.1 \pm 8.5^{35-37}$	$619.1 \pm 9.8^{27-33}$	$443.1 \pm 6.2^{65-70}$
	125	5	$639.0 \pm 14.2^{14-22}$	$445.3 \pm 4.7^{64-70}$	$646.0 \pm 12.4^{10-18}$	$524.2 \pm 7.0^{34-37}$	$610.5 \pm 12.7^{32,33}$	433.9 ± 3.3^{70}

125	10	647.1 ± 12.8[9-17]	446.5 ±1.7[62-70]	663.2 ± 4.9[2-6]	527.9 ± 14.2[34-36]	618.2 ± 9.9[29-33]	434.1 ± 3.7[70]
125	15	643.0 ± 7.8[13-20]	449.7 ± 5.5[58-69]	658.3 ± 8.5[5-11]	535.2 ± 9.0[34]	614.0 ± 8.1[31-33]	442.5 ± 9.9[66-70]

Table 5.5.ANOVA table for factors affecting pellet bulk density of the untreated and AFEX™ pellets

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Feedstock (FS)	2	55098.0	27549.0	331.56	<.0001
Screen size (SS)	2	342.4	171.2	2.06	0.1311
FS*SS	3	1805.6	601.8	7.24	0.0001
Temperature (T)	2	588.2	294.1	3.54	0.0716
FS*T	4	711.7	177.9	2.14	0.0787
SS*T	4	269.0	67.2	0.81	0.5210
FS*SS*T	6	1026.1	171.0	2.06	0.0617
Moisture content (MC)	2	8196.3	4098.1	49.32	<.0001
FS*MC	4	1846.1	461.5	5.55	0.0003
SS*MC	4	273.0	68.2	0.82	0.5134
FS*SS*MC	6	609.1	101.5	1.22	0.2984
T*MC	4	1055.0	263.7	3.17	0.0156
FS*T*MC	8	2107.9	263.4	3.17	0.0024
SS*T*MC	8	333.5	41.6	0.50	0.8534
FS*SS*T*MC	12	731.7	60.9	0.73	0.7165

Table 5.6. Pellet hardness of untreated and AFEX™ pretreated corn stover, prairie cord grass, and switchgrass

Screen size (mm)	Barrel temperature (°C)	Moisture content (% wb)	Corn stover		Prairie cord grass		Switchgrass	
			AFEX™	Untreated	AFEX™	Untreated	AFEX™	Untreated
2	75	5	1442.9 ± 71.6$^{26-28}$	132.5 ± 23.7$^{51-56}$	1367.3 ± 62.3$^{28-31}$	168.3 ± 52.1$^{44-54}$	1178.3 ± 43.1$^{36-38}$	117.4 ± 9.9$^{52-56}$
	75	10	2047.2 ± 82.6^{9,10}	158.2 ± 48.2$^{45-55}$	1487.9 ± 38.6$^{23-26}$	212.4 ± 40.4$^{42-50}$	1352.0 ± 41.4^{30,31}	130.9 ± 23.2$^{51-56}$
	75	15	2303.8 ± 85.2^{4,5}	157.4 ± 15.3$^{45-55}$	1455.0 ± 86.3$^{25-27}$	225.8 ± 18.5$^{42-45}$	1273.2 ± 29.4$^{32-35}$	138.5 ± 16.8$^{50-56}$
	100	5	1628.6 ± 24.7$^{18-20}$	135.4 ± 19.7$^{51-56}$	1856.1 ± 54.4$^{13-16}$	222.5 ± 15.5$^{42-45}$	1214.4 ± 101.3$^{34-37}$	127.8 ± 20.0$^{51-56}$
	100	10	2102.2 ± 27.6^{8,9}	157.3 ± 28.1$^{45-55}$	1854.0 ± 20.2$^{13-16}$	248.6 ± 24.2^{42,43}	1253.9 ± 65.4$^{33-36}$	147.5 ± 14.6$^{46-56}$
	100	15	2134.5 ± 71.2^{7,8}	198.5 ± 25.2$^{42-51}$	1870.3 ± 46.9$^{12-15}$	238.5 ± 11.2$^{42-44}$	1247.9 ± 53.4$^{33-36}$	154.5 ± 12.4$^{45-55}$
	125	5	1539.4 ± 29.9$^{22-24}$	184.3 ± 30.8$^{43-53}$	1944.9 ± 48.6^{11,12}	218.5 ± 54.8$^{42-47}$	1158.6 ± 47.8$^{37-39}$	124.3 ± 17.6$^{51-56}$
	125	10	2004.8 ± 39.4^{10,11}	214.8 ± 12.4$^{42-49}$	2028.0 ± 88.6^{9,10}	267.5 ± 38.4^{42}	1298.5 ± 84.3$^{31-33}$	143.5 ± 28.5$^{47-56}$
	125	15	2342.8 ± 53.9^{3,4}	238.5 ± 19.4$^{42-44}$	1367.0 ± 75.1$^{29-31}$	249.5 ± 56.3^{42,43}	1265.8 ± 53.7$^{32-35}$	162.8 ± 11.8$^{44-55}$
4	75	5	1484.3 ± 86.3$^{23-26}$	125.6 ± 22.8$^{51-56}$	1388.0 ± 85.2$^{27-30}$	158.3 ± 27.8$^{45-55}$	1106.4 ± 78.3$^{38-40}$	104.5 ± 22.3$^{54-56}$
	75	10	1689.3 ± 78.3^{18}	137.5 ± 34.1$^{50-56}$	1580.0 ± 102.5$^{20-22}$	212.4 ± 40.4$^{42-50}$	1298.6 ± 81.4$^{31-33}$	114.8 ± 10.2$^{52-56}$
	75	15	2014.7 ± 75.2^{10,11}	145.3 ± 18.4$^{47-56}$	2202.0 ± 67.2^{6,7}	184.1 ± 24.6$^{43-53}$	1293.5 ± 64.1$^{31-33}$	130.4 ± 7.1$^{51-56}$
	100	5	1527.9 ± 62.3$^{22-25}$	126.4 ± 35.1$^{51-56}$	2405.0 ± 62.3$^{1-3}$	198.7 ± 12.5$^{42-51}$	1147.7 ± 54.8$^{37-39}$	120.8 ± 16.5$^{52-56}$
	100	10	1798.9 ± 52.1$^{15-17}$	147.3 ± 15.1$^{46-56}$	2389.0 ± 85.2^{2,3}	198.5 ± 21.6$^{42-51}$	1189.3 ± 91.5^{36,37}	140.6 ± 17.3$^{49-56}$
	100	15	2247.1 ± 28.2^{5,6}	160.4 ± 17.5$^{45-55}$	2474.2 ± 18.3^{1}	218.2 ± 13.5$^{42-47}$	1268.1 ± 38.4$^{32-35}$	154.1 ± 11.4$^{45-55}$
	125	5	1547.6 ± 33.4^{22,23}	134.9 ± 24.8$^{51-56}$	2153.2 ± 61.6^{7,8}	214.8 ± 17.3$^{42-49}$	1198.3 ± 53.8$^{35-37}$	120.3 ± 21.2$^{52-56}$
	125	10	1847.2 ± 43.2$^{13-17}$	182.3 ± 18.7$^{43-53}$	2342.2 ± 84.7^{3,4}	237.6 ± 12.5$^{42-44}$	1275.3 ± 51.7$^{32-34}$	142.6 ± 16.3$^{48-56}$
	125	15	2147.4 ± 44.3^{7,8}	190.4 ± 28.6$^{43-51}$	2424.3 ± 67.8^{1,2}	227.9 ± 17.4$^{42-45}$	1212.1 ± 29.7$^{34-37}$	157.6 ± 15.9$^{45-55}$
8	75	5	1385.5 ± 64.8$^{27-30}$	73.6 ± 16.8^{56}	1429.5 ± 57.1$^{26-29}$	98.7 ± 18.3$^{54-56}$	988.7 ± 59.8^{41}	98.3 ± 28.2$^{54-56}$
	75	10	1589.4 ± 54.7$^{19-22}$	99.7 ± 34.2$^{54-56}$	1526.5 ± 26.3$^{22-25}$	125.4 ± 16.5$^{51-56}$	1302.7 ± 34.1$^{31-33}$	114.5 ± 8.2$^{52-56}$
	75	15	1625.8 ± 25.9$^{18-21}$	89.3 ± 29.5^{55,56}	1905.6 ± 71.2^{12,13}	118.8 ± 10.5$^{52-56}$	1253.2 ± 54.8$^{33-36}$	129.4 ± 15.7$^{51-56}$
	100	5	1338.3 ± 48.7$^{30-32}$	115.8 ± 23.4$^{52-56}$	1467.0 ± 49.6$^{24-26}$	135.8 ± 14.3$^{51-56}$	1159.3 ± 81.0$^{37-39}$	110.5 ± 20.4$^{53-56}$
	100	10	1789.4 ± 67.2^{16,17}	139.4 ± 12.7$^{49-56}$	1663.5 ± 75.1^{18,19}	157.8 ± 18.5$^{45-55}$	1058.1 ± 65.1^{40,41}	125.4 ± 12.9$^{51-56}$
	100	15	1772.4 ± 61.8^{17}	129.5 ± 24.8$^{51-56}$	1877.4 ± 17.2$^{12-14}$	138.7 ± 24.2$^{50-56}$	1165.9 ± 73.4^{37,38}	124.9 ± 9.9$^{51-56}$
	125	5	1442.7 ± 62.4$^{26-29}$	105.2 ± 22.5$^{54-56}$	1368.5 ± 70.3$^{28-31}$	134.3 ± 27.9$^{51-56}$	1087.8 ± 79.1^{39,40}	120.6 ± 11.4$^{52-56}$

125	10	1678.3 ± 84.2[18]	126.7 ± 29.9[51-56]	1552.4 ± 87.2[21-23]	184.3 ± 24.1[43-53]	1212.8 ± 27.8[34-37]	133.1 ± 15.2[51-56]
125	15	1653.4 ± 42.3[18-20]	138.4 ± 18.7[50-56]	1829.5 ± 29.5[14-17]	157.5 ± 13.6[45-55]	1248.6 ± 68.1[33-36]	135.4 ± 11.8[51-56]

Table 5.7. ANOVA table for the factors affecting hardness of pellets produced from untreated feedstocks

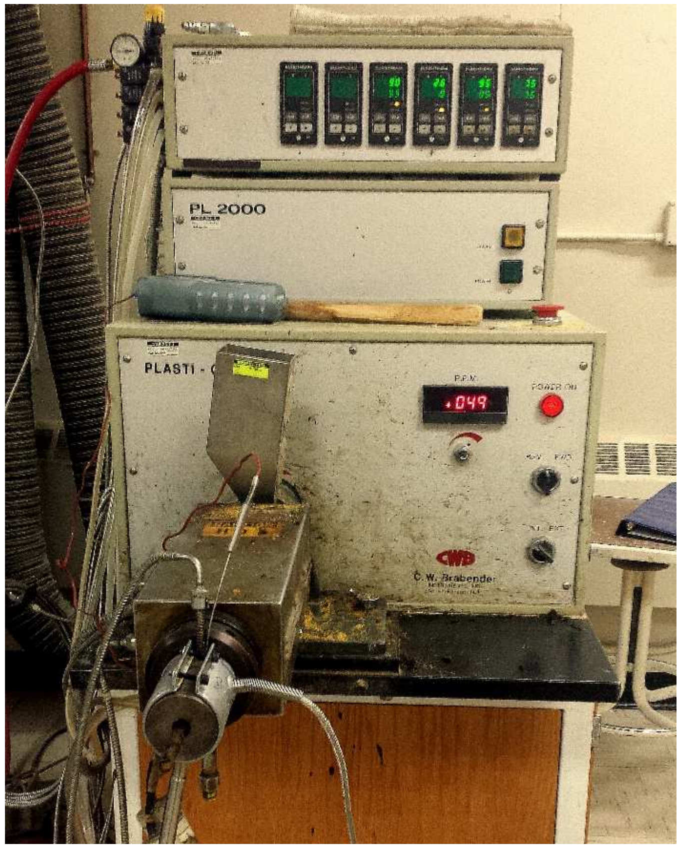
Source	DF	Type I SS	Mean Square	F Value	Pr > F
Temperature (T)	2	28355.1800	14177.5900	19.26	<.0001
Screen size (SS)	2	115764.9267	57882.4633	78.63	<.0001
T*SS	4	153.0533	38.2633	0.05	0.9948
Moisture content (MC)	2	14983.0200	7491.5100	10.18	0.0002
T*MC	4	2665.9600	666.4900	0.91	0.4674
SS*MC	4	1522.4933	380.6233	0.52	0.7235
T*SS*MC	8	720.3667	90.0458	0.12	0.9981

Table 5.8. Chemical composition of untreated corn stover, prairie cord grass, and switchgrass

Feedstock	Corn stover	Prairie cord grass	Switchgrass
Glucan (%)	34.3	37.8	32.2
Xylan (%)	18.5	22.6	14.8
Arabinan (%)	2.5	2.9	2.3
Lignin (%)	15.7	15.3	13.3

Table 5.9. *p*-value and model equations for the glucose and xylose yields from the pellets produced from untreated corn stover, prairie cord grass, and switchgrass.

Feedstocks	Model equations	*p*-value	R^2
Untreated corn stover	$Y_{glucose}=61.81+0.57x_1-1.46x_2+1.88x_1x_3-1.59x_2^2$	0.045	0.82
	$Y_{xylose}=30.60+0.60x_1-0.17x_2-1.46x_1x_3-1.20x_2x_3$	0.009	0.78
Untreated prairie cord grass	$Y_{glucose}=26.02+0.52x_1-0.12x_2+0.12x_2x_3-0.002x_1^2$	0.032	0.87
	$Y_{xylose}=26.75+0.24x_1-0.35x_2-2.51x_3^2$	0.044	0.80
Untreated switchgrass	$Y_{glucose}=49.15+1.02x_1-1.05x_1x_2+0.75x_1^2$	0.001	0.82
	$Y_{xylose}=31.99+0.83x_1+1.95x_3-1.35x_2x_3-0.83x_3^2$	0.007	0.72



(a)

(b)

(c)

Fig. 5.1. Lab scale extruder and the samples

(a) Lab scale extruder (b) Untreated, AFEX™ pretreated prairie cord grass (c) Untreated pellets and AFEX™ pellets

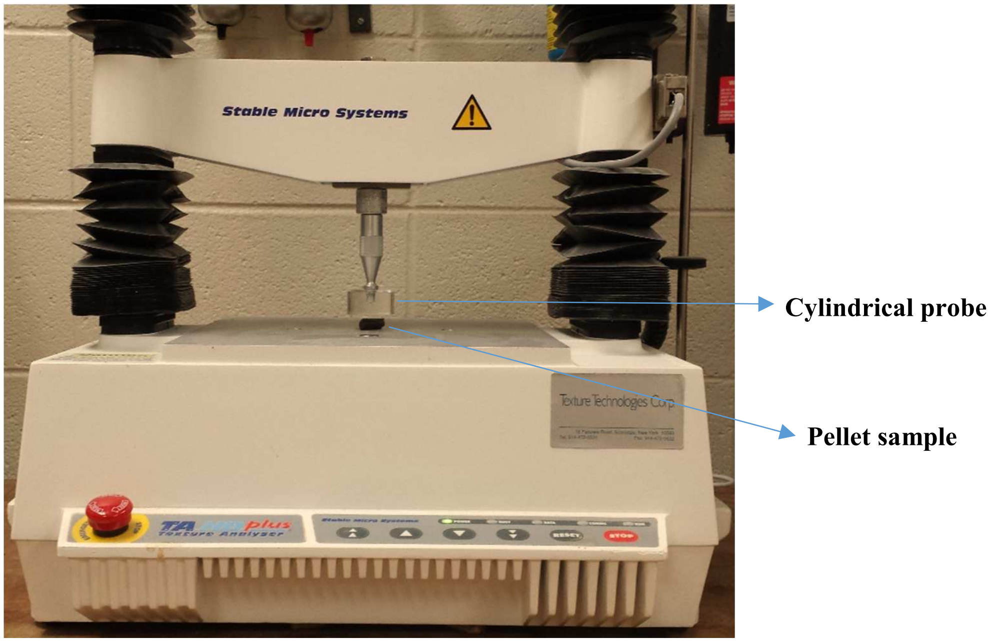


Fig. 5.2. Pellet hardness test using Texture analyzer.

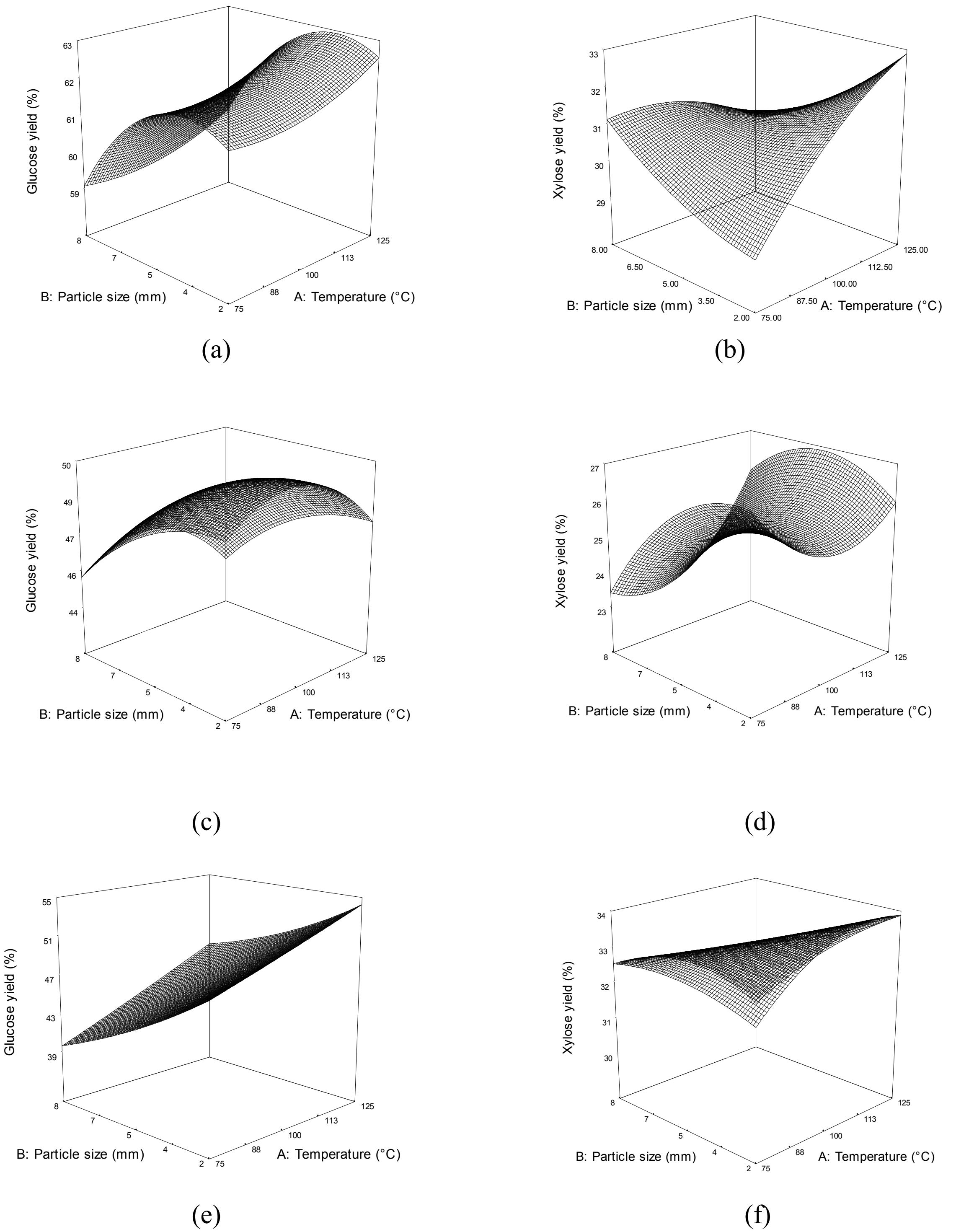


Fig. 5.3. Response surface plots showing the effects of temperature and particle size (hammer mill screen size) and glucose and xylose yields at 10% moisture content.

(a) Glucose yields of untreated corn stover pellets; (b) Xylose yields of untreated corn stover pellets; (c) Glucose yields of untreated prairie cord grass pellets; (d) Xylose yields of untreated prairie cord grass pellets; (e) Glucose yields of untreated switchgrass pellets; (f) Xylose yields of untreated switchgrass pellets.

6. UNDERSTANDING THE IMPACTS OF AFEX™ PRETREATMENT AND DENSIFICATION ON THE FAST PYROLYSIS OF CORN STOVER, PRAIRIE CORD GRASS, AND SWITCHGRASS

6.1. Abstract

Lignocellulosic feedstocks corn stover, prairie cord grass, and switchgrass were subjected to ammonia fiber expansion (AFEX™) pretreatment and densified using extrusion pelleting and ComPAKco densification technique. The effects of AFEX™ pretreatment and densification were studied on the fast pyrolysis product yields. Feedstocks were milled in a hammer mill using three different screen sizes (2, 4, and 8 mm) and were subjected to AFEX™ pretreatment. The untreated and AFEX™ pretreated feedstocks were moisture adjusted at three levels (5, 10, and 15% wb). and were extruded using a lab scale single screw extruder. The barrel temperature of the extruder was maintained at 75, 100, and 125°C. Durability of the extruded pellets made from AFEX™ pretreated corn stover, prairie cord grass, and switchgrass varied from 94.5% to 99.2%, 94.3% to 98.7, and 90.1% to 97.5% respectively. Results of the thermogravimetric analysis showed the decrease in the decomposition temperature of the all the feedstocks after AFEX™ pretreatment indicating the increase in thermal stability. Loose and densified feedstocks were subjected to fast pyrolysis in a lab scale reactor and the bio-char and bio-oil yields were measured. Bio-char obtained from the AFEX™ pretreated feedstocks exhibited increased bulk and particle density compared to the untreated feedstocks. The properties of the bio-oil were statistically similar for the untreated, AFEX™ pretreated, and AFEX™ pretreated densified feedstocks. Based on the bio-char and bio-oil yields, the AFEX™ pretreated feedstocks and the densified AFEX™

pretreated feedstocks (pellets and PAKs) exhibited similar behavior. Hence, it can be concluded that densifying the AFEX™ pretreated feedstocks could be a viable option in the biomass processing depots to reduce the transportation costs and the logistical impediments without affecting the product yields.

6.2. Introduction

Biofuels production from the lignocellulosic biomass could be an attractive approach to reduce the expensive fossil fuels import and to reduce the greenhouse gas emissions. Researchers are being carried out to overcome the challenges associated with the lignocellulosic biomass and to make the biofuels economically competitive with petroleum based transportation fuels. The principle challenge associated in establishing the lignocellulosic biomass based biorefineries is to make the biomass logistics economically and ecologically viable (Hess *et al.,* 2009). Because of the low bulk density nature of the lignocellulosic biomass, the difficulties arise while handling, transporting, and storing which significantly influences the feedstock costs and quality. Size reduction and densification of lignocellulosic biomass plays a vital role in biomass supply chain by improving the handling, transportation, and storage costs (Tumuluru *et al.,* 2011; Mia *et al.,* 2013). The most commonly used methods of densification are pelleting, briquetting, and extrusion processing (Tumuluru *et al.,* 2010). Eranki *et al* (2011a) explored the concept of Regional Biomass Processing Depots (RBPD), which produce pretreated and densified biomass promoting the use of existing logistics systems and economic long distance hauling. RBPD proved to yield same total energy and less greenhouse gas emissions compared to the centralized processing facilities (Eranki and Dale, 2011b).

The composite chemical structure of the lignocellulosic biomass makes it difficult for efficient and economic conversion into biofuels. Lignin, the protective layer encompassing the cellulose and hemicellulose sugar components hinders the enzymatic conversion. Pretreatment is the vital process to break and alter the structure of lignin, providing the access to the cellulose and hemicellulose (Balan *et al.,* 2009). Several pretreatment methods (physical, chemical, and biological) to alter the complex structure and their impacts on the sugar yields were studied extensively (Alvira *et al.,* 2010). Ammonia Fiber Expansion (AFEX™) is one of the biomass pretreatment technologies, which employs physical (high temperature and pressure) and chemical (ammonia) processes to break the complex chemical structure (Balan *et al.,* 2009; Dale, 1986). AFEX™ pretreatment is a promising option in depot processing facility for delivering high value densified biomass (Bonner *et al.,* 2015).

Biofuels can be produced via thermochemical conversion, by thermally degrading the biomass to yield solid bio-char, liquid bio-oil, and gaseous products. Fast pyrolysis is on the thermochemical conversion technologies, proved to be a feasible and viable route to produce renewable liquid fuels (Bridgwater and Peacocke, 2000). Fast pyrolysis involves rapid heating of the biomass in an inert atmosphere to yield dark brown liquid, when the products are condensed (Bridgwater, 2012). RBPDs can be configured to supply the feedstocks in the form best suitable for biochemical and thermochemical conversion process (Eranki and Dale, 2011b). Several researches were carried out to study the impacts of biomass pretreatment and densification on sugar yields through biochemical conversion (Theerarattananoon *et al.,* 2012; Hoover *et al.,* 2014; Rijal *et al.,* 2014; Sundaram *et al.,* 2016). Based on the literature review, the studies on the impacts of lignocellulosic biomass pretreatment on thermochemical conversion are very limited (Amin *et al.,* 2012; Kasparbauer, 2009). Hence, it is imperative to study the impacts of biomass pretreatment on products yield through thermochemical conversion. This research was developed to investigate the impacts of AFEX™ pretreatment and densification on pyrolysis behavior of corn stover, prairie cord grass, and switchgrass. The specific objectives were to study the impacts of AFEX™ pretreatment and selected variables viz. extruder barrel temperature (75, 100, and 125°C), hammer mill screen size (2, 4, and 8 mm), and feedstock moisture content (5, 10, and 15% wet basis) on pellet durability, bio-oil, and bio-char yields from corn stover, prairie cord grass, and switchgrass. Besides, the densified products (PAKs) produced using a ComPAK co device (Karki *et al.,* 2015) was also subjected to fast pyrolysis. The pyrolysis yields and the properties of the bio-char and bio-oil obtained from pellets and PAKs were compared.

6.3. Materials and methods

6.3.1. Biomass preparation and AFEX™ pretreatment

The feedstocks corn stover, prairie cord grass, and switchgrass procured from the local farm in Brookings, South Dakota were dried and milled using hammer mills fitted with screen size of 2, 4 (Thomas wiley laboratory mill, Swedesboro, NJ), and 8 mm (Speed King, Winona Attrition Mill Co., Winona, MN). AFEX™ pretreatment was carried out at Biomass conversion research laboratory (BCRL), Michigan State University. The optimum conditions used for the AFEX™ pretreatment of the feedstocks are given in Table 6.1 (Sundaram *et al.,* 2015; Sundaram and Muthukumarappan, 2016). Moisture content of the samples were determined using ASABE Standard (ASASBE, 2006) and the moisture content was adjusted to 5, 10, and 15% on a wet weight basis by adding calculated quantity of water. The moisture adjusted samples were packed in plastic bags and stored in the refrigerator. The samples were brought to the room temperature, prior to the extrusion pelleting.

6.3.2. Extrusion pelleting and ComPAK co densification

Moisture adjusted untreated and AFEX™ pretreated corn stover, prairie cord grass, and switchgrass samples were pelleted using a laboratory scale single screw extruder (Brabender Plasti-corder Extruder model PL 2000, Hackensack, NJ). Feedstocks were extruded at three different barrel and die temperature (75, 100, and 125°C). Compression ratio of 3:1, barrel length to screw diameter of 20:1, and the screw speed of 50 rpm was maintained for all the samples. 200 g of moisture adjusted samples were fed manually and the samples were pelleted at three different temperatures. Karki *et al* (2015) used the ComPAK co system to densify the AFEX™ pretreated corn stover, prairie cord grass, and switchgrass. The authors termed the densified product obtained from the ComPAK co systems as 'PAKs'. Fig.6.1 shows the untreated, AFEX™ pretreated, untreated pelleted, AFEX™ pretreated pelleted, AFEX™ pretreated PAKs, bio-char, and bio-oil obtained from corn stover.

6.3.3. Biomass characterization

The moisture content of the samples was determined by drying the samples at 103±2°C for a period of 24 h (ASABE, 2006). The volatile matter and ash content of the samples were determined by following ASTM standards (ASTM D3175-11, 2011; ASTM D3174-12, 2012). The fixed carbon was determined by considering the mass of the sample after the volatile matter was driven off. The elements carbon, hydrogen, and oxygen content of the biomass was determined using an elemental analyzer (CE440 Exeter Analytical Ltd, UK). Higher heating values of the samples were determined using an auto bomb calorimeter (IKA C2000, Wilmington, NC). All the characterization was carried out in triplicates. Thermogravimetric analysis (TGA) tests were carried out for the untreated, AFEX™ pretreated, untreated pelleted, and AFEX™ pretreated pelleted samples using Pyris™ 1 TGA instrument (Perkin Elmer Inc, Waltham, MA). About 5 to 20 mg of samples were taken in a crucible and heated from room temperature to 900°C at a heating rate of 30°C min^{-1}.

6.3.4. Pyrolysis experimental setup

Pyrolysis of untreated, AFEX™ pretreated, untreated pelleted, and AFEX™ pretreated pelleted corn stover, prairie cord grass, and switchgrass samples were carried out in a cylindrical stainless reactor. The cylindrical reactor tubing was 508 mm long with an internal diameter of 25.4 mm. The samples were packed between the bed of quartz wool (6625-01, GM associates, Oakland, CA) and steel wool (Grade#1, Rhodes American) inside the cylindrical reactor. The packed reactor was placed inside an electric furnace (Lindberg Blue M™, Thermo Scientific) controlled by a program controller. Compressed nitrogen was purged inside the reactor to maintain the inert atmosphere during pyrolysis process. Before starting the furnace, nitrogen gas was purged inside the reactor for 10 min to remove the air inside the reactor. Thermocouple was placed inside the reactor to read the actual temperature inside the reactor. Heating rate of the furnace was set at 30°C min^{-1} and the pyrolysis temperature was set at 400°C. As the temperature increased, gases produced were condensed using a condenser placed underneath the reactor. The condenser unit consisted of a conical flask with a nose placed inside an ice bath. The condensed liquid product was collected in the conical flask and the non-condensed gases were sent to an exhaust hood. The condensed liquid and the char left inside the reactor were collected and weighed. Fig.6.2 shows the schematic of pyrolysis experimental setup.

6.3.5. Bio-char and bio-oil characterization

Viscosity of the bio-oil samples was determined by using a viscoanalyzer (ATS Rheosystems, NJ) at 20°C. The pH values were determined by using a Fisher scientific digital pH meter (Accument basic AB15, Pittsburg, PA). Higher heating value of the bio-oil samples was determined using an auto bomb calorimeter (IKA C2000, Wilmington, NC). The density of the bio-oil samples was determined by diving the mass of the samples to its volume at room temperature. Bulk density of the bio-char samples was determined by dividing the mass of the sample by the known volume of sample taken in a cylindrical container. Particle density of the bio-char samples was determined using a multivolume gas (Micrometritics 1305, Norcross, GA).

6.3.6. Statistical analysis

Statistical analysis was carried out using SAS statistical software (SAS 9.3, SAS Institute Inc. Cary, NC) at 5 % level of significance. PROC GLM procedure in SAS software was used to determine the least significant difference (LSD) values and main and interaction effects at $p < 0.05$.

6.4. Results and discussion

6.4.1. Biomass characterization

Table 6.2 shows the results of proximate and ultimate analysis and heating values of the untreated and AFEX™ pretreated corn stover, prairie cord grass, and switchgrass. The volatile content of the samples was in the range of 77.3 to 81.9%. Maximum volatile matter was observed in the switchgrass samples and the corn stover samples had lowest volatile content. Compared to the switchgrass samples, corn stover and prairie cord grass samples had more ash content. The elemental carbon content of the samples was in the range of 46.4 to 47.3% and the oxygen and hydrogen contents were in the range of 42.4 to 43.5% and 5.7 to 5.8%, respectively. The heating values of the samples did not show much variance and the values ranged from 18.1 to 18.9 MJ/kg. The carbon and hydrogen contents of the corn stover sample were similar to the values reported by Evans *et al* (1988) and Kumar *et al* (2008), except for the oxygen content, which was slightly higher in this study. In the case of prairie cord grass and switchgrass samples, the proximate and ultimate analysis properties were similar to the values reported by Moutsoglou (2012). It can be inferred from the Table 6.2, that the means of proximate, ultimate analysis, and heating values of the samples did not vary significantly ($p<0.001$). In other words, AFEX™ pretreatment did not have any significant influence in the proximate, ultimate properties, and heating values of the feedstocks. The retention of the biomass components (cellulose, hemicellulose, and lignin) and the composition after pretreatment is one of the unique features of the AFEX™ pretreatment (Campbell *et al.,* 2013). This could be the reason for no significant difference in the properties of the untreated and AFEX™ pretreated samples.

The thermal degradation behavior of the samples was studied using thermogravimetric analysis and Fig.6.3 shows the thermogravimetric (TG) and differential thermogravimetric (DTG) curves for the untreated and AFEX™ pretreated corn stover, prairie cord grass, and switchgrass. The peak in the derivative weight loss curve indicates the maximum rate of weight loss occurred at that temperature. Yang *et al* (Yang *et al.,* 2007) studied the pyrolytic behavior of hemicellulose, cellulose, and lignin and noticed the degradation temperature of hemicellulose and cellulose between 220°C and 400°C. Prins *et al* (2006) also observed the two-step mechanism involved in the degradation of wood. During the first step, degradation of hemicellulose occurs around 200°C followed by cellulose degradation in the second step. In Fig.6.3, the first peak in the derivative weight loss curve corresponds to the hemicellulose degradation followed by the cellulose degradation. Derivative weight loss curves for the untreated and AFEX™ pretreated prairie cord grass and switchgrass showed well defined first and second peaks corresponding to hemicellulose and cellulose degradation. The hemicellulose degradation temperature for the untreated and AFEX™ pretreated prairie cord grass was 325°C and 317°C. For the untreated and AFEX™ pretreated switchgrass, the degradation temperature was 353°C and 347°C. The difference in the hemicellulose degradation temperature of the untreated and AFEX™ pretreated prairie cord grass and switchgrass designates the impacts of the pretreatment. AFEX™ pretreatment impacts structural changes in the biomass and partial hydrolyzing of hemicellulose components is one among the structural changes (Dale, 1986). For the untreated and AFEX™ pretreated corn stover, the hemicellulose peak was not observed. The rate of weight loss decreased after 400°C indicating the degradation of lignin. Yang *et al* (2007) observed the lignin decomposition from 160°C to 900°C and Randriamanantena *et al* (2009) observed the three stages of lignin degradation beginning from 115°C. From Fig.6.3 it can be observed, that the maximum rate of weight losses occurred at 388°C, 382°C, and 410°C for AFEX™ pretreated corn stover, prairie cord grass, and switchgrass respectively. For the untreated corn stover, prairie cord grass, and switchgrass the maximum rate of weight loss occurred at 385°C, 381°C, and 381°C respectively. Increase in the cellulose degradation temperature after AFEX™ pretreatment was observed, and this could be due to the lignin mobilization to the surface of the biomass after pretreatment. During the AFEX™ pretreatment, the ammonia solubilizes the lignin and redeposit on the surface of the biomass (Dale, 1986; Campbell *et al.,* 2013; Bals *et al.,* 2010). The mobilized lignin on the surface could have hindered the cellulose degradation, leading the reduction in the degradation temperature.

6.4.2. Effect of barrel temperature, moisture content, and screen size on pellet durability

Pellet durability describes the ability of pellets to resist against the forces acting on pellets during handling, transportation, and storage. Table 6.3 shows the durability of untreated and AFEX™ pretreated corn stover, prairie cord grass, and switchgrass pellets. Durability of the pellets made from AFEX™ pretreated corn stover, prairie cord grass, and switchgrass varied from 94.5% to 99.2%, 94.3% to 98.7, and 90.1% to 97.5% respectively. For the pellets made from untreated corn stover, prairie cord grass, and switchgrass the durability varied from 26.5% to 80.5%, 33.5% to 68.1%, and 30.4% to 72% respectively. Karki *et al* (2015) reported the durability range of the ComPAK co densified corn stover, prairie cord grass, and switchgrass as 92.6 to 95.2%, 87.1-92.1%, 78.2 to 91.1% respectively. In this study, higher pellet durability was observed for AFEX™ pretreated biomass pellets compared to the untreated biomass pellets and this can be attributed to the increased availability of lignin present in the pretreated biomass for better binding during the pelleting process. Lignin, one of the natural binders present in the lignocellulosic biomass gets mobilized to the surface after the AFEX™ pretreatment (Dale, 1986; Bals *et al.,* 2010; Chundawat *et al.,* 2007) and this availability of lignin during the pelleting process have contributed for the maximum pellet durability. The increased durability of AFEX™ pretreated pellets can resist tougher conditions during handling, transportation, and storage compared to untreated pellets. Campbell *et al* (Campbell *et al.,* 2013) indicated that high durability of AFEX™ pellets are suitable to be stored, handled and shipped without producing much fines.

Temperature had a significant impact ($p<0.05$) only on the durability of pellets made from untreated corn stover, prairie cord grass, and switchgrass. Increase in the barrel temperature had significant effect on the bonding mechanisms, resulting in higher durability of pellets**.** Shaw *et al* (2009) reported the increased tensile strength of the poplar wood pellets to the increased packing and bonding of the particles, when the die temperature was increased from 70°C to 100°C. The increase in durability for pellets made from untreated samples with increase in barrel temperature can be attributed to the gelatinization of corn starch as a binding agent. Lee *et al* (2000) observed the positive correlation between the twin screw extruder barrel temperature and the degree of gelatinization. Pellets made from AFEX™ pretreated samples appeared darker than the pellets made from untreated samples and the reason is presence of cleaved-lignin phenolic fragments and other extractives on the surface of biomass upon AFEX™

pretreatment (Chundawat *et al.,* 2007). Lignin, an aromatic polymer component undergoes softening during the pelleting process, which aids in the binding of particles. Kashaninejad and Tabil (2011) stated that when the biomass is heated during densification, the available lignin melts and become soft exhibiting thermosetting properties. In this extrusion pelleting study, the feedstock was subjected to heating, mixing, and shearing inside the barrel and these effects could have increased the temperature resulting in thermal softening of lignin.

Moisture content had a significant effect (p<0.001) effect on the durability of the pellets produced from untreated and AFEX™ pretreated feedstocks. Increase in the durability of the pellets was observed with increase in the feedstocks moisture content. Kaliyan and Morey (2009) observed the decrease in the glass transition temperature of the corn stover and switchgrass increase in the moisture content from 10% to 20%. Glass transition temperature indicates the transformation of materials from glassy to rubbery state (Roos, 1995). With increase in the moisture content, the feedstock becomes soft and increase in inter-particle contact will occur when the feedstock is forced against the die in screw press compaction (Grover and Mishra, 1996). With increase in the moisture content, the feedstocks could have subjected to better heating, mixing, shearing, and size reduction inside the extruder promoting better particle binding. Under high pressures in the presence of moisture, the natural binders present in the biomass can be activated (Kaliyan and Morey, 2010). In this study, moisture content increase could have activated the lignin present on the surface of AFEX™ pretreated biomass and this could be the reason for increased pellet durability.

Hammer mill screen size had significant effect (p<0.001) on the durability of the pellets produced from untreated corn stover, prairie cord grass, and switchgrass. The first stage in the densification process is the particle rearrangement and Mani *et al* (2004) showed that the smaller particle size samples rearrange quickly than the larger samples to a form closely packed mass. Besides, finer particles accept more moisture than larger particles (Kaliyan and Morey, 2009) and this effect could have made the smaller screen size samples soft resulting in higher degree of compaction inside the extruder barrel. Pellets produced from 8 mm screen size samples had cracks and McBain (1966) indicated that larger particles are fissure points that causes cracks in the compacts. In the case of AFEX™ pretreated samples, the screen size had no significant impact (p>0.05) on the pellet durability. However, pellets with maximum durability were produced from 2 mm and 4 mm screen size samples. Increase in the durability for smaller screen size samples can be attributed to the increased surface availability for binding. Density and durability of the pellets are inversely proportional to the particle size because of the increased surface area during the compaction process (Tumuluru *et al.,* 2010).

6.4.3. Effect of AFEX™ pretreatment and extrusion pelleting on pyrolysis yields

Untreated, AFEX™ pretreated, Untreated pelleted, AFEX™ pretreated pelleted, ComPAKco densified corn stover, prairie cord grass, and switchgrass were subjected to pyrolysis. Table 6.4 shows the pyrolysis yields of the untreated and AFEX™ pretreated corn stover, prairie cord grass, and switchgrass. The yields of bio-oil and bio-char varied from 45.9% to 48% and 22.0 to 24.9%, respectively. The non-condensable gas yield varied from 27.3% to 31.6%. Statistical analysis showed that the hammer mill screen size did not influence (p>0.05) the yields of pyrolysis products. The results showed that the product yields of the pyrolysis were not affected (*p*>0.05) by the AFEX™ pretreatment in corn stover, prairie cord grass, and switchgrass. It can be observed from the Fig.6.4 that the decomposition of AFEX™ pretreated feedstocks was slower compared to the untreated feedstocks. This results indicate the increase in the thermal stability of the feedstocks after AFEX™ pretreatment. Harun *et al* (2013) observed the increase in the nitrogen of AFEX™ pretreated rice straw compared to the untreated rice straw and the authors indicated the increase in nitrogen to the addition of ammonia to the biomass during the AFEX™ pretreatment. In this study, the slow decomposition of AFEX™ pretreated feedstocks could be due to the increase in the nitrogen content of the biomass after pretreatment. Fig.6.4 shows the weight loss curve for untreated, AFEX™ pelleted, AFEX™ ComPAKco densified corn stover, prairie cord grass, and switchgrass (2 mm screen size). The decomposition of the AFEX™ pretreated feedstocks, extrusion pelleted AFEX™ pretreated feedstocks, and ComPAKco densified feedstocks were slower compared to the untreated feedstocks. In other words, extrusion pelleting and ComPAKco densification did not have any influence on the decomposition behavior of the AFEX™ pretreated corn stover, prairie cord grass, and switchgrass. Singh *et al* (2013) indicated the decrease in the decomposition of ionic liquid pretreated biomass to depolymerization of lignin. Lignin depolymerization is one of the important impacts of AFEX™ pretreatment and this also could have decreased the decomposition temperature of the AFEX™ pretreated biomass resulting in higher thermal stability.

Table 6.5 shows the properties of the bio-char and bio-oil obtained from the untreated and AFEX™ pretreated corn stover, prairie cord grass, and switchgrass. The bio-oils obtained were brown colored having pungent odor. The pH value serves as an indicator of corrosiveness. The pH values of the bio-oil obtained from untreated and AFEX™ pretreated feedstocks ranged from 2.25 to 2.77. The acidic nature of the bio-oil is due to the presence of acetic and formic acid (Pattiya, 2011). The density of the bio-oils produced from the untreated and AFEX™ pretreated feedstocks were higher than the density of water and this could be due to the presence of ash (Zhang *et al.,* 2007). The densities of the bio-oil ranged from 1.20 to 1.26 g cm^{-3}. The dynamic viscosity of the bio-oils is shown in Table 6.5 and the values showed the insignificant effect of AFEX™ pretreatment on the feedstocks. The viscosity values ranged from 2.2 to 2.9 cP at 20°C. Karunanithy and Muthukumarappan (2011) also reported the similar viscosity values of the bio-oils obtained from aspen, canola, and corn cobs pyrolyzed with the assistance of microwave. Heating value of the bio-oils ranged from 14.9 to 15.8 MJ/kg. From the literatures, it was observed that the heating values of the bio-oils varied between 15.0 and 40.4 MJ/kg (Yu *et al.,* 2007; Anouti *et al.,* 2016). The poor heating values of the bio-oil could be due to the presence of water. Water content in the bio-oil ranges from 15-35% wt (Pandey *et al.,* 2011) comprising pyroligneous water produced during the dehydration of carbohydrates (Dobele *et al.,* 2007). No statistical significance (p>0.05) in the pH, oil density, viscosity, and heating values was observed between the untreated and the AFEX™ pretreated feedstocks.

Bulk density of the bio-chars obtained from the untreated and AFEX™ pretreated feedstocks was lower than the bulk densities of the untreated and AFEX™ pretreated feedstocks as reported by Sundaram *et al* (2015). Different components of lignocellulosic biomass thermally decompose at different temperature. Hemicellulose decomposes initially followed by cellulose decomposes into volatile product at 400°C

(Randriamanantena *et al.,* 2009). These volatilizations of cellulose and hemicellulose components could be the reason for decrease in the mass of the biomass leading to the reduction in the bulk density of bio-chars. AFEX™ pretreated feedstocks showed increased bulk and particle density compared to the untreated feedstocks and the statistical analysis showed the significant effect ($p<0.05$) of pretreatment on bulk and particle density. During AFEX™ pretreatment, the biomass undergoes swelling at moderate temperature and pressure, and with the drop in pressure the disruption of lignocellulosic structure occurs (Dale, 1986; Chundawat *et al.,* 2011). The mobilization of lignin to the outer surface of the biomass due to the disruption of the matrix structure could have retained some of the volatile compounds in the char resulting in increased bulk and particle densities.

Bio-oil yields of the pellets produced from AFEX™ corn stover, prairie cord grass, and switchgrass varied from 44.3% to 46.8%, 43.2% to 47.5%, and 42.4% to 47.3% respectively. The bio-char yields varied from 24.7% to 25.3%, 24.2% to 25.7%, and 23.5% to 24.9% respectively for AFEX™ corn stover, prairie cord grass, and switchgrass. The yields of bio-oil, bio-char, and syngas from the pellets produced from untreated and AFEX™ pretreated prairie cord grass are shown in Table 6.6 and Table 6.7 shows the yields from AFEX™ ComPAKs. It can be observed that the yields from the pellets and PAKs were in the range of unpelleted samples shown in Table 6.4. In other words, extrusion pelleting and ComPAKco densification did not have any significant influence on the yields of fast pyrolysis.

Table 6.8 and 6.9 shows the properties of the bio-oil and bio-char obtained from pyrolysis of untreated and AFEX™ pretreated prairie cord grass pellets. It can be witnessed that the properties of the fast pyrolysis products from the unpelleted and pelleted samples was not significantly different. In other words, the properties of the bio-oil and bio-char obtained from the pelleted samples were in the range of the unpelleted samples. Therefore, based on the product yields and quality of the products obtained, it can be concluded that the extrusion and ComPAK co densified AFEX™ pretreated feedstocks behaved like the AFEX™ pretreated feedstocks during the pyrolysis process. Densification of the pretreated biomass will reduce the transportation costs and environmental impacts associated with the biomass logistics (Eranki and Dale, 2011b). Hence densification of AFEX™ pretreated lignocellulosic feedstock for the pyrolysis process would reduce the logistical impediments without affecting the products yield.

6.5. Conclusions

The study showed that the durability of the AFEX™ pretreated corn stover, prairie cord grass, and switchgrass pellets ranged from 94.5% to 99.2%, 94.3% to 98.7, and 90.1% to 97.5% respectively. A significant increase in the pellet durability was noticed for the pellets made from AFEX™ pretreated feedstocks compared to the untreated feedstocks. Decrease in the degradation temperature was observed for all the feedstocks subjected to AFEX™ pretreatment, indicating the increased thermal stability of the feedstocks after pretreatment. The yields of bio-oil and bio-char varied from 45.9% to 48% and 22.0 to 24.9%, respectively for the untreated and AFEX™ pretreated feedstocks. Hammer mill screen size did not have any significant influence on the products yield from the fast pyrolysis. No significant difference in the bio-oil and bio-char yields was observed for the untreated and AFEX™ pretreated feedstocks when subjected to fast pyrolysis. Similarly, the densification (pelleting and ComPAK co technique) had no significant effect on the products yield indicating the feasible option to densify the AFEX™ pretreated feedstocks in the processing depots without affecting the product yields.

Table 6.1. AFEX™ pretreatment conditions employed for different biomass*

Conditions	Corn stover	Prairie cord grass	Switchgrass
Ammonia loading, NH3 to dry biomass loading (w/w)	1:1	1:2	1:2
Moisture content (db %)	60	40	50
Pretreatment soaking time (min)	15	30	30

*Pretreatment was carried out at 100°C

Table 6.2. Proximate and ultimate analysis, and high heating value of untreated and AFEX™ pretreated feedstocks

Feedstock	Screen size (mm)	Moisture content (%)	Volatile matter (%)	Ash content (%)	Fixed carbon (%)	C (%)	H (%)	O (%)	HHV (MJ/kg)
Untreated Corn stover	2	5.1 ± 0.1$^{6-8}$	77.8 ± 0.3^{6,7}	3.5 ± 0.2$^{4-6}$	18.6 ± 0.1^{1,2}	47.2 ± 0.2^{1,2}	5.8 ± 0.1$^{4-6}$	42.7 ± 0.2$^{7-9}$	18.8 ± 0.1^{1}
	4	5.6 ± 0.1$^{3-5}$	77.5 ± 0.8^{6,7}	3.6 ± 0.3$^{3-6}$	18.8 ± 0.5^{1,2}	47.3 ± 0.1^{1,2}	5.8 ± 0.1$^{4-6}$	42.6 ± 0.2^{8,9}	18.9 ± 0.1^{1}
	8	5.3 ± 0.3^{5,6}	77.9 ± 1.0^{6,7}	3.9 ± 0.2^{2,3}	18.1 ± 0.7^{2}	46.9 ± 0.1$^{3-6}$	5.7 ± 0.1$^{6-8}$	42.6 ± 0.3^{9,10}	18.7 ± 0.2^{1,2}
Untreated Prairie cord grass	2	5.3 ± 0.1^{5,6}	79.6 ± 0.4^{5}	3.8 ± 0.4$^{2-5}$	16.5 ± 0.4^{3}	46.7 ± 0.3$^{7-9}$	5.7 ± 0.1$^{5-7}$	42.9 ± 0.2^{6,7}	18.3 ± 0.1$^{3-6}$
	4	5.6 ± 0.1^{3,4}	81.1 ± 0.5$^{1-4}$	3.6 ± 0.4$^{3-6}$	15.2 ± 0.9$^{4-6}$	46.6 ± 0.4$^{7-9}$	5.8 ± 0.1$^{4-6}$	43.1 ± 0.2^{4,5}	18.1 ± 0.3^{6}
	8	5.8 ± 0.2^{2,3}	80.8 ± 0.4^{3,4}	3.3 ± 0.3^{6,7}	15.7 ± 0.7$^{3-5}$	46.8 ± 0.3$^{5-7}$	5.8 ± 0.1^{3,4}	43.2 ± 0.1$^{3-5}$	18.3 ± 0.2^{5,6}
Untreated Switchgrass	2	5.7 ± 0.1^{3}	80.7 ± 0.6^{3,4}	2.8 ± 0.4^{8,9}	16.4 ± 0.3^{3}	47.3 ± 0.2^{1,2}	5.8 ± 0.1^{1,2}	43.3 ± 0.2$^{1-3}$	18.5± 0.1$^{2-5}$
	4	6.1 ± 0.1^{2}	81.3 ± 0.7$^{1-3}$	2.6 ± 0.2^{9}	16.0 ± 0.7^{3,4}	47.3 ± 0.2^{1}	5.8 ± 0.1^{1}	43.5 ± 0.2^{1}	18.4 ± 0.2$^{2-5}$
	8	5.1 ± 0.1$^{6-8}$	81.0 ± 0.3$^{2-4}$	2.8 ± 0.3^{8,9}	16.1 ± 0.6^{3}	47.2 ± 0.3$^{1-3}$	5.8 ± 0.1^{1,2}	43.4 ± 0.1^{1,2}	18.4 ± 0.2$^{2-5}$
AFEX™ Corn stover	2	4.8 ± 0.4^{8}	77.3 ± 0.3^{7}	3.6 ± 0.2$^{3-6}$	19.0 ± 0.4^{1}	47.3 ± 0.2^{1,2}	5.8 ± 0.1$^{4-6}$	42.6 ± 0.1^{8,9}	18.3 ± 0.1^{5,6}
	4	5.9 ± 0.2^{2,3}	78.2 ± 0.1^{6}	3.5 ± 0.1^{5,6}	18.2 ± 0.1^{2}	47.2 ± 0.1$^{1-4}$	5.8 ± 0.1$^{4-6}$	42.8 ± 0.1^{7,8}	18.4 ± 0.1$^{3-6}$
	8	7.0 ± 0.1^{1}	76.6 ± 0.2^{8}	4.0 ± 0.2^{1,2}	19.3 ± 0.2^{1}	47.1 ± 0.2$^{1-5}$	5.7 ± 0.1$^{6-8}$	42.4 ± 0.1^{10}	18.3 ± 0.2^{5,6}
AFEX™ Prairie cord grass	2	5.2 ± 0.4^{6,7}	80.5 ± 0.2^{4}	4.4 ± 0.1^{1}	15.0 ± 0.2^{5,6}	46.1 ± 0.1^{10}	5.7 ± 0.1^{8}	42.7 ± 0.1^{7,8}	18.4 ± 0.2$^{3-6}$
	4	5.4 ± 0.2$^{4-6}$	81.0 ± 0.4$^{2-4}$	3.7 ± 0.1$^{2-5}$	15.1 ± 0.4^{5,6}	46.5 ± 0.1^{8,9}	5.8 ± 0.1$^{4-6}$	43.1 ± 0.1^{5}	18.3 ± 0.1^{5,6}
	8	5.4 ± 0.2$^{4-6}$	81.3 ± 0.2$^{1-3}$	3.9 ± 0.2$^{2-4}$	14.7 ± 0.4^{6}	46.4 ± 0.2^{9,10}	5.7 ± 0.1$^{4-7}$	43.0 ± 0.1^{5,6}	18.3 ± 0.1$^{3-6}$
AFEX™ Switchgrass	2	5.2 ± 0.3^{6,7}	80.9 ± 0.2$^{2-4}$	3.0 ± 0.1^{7,8}	16.0 ± 0.3^{3}	47.1 ± 0.1$^{1-5}$	5.8 ± 0.1^{2,3}	43.3 ± 0.1$^{2-4}$	18.2 ± 0.4^{5,6}
	4	4.9 ± 0.1^{7,8}	81.9 ± 0.3^{1}	2.8 ± 0.1^{8,9}	15.2 ± 0.4^{5,6}	47.0 ± 0.1$^{2-5}$	5.8 ± 0.1^{1,2}	43.5 ± 0.1^{1}	18.6 ± 0.1$^{1-3}$
	8	5.1 ± 0.2$^{6-8}$	81.6 ± 0.4^{1,2}	3.1 ± 0.2^{7,8}	15.2 ± 0.3^{5,6}	46.9 ± 0.1$^{4-6}$	5.8 ± 0.1^{2,3}	43.4 ± 0.1^{1,2}	18.6 ± 0.1$^{1-3}$

Means sharing the same superscript numbers for a given property between the columns are not significantly different ($p < 0.05$).

Table 6.3. Pellet durability of untreated and AFEX™ pretreated corn stover, prairie cord grass, and switchgrass pellets

Temp (°C)	Moisture content (%) wb	Screen size (mm)	AFEX™ corn stover	Untreated corn stover	AFEX™ prairie cord grass	Untreated prairie cord grass	AFEX™ switchgrass	Untreated switchgrass
75	5	2	98.6±0.4^{1}	42.1±3.6$^{29-32}$	97.3±2.4^{1,2}	44.1±2.0$^{26-31}$	96.1±0.7^{1,2}	47.1±4.2$^{24-30}$
		4	98.2±0.3^{1}	39.8±5.6$^{30-34}$	97.1±0.9^{1,2}	37.8±3.0$^{31-34}$	95.2±2.3^{1,2}	38.4±1.8$^{31-34}$
		8	96.4±1.3^{1,2}	28.3±2.9^{35,36}	94.5±0.2^{1,2}	35.3±5.4$^{32-35}$	90.1±1.6^{2}	35.1±2.2$^{32-35}$
	10	2	99.2±0.3^{1}	40.4±4.2$^{30-34}$	98.2±1.7^{1}	45.4±3.4$^{25-31}$	95.4±0.5^{1,2}	48.9±5.1$^{22-29}$
		4	98.1±1.5^{1}	34.6±7.9$^{32-35}$	97.8±1.4^{1,2}	39.6±1.8$^{30-34}$	94.9±1.4^{1,2}	39.0±0.8$^{31-33}$
		8	94.5±4.1^{1,2}	26.5±4.2^{36}	95.3±2.1^{1,2}	33.5±4.2$^{33-36}$	91.3±2.4^{1,2}	30.4±4.5$^{34-36}$
	15	2	98.7±1.2^{1}	58.5±4.3$^{11-20}$	98.4±1.2^{1}	49.5±10.3$^{22-29}$	93.3±0.9^{1,2}	50.1±3.3$^{22-28}$
		4	98.7±1.3^{1}	52.5±3.6$^{18-25}$	98.6±1.8^{1}	52.5±3.8$^{18-25}$	94.3±1.3^{1,2}	49.0±4.9$^{22-29}$
		8	95.6±3.7^{1,2}	40.5±4.8$^{30-34}$	94.3±0.7^{1,2}	42.5±5.8$^{28-32}$	92.9±1.8^{1,2}	40.4±3.0$^{30-34}$
100	5	2	98.9±0.6^{1}	60.5±3.6$^{9-17}$	97.8±1.6^{1,2}	52.5±2.1$^{18-25}$	96.3±0.6^{1,2}	55.6±4.3$^{12-23}$
		4	98.2±1.4^{1}	58.8±2.6$^{11-20}$	98.3±0.8^{1}	53.5±6.6$^{16-24}$	94.4±1.1^{1,2}	55.3±2.5$^{12-23}$
		8	96.3±1.4^{1,2}	52.3±4.3$^{19-25}$	98.2±0.4^{1}	45.3±1.3$^{25-31}$	93.3±0.1^{1,2}	43.3±2.8$^{27-31}$
	10	2	99.1±0.4^{1}	72.5±3.5$^{3-7}$	98.2±1.5^{1}	59.5±7.1$^{10-19}$	95.2±2.5^{1,2}	60.1±0.8$^{10-19}$
		4	97.4±2.0^{1,2}	75.3±4.3$^{3-5}$	97.8±2.0^{1,2}	58.3±7.5$^{11-21}$	96.3±0.8^{1,2}	55.2±4.4$^{12-23}$
		8	94.7±2.7^{1,2}	55.2±8.2$^{13-23}$	93.2±2.7^{1,2}	52.3±0.6$^{19-25}$	94.1±1.2^{1,2}	49.6±3.8$^{22-29}$
	15	2	98.2±1.4^{1}	80.2±4.6^{3}	98.6±1.4^{1}	62.5±3.4$^{8-14}$	96.4±1.3^{1,2}	65.0±3.5$^{7-11}$
		4	97.5±2.0^{1,2}	74.7±6.1$^{3-6}$	97.8±1.0^{1,2}	58.4±4.9$^{11-21}$	96.0±1.0^{1,2}	61.7±4.7$^{8-15}$
		8	94.8±3.7^{1,2}	55.5±1.5$^{12-23}$	94.9±3.1^{1,2}	48.5±1.7$^{23-29}$	94.2±0.4^{1,2}	51.5±4.2$^{20-26}$
125	5	2	98.9±0.3^{1}	60.5±5.2$^{9-17}$	98.2±0.3^{1}	62.8±7.5$^{8-13}$	96.8±0.7^{1,2}	60.1±3.8$^{10-19}$
		4	97.5±2.0^{1,2}	54.6±2.6$^{14-24}$	97.9±0.1^{1,2}	52.6±1.8$^{17-25}$	95.2±1.6^{1,2}	54.9±3.2$^{13-24}$
		8	97.2±1.8^{1,2}	50.5±3.2$^{21-27}$	97.8±0.3^{1,2}	53.4±1.6$^{16-24}$	92.6±0.5^{1,2}	56.6±4.5$^{12-22}$
	10	2	98.9±0.1^{1}	80.5±3.4^{3}	98.5±0.9^{1}	65.1±3.5$^{7-11}$	97.5±0.8^{1,2}	72.0±4.4$^{4-7}$
		4	98.3±0.7^{1}	78.3±5.9^{3,4}	98.2±1.4^{1}	63.2±9.1$^{8-12}$	95.2±1.3^{1,2}	66.9±5.2$^{6-10}$
		8	96.3±3.4^{1,2}	56.3±4.3$^{12-23}$	95.9±2.1^{1,2}	54.1±5.5$^{15-24}$	92.9±0.8^{1,2}	54.0±2.1$^{15-24}$
	15	2	98.8±0.6^{1}	78.5±7.6^{3,4}	98.7±0.3^{1}	68.1±5.7$^{5-9}$	95.9±0.5^{1,2}	68.1±5.9$^{5-9}$
		4	97.7±1.3^{1,2}	80.3±5.4^{3}	98.2±1.4^{1}	60.9±6.9$^{8-16}$	95.2±0.6^{1,2}	68.7±5.1$^{5-8}$
		8	95.4±2.4^{1,2}	60.3±4.6$^{9-18}$	95.3±2.3^{1,2}	54.1±3.3$^{15-24}$	92.4±1.0^{1,2}	56.3±3.1$^{12-23}$

Means sharing the same superscript numbers between the columns are not significantly different ($p < 0.05$).

Table 6.4. Pyrolysis yields from untreated and AFEX™ pretreated feedstocks

Feedstock	Screen size (mm)	Bio-oil (%)	Bio-char (%)	Syngas (%)
Untreated corn stover	2	47.3^{a-c}	23.9^{a-e}	28.8^{a-c}
	4	46.9^{c}	24.7^{ab}	28.4^{a-c}
	8	46.1^{bc}	24.5^{a-c}	29.4^{a-c}
Untreated prairie cord grass	2	48.0^{ab}	24.4^{a-c}	27.5^{bc}
	4	46.5^{bc}	24.9^{a}	28.6^{a-c}
	8	49.0^{a}	23.7^{a-e}	27.3^{c}
Untreated switchgrass	2	47.8^{a-c}	22.0^{ef}	30.2^{a-c}
	4	46.3^{bc}	23.8^{a-e}	29.9^{a-c}
	8	46.1^{bc}	22.6^{c-f}	31.3^{a}
AFEX™ corn stover	2	48.1^{ab}	22.4^{d-f}	29.5^{a-c}
	4	46.9^{a-c}	22.0^{ef}	31.1^{ab}
	8	46.3^{bc}	22.9^{b-f}	30.8^{a-c}
AFEX™ prairie cord grass	2	47.7^{c}	23.6^{a-e}	28.7^{bc}
	4	47.5^{bc}	23.9^{a-e}	28.6^{a-c}
	8	47.8^{c}	23.9^{a-f}	28.3^{c}
AFEX™ switchgrass	2	48.1^{ab}	22.8^{c-f}	29.1^{a-c}
	4	45.9^{bc}	22.5^{d-f}	31.6^{a}
	8	46.3^{bc}	24.1^{a-d}	29.6^{a-c}

Means sharing the same superscript letters between the columns are not significantly different ($p < 0.05$).

Table 6.5. Properties of the bio-oil and bio-char obtained from untreated and AFEX™ pretreated feedstocks

Feedstock	Screen size (mm)	Bio-oil				Bio-char	
		pH	Oil density (g cm^{-3})	Viscosity (cP)	Heating value (MJ/kg)	Bulk density (g cm^{-3})	Particle density (g cm^{-3})
Untreated corn stover	2	2.67^{a}	1.25^{a}	2.6^{abc}	15.3^{cde}	0.05^{h}	0.43^{hi}
	4	2.76^{a}	1.21^{a}	2.5^{abc}	15.8^{a}	0.06^{fg}	0.51^{gf}
	8	2.67^{a}	1.26^{a}	2.5^{abc}	15.5$^{a\text{-}d}$	0.07^{f}	0.56^{f}
Untreated prairie cord grass	2	2.59^{ab}	1.25^{a}	2.5^{abc}	15.2^{ef}	0.06^{fg}	0.46^{gh}
	4	2.26^{b}	1.21^{a}	2.4^{abc}	15.4$^{b\text{-}e}$	0.06^{fg}	0.49^{gh}
	8	2.58^{ab}	1.24^{a}	2.4^{abc}	15.5$^{a\text{-}d}$	0.06^{fg}	0.48^{gh}
Untreated switchgrass	2	2.77^{a}	1.25^{a}	2.1^{c}	14.9^{f}	0.04^{h}	0.40^{i}
	4	2.66^{a}	1.20^{a}	2.2^{bc}	15.0^{ef}	0.06^{fg}	0.47^{gh}
	8	2.54^{ab}	1.20^{a}	2.2^{bc}	14.9^{f}	0.06^{fg}	0.47^{gh}
AFEX™ corn stover	2	2.74^{a}	1.24^{a}	2.6^{abc}	15.5^{ef}	0.15^{b}	0.82^{c}
	4	2.46^{ab}	1.20^{a}	2.4^{abc}	15.7^{ab}	0.18^{a}	0.90^{b}
	8	2.25^{b}	1.21^{a}	2.9^{a}	15.8^{a}	0.19^{a}	1.12^{a}
AFEX™ prairie cord grass	2	2.52^{ab}	1.25^{a}	2.4^{abc}	15.6^{abc}	0.12^{c}	0.73^{de}
	4	2.62^{ab}	1.24^{a}	2.5^{abc}	15.5$^{a\text{-}d}$	0.13^{c}	0.76^{cd}
	8	2.53^{ab}	1.20^{a}	2.2^{bc}	15.5$^{a\text{-}d}$	0.13^{c}	0.90^{b}
AFEX™ switchgrass	2	2.42^{ab}	1.24^{a}	2.5^{abc}	15.2^{def}	0.10^{d}	0.67^{e}
	4	2.46^{ab}	1.24^{a}	2.7^{ab}	15.0^{f}	0.11^{d}	0.75^{d}
	8	2.45^{ab}	1.25^{a}	2.4^{abc}	15.3^{cde}	0.12^{c}	0.77^{cd}

Means sharing the same superscript letters for a given property between the columns are not significantly different ($p < 0.05$).

Table 6.6. Fast pyrolysis yields from untreated and AFEX™ pretreated corn stover pellets

Temp (°C)	Moisture (% wb)	Screen size (mm)	Untreated corn stover pellets			AFEX corn stover pellets		
			Bio-oil (%)	Bio-char (%)	Syngas (%)	Bio-oil (%)	Bio-char (%)	Syngas (%)
75	5	2	46.1	26.8	27.1	46.8	24.4	28.8
75	5	4	46.7	24.0	29.3	45.9	26.6	27.5
75	5	8	46.4	23.5	30.2	44.0	23.3	32.7
75	10	2	45.0	22.0	33.0	47.6	23.4	29.0
75	10	4	44.8	23.8	31.4	45.6	25.9	28.5
75	10	8	45.6	24.7	29.7	45.6	26.9	27.5
75	15	2	46.9	23.9	29.2	46.6	23.9	29.5
75	15	4	48.4	25.2	26.4	47.9	27.8	24.3
75	15	8	47.5	25.3	27.2	47.0	26.8	26.2
100	5	2	45.0	27.1	27.9	46.9	24.2	29.0
100	5	4	45.9	26.8	27.3	45.7	24.7	29.6
100	5	8	47.7	23.6	28.8	45.8	25.6	28.6
100	10	2	46.8	26.9	26.3	44.8	24.8	30.5
100	10	4	48.3	25.3	26.4	46.2	23.4	30.4
100	10	8	45.9	25.8	28.3	44.4	25.1	30.5
100	15	2	47.8	25.3	27.0	48.4	27.4	24.2
100	15	4	46.3	21.3	32.4	45.4	24.7	29.8
100	15	8	46.1	25.5	28.4	45.5	25.5	29.0
125	5	2	46.7	23.4	30.0	47.0	26.0	26.9
125	5	4	46.0	23.5	30.5	48.8	25.1	26.1
125	5	8	46.0	25.2	28.7	44.9	25.7	29.4
125	10	2	45.1	26.8	28.1	46.9	25.2	27.8
125	10	4	47.7	24.7	27.7	47.8	26.2	26.0
125	10	8	46.8	25.6	27.6	47.4	22.8	29.8
125	15	2	47.3	21.9	30.8	47.2	25.4	27.5
125	15	4	45.9	28.4	25.7	46.9	25.5	27.6
125	15	8	47.8	24.4	27.8	47.0	25.8	27.2

Table 6.7. Fast pyrolysis yields from untreated and AFEX™ pretreated prairie cord grass pellets

Temp (°C)	Moisture (% wb)	Screen size (mm)	Untreated prairie cord grass pellets			AFEX™ prairie cord grass pellets		
			Bio-oil (%)	Bio-char (%)	Syngas (%)	Bio-oil (%)	Bio-char (%)	Syngas (%)
75	5	2	43.2	25.2	31.6	47.0	24.8	28.2
		4	45.3	24.3	30.4	46.2	23.4	30.4
		8	46.5	24.9	28.6	47.2	24.1	28.7
	10	2	47.2	25.2	27.6	47.8	23.9	28.3
		4	43.8	24.3	31.9	48.0	24.6	27.4
		8	47.2	25.3	27.5	46.5	23.7	29.8
	15	2	46.6	24.7	28.7	45.9	23.9	30.2
		4	45.4	25.2	29.4	47.2	23.5	29.3
		8	47.2	24.6	28.2	48.5	24.0	27.5
100	5	2	46.5	24.9	28.6	46.8	24.8	28.4
		4	45.2	25.2	29.6	47.3	23.5	29.2
		8	46.2	25.2	28.6	48.2	25.4	26.4
	10	2	45.9	25.7	28.4	47.2	23.4	29.4
		4	46.3	26.9	26.8	47.6	25.2	27.2
		8	47.2	24.9	27.9	46.8	24.3	28.9
	15	2	46.2	25.2	28.6	45.3	24.0	30.7
		4	47.5	24.3	28.2	46.5	23.9	29.6
		8	45.9	25.6	28.5	48.4	25.1	26.5
125	5	2	45.3	25.2	29.5	47.3	23.4	29.3
		4	47.2	24.9	27.9	45.2	25.2	29.6
		8	46.3	25.3	28.4	46.4	24.3	29.3
	10	2	45.2	25.2	29.6	43.2	24.8	32.0
		4	47.2	24.9	27.9	45.2	23.9	30.9
		8	46.2	26.2	27.6	48.9	24.3	26.8
	15	2	45.7	24.5	29.8	48.2	25.2	26.6
		4	46.9	26.1	27.0	47.5	24.7	27.8
		8	47.2	24.6	28.2	46.5	23.9	29.6

Table 6.8. Fast pyrolysis yields from untreated and AFEX™ pretreated switchgrass pellets

Temp (°C)	Moisture (%)	Screen size (mm)	Untreated switchgrass pellets			AFEX switchgrass pellets		
			Bio-oil (%)	Bio-char (%)	Syngas (%)	Bio-oil (%)	Bio-char (%)	Syngas (%)
75	5	2	46.1	25.0	28.9	46.1	25.3	28.6
		4	46.4	25.6	28.0	45.8	25.3	28.9
		8	45.3	24.6	30.1	45.6	25.4	29.0
	10	2	47.0	25.9	27.1	46.0	26.3	27.7
		4	46.7	25.2	28.1	46.0	26.4	27.6
		8	45.7	24.4	29.9	45.8	25.8	28.4
	15	2	45.3	26.0	28.7	45.7	26.4	27.9
		4	45.3	24.7	30.0	45.6	25.9	28.4
		8	46.4	24.6	29.0	45.7	25.3	29.0
100	5	2	46.8	25.6	27.6	46.3	27.0	26.7
		4	46.4	25.1	28.5	46.0	26.7	27.3
		8	45.8	25.1	29.1	45.9	25.7	28.4
	10	2	47.0	25.3	27.7	45.9	25.3	28.8
		4	46.4	24.7	28.9	46.4	25.3	28.3
		8	46.4	25.7	27.9	45.7	26.4	27.9
	15	2	47.0	25.3	27.7	46.2	26.8	27.0
		4	46.7	24.5	28.8	45.8	26.4	27.8
		8	46.3	25.3	28.4	46.1	25.8	28.1
125	5	2	46.4	26.6	27.0	47.8	25.1	27.0
		4	46.3	24.8	28.8	47.2	25.1	27.7
		8	46.1	26.4	27.5	46.7	25.1	28.2
	10	2	46.2	25.2	28.6	46.2	25.2	28.7
		4	46.3	24.9	28.8	47.9	25.5	26.7
		8	46.0	25.5	28.5	46.1	25.6	28.3
	15	2	46.2	26.6	27.2	47.1	27.0	25.9
		4	45.6	26.8	27.6	47.3	26.7	26.0
		8	47.2	27.0	25.8	46.1	25.7	28.2

Table 6.9. Fast pyrolysis yields from AFEX™ ComPAKs.

Moisture (% wb)	Screen size (mm)	Bio-oil (%)	Bio-char (%)	Syngas (%)
Corn stover	2	45.7	23.9	30.4
	4	46.2	24.3	29.4
	8	45.3	24.5	30.2
Prairie cord grass	2	46.4	25.2	29.4
	4	46.2	24.6	29.2
	8	47.1	25.3	27.6
Switchgrass	2	45.8	24.1	30.1
	4	44.9	24.7	30.4
	8	45.3	24.0	30.7

Table 6.10. Properties of the bio-oil and bio-char from untreated prairie cord grass pellets

Temp (°C)	Moisture (% wb)	Screen size (mm)	pH	Oil density (g cm^{-3})	Viscosity (cP)	Heating value (MJ/kg)	Bulk density (g cm^{-3})	Particle Density (g cm^{-3})
75	5	2	2.47	1.23	1.8	15.3	0.08	0.46
		4	2.70	1.24	2.1	15.3	0.08	0.58
		8	2.48	1.24	2.4	15.4	0.09	0.48
	10	2	2.36	1.20	2.1	15.4	0.08	0.57
		4	3.03	1.21	1.9	15.3	0.07	0.55
		8	2.65	1.22	2.1	15.5	0.06	0.56
	15	2	2.90	1.20	2.2	15.3	0.06	0.53
		4	2.73	1.19	2.3	15.4	0.05	0.47
		8	2.79	1.24	2.0	15.4	0.06	0.49
100	5	2	2.57	1.24	2.3	15.4	0.05	0.52
		4	2.3	1.22	2.4	14.9	0.06	0.56
		8	3.05	1.21	2.2	15.6	0.07	0.49
	10	2	2.41	1.21	2.4	14.8	0.06	0.52
		4	2.37	1.23	2.4	15.1	0.05	0.53
		8	2.58	1.20	2.2	15.3	0.04	0.39
	15	2	2.30	1.25	2.4	15.6	0.07	0.46
		4	2.65	1.20	2.2	14.9	0.08	0.40
		8	2.66	1.21	2.4	15.0	0.07	0.53
125	5	2	2.56	1.24	2.4	15.1	0.05	0.56
		4	2.79	1.25	2.4	15.4	0.07	0.48
		8	2.40	1.24	2.1	15.5	0.05	0.55
	10	2	2.93	1.22	2.4	15.2	0.06	0.48
		4	2.57	1.23	2.3	15.5	0.07	0.43
		8	2.66	1.25	2.5	15.4	0.04	0.40
	15	2	2.79	1.21	2.4	15.4	0.07	0.52
		4	2.61	1.22	1.9	15.0	0.05	0.54
		8	2.47	1.21	2.3	15.2	0.05	0.52

Table 6.11. Properties of the bio-oil and bio-char from AFEX™ prairie cord grass pellets

Temp (°C)	Moisture (% wb)	Screen size (mm)	pH	Oil density (g cm^{-3})	Viscosity (cP)	Heating value (MJ/kg)	Bulk density (g cm^{-3})	Particle Density (g cm^{-3})
75	5	2	2.30	1.26	2.8	15.4	0.13	0.74
		4	2.65	1.23	2.2	15.5	0.14	0.73
		8	2.83	1.25	2.4	15.5	0.13	0.76
	10	2	2.56	1.23	2.3	15.2	0.14	0.74
		4	2.70	1.24	2.4	15.4	0.13	0.77
		8	2.91	1.23	2.7	15.7	0.12	0.74
	15	2	2.40	1.23	2.2	15.8	0.16	0.75
		4	2.73	1.21	2.4	15.6	0.15	0.71
		8	2.81	1.23	2.3	15.2	0.15	0.74
100	5	2	2.67	1.23	2.3	15.7	0.13	0.75
		4	2.72	1.24	2.5	15.3	0.15	0.76
		8	2.45	1.21	2.4	15.4	0.12	0.73
	10	2	2.67	1.22	2.6	15.4	0.12	0.74
		4	2.54	1.21	2.7	15.6	0.11	0.75
		8	2.64	1.24	2.4	15.6	0.12	0.75
	15	2	2.72	1.27	2.4	15.2	0.13	0.73
		4	2.59	1.25	2.7	15.8	0.11	0.76
		8	2.63	1.25	2.5	15.4	0.14	0.74
125	5	2	2.88	1.24	1.9	15.3	0.13	0.76
		4	2.29	1.25	2.7	15.2	0.13	0.70
		8	2.70	1.24	2.4	15.4	0.14	0.73
	10	2	2.32	1.23	2.2	15.3	0.13	0.74
		4	2.54	1.23	2.4	15.4	0.14	0.74
		8	2.49	1.25	2.6	15.4	0.12	0.73
	15	2	2.66	1.21	2.5	15.2	0.14	0.77
		4	2.73	1.22	2.5	15.6	0.12	0.75
		8	2.47	1.25	2.2	15.6	0.15	0.74

Fig. 6.1. Untreated, AFEX™ pretreated, untreated pelleted, AFEX™ pretreated pelleted, AFEX™ pretreated PAKs, bio-char, and bio-oil obtained from corn stover.

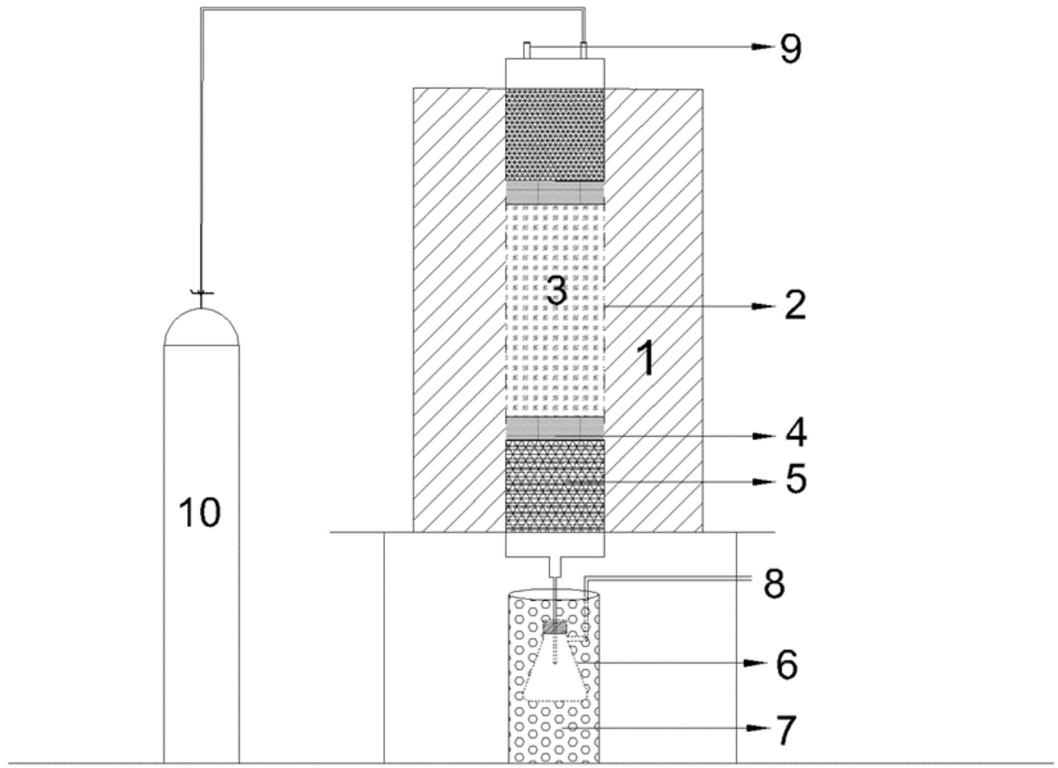
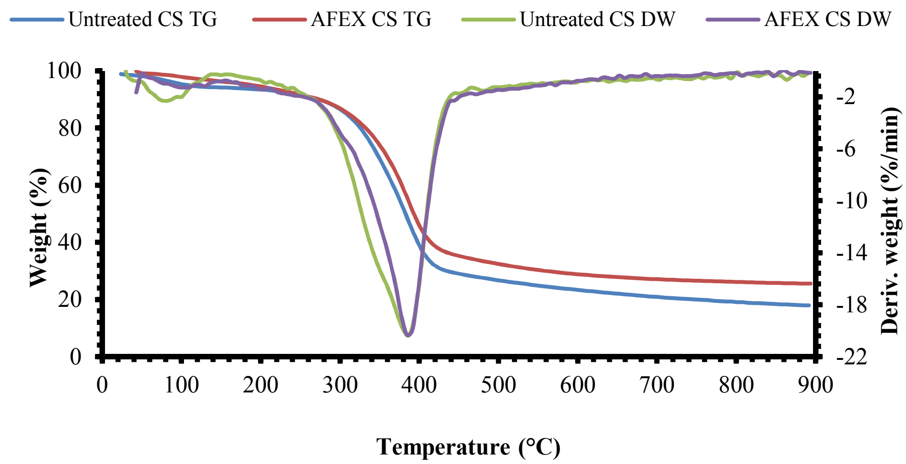
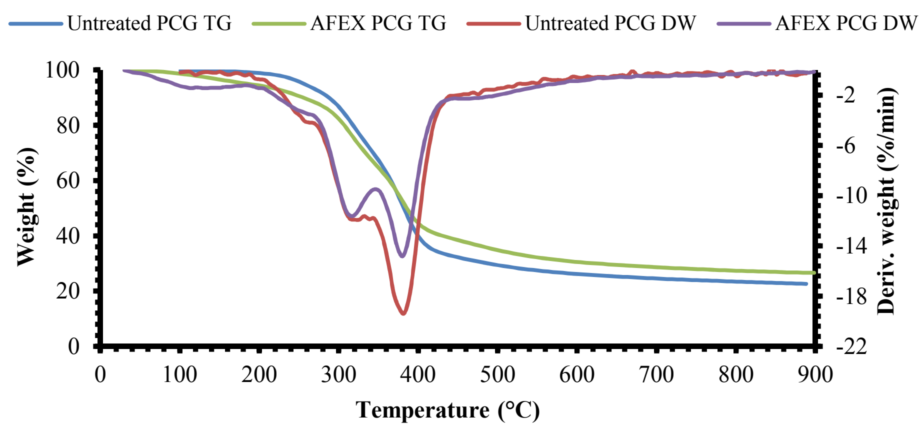


Fig. 6.2. Pyrolysis experimental setup

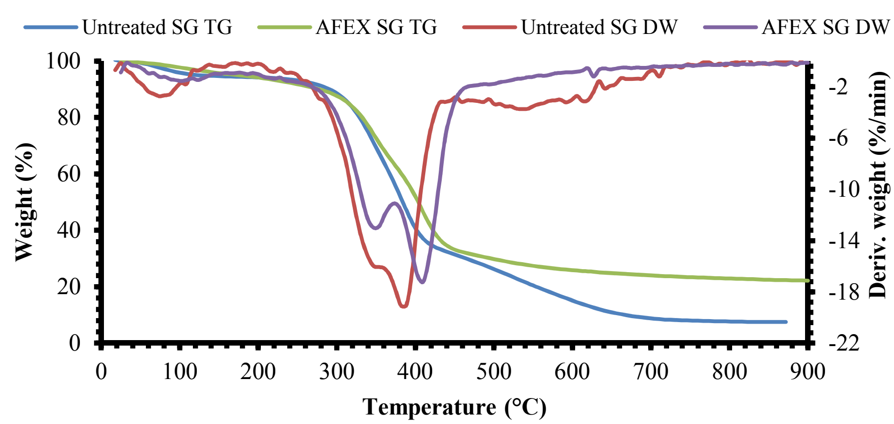
(1) Electric furnace; (2) Stainless steel reactor; (3) Biomass sample; (4) Quartz wool; (5) Steel wool; (6) Conical flask with nose; (7) Ice bath; (8) Exhaust; (9); Thermocouple; (10) Compressed nitrogen cylinder



(a) Corn stover

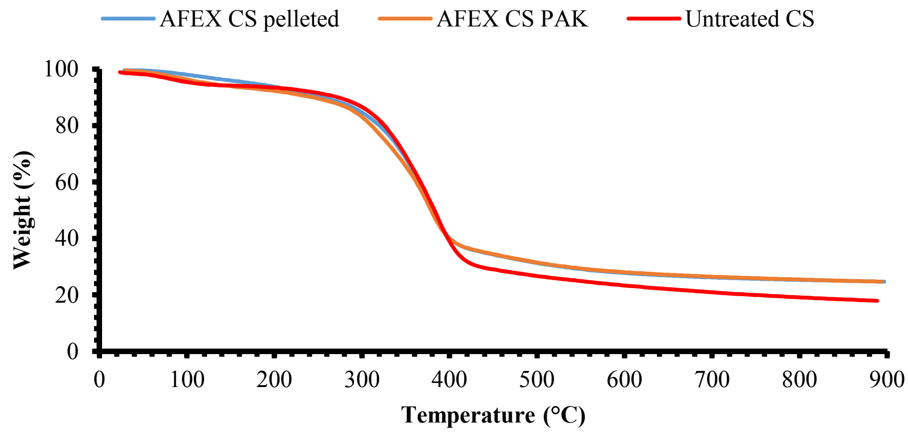


(b) Prairie cord grass

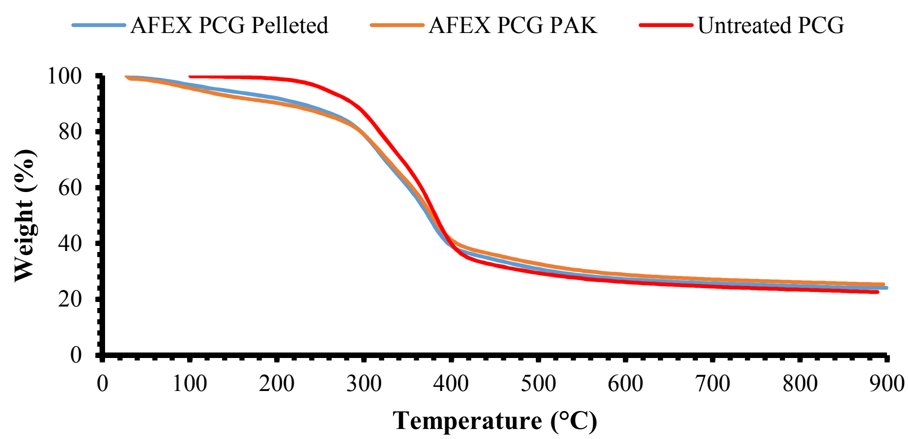


(c) Switchgrass

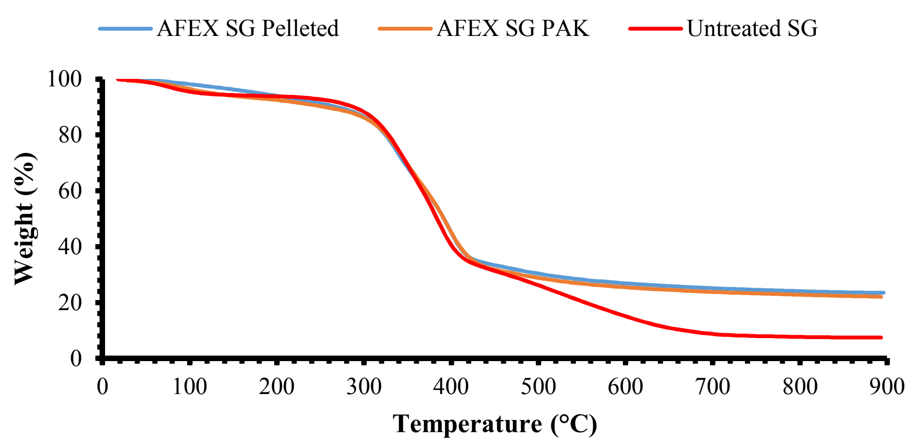
Fig. 6.3. Thermogravimetric (TG) and Derivative weight (DW) loss curve for untreated and AFEX™ pretreated corn stover, prairie cord grass, and switchgrass.



(a) Corn stover



(b) Prairie cord grass



(c) Switchgrass

Fig. 6.4. Thermogravimetric (TG) loss curve for 2 mm untreated, pelleted AFEX™ pretreated, and ComPAKco densified AFEX™ corn stover (CS), prairie cord grass (PCG), and switchgrass (SG).

7. CONCLUSIONS AND RECOMMENDATIONS

7.1. Conclusions

Lignocellulosic biomasses corn stover, prairie cord grass, and switchgrass were subjected to Ammonia Fiber Expansion (AFEX) pretreatment and the impacts were studied on the densification behavior, quality of the densified products, and the yields of the end products. The compression behavior of corn stover, prairie cord grass, and switchgrass was studied to understand the impacts of AFEX pretreatment. Feedstocks were compressed using a single pelleting unit and the pellet unit density was recorded. The factors moisture content, compressive load, and hammer mill screen sizes were varied and the compressive behavior was studied using powder compaction models (Jones, Walker, and Kawakita and Ludde). The constant values from the models indicated the impact of AFEX™ pretreatment, which made the biomass easier to compress at low pressure. Also the models indicate, at moisture content in the range of 16%- 20% AFEX pretreated biomasses require less pressure to produce highly compacted pellets.

The blending effects were studied using AFEX pretreated corn stover and switchgrass on pellet unit density, pellet hardness, specific energy consumption for pellets production, and the sugar yields. A single pelleting unit was employed in the study and the pellets produced from AFEX™ pretreated samples reached their maximum pellet unit densities at lower pressure. Pellet hardness was tested by applying the force to the pellets and recording the maximum force required to break. Results showed that the pellets produced from the small screen size sample at a higher applied pressure required more force to break. Besides, blend with higher proportion of AFEX™ pretreated corn stover produced harder pellets. Specific energy consumption for the pellets production varied from 11.4 to 57.9 kW h t^{-1}, and due to low bulk density of switchgrass, blends with a higher proportion of switchgrass consumed more energy for pellet production. Glucose yields of the AFEX™ pretreated samples were enhanced by 4–4.5 times and the xylose yields by 2–2.5 times compared to the untreated samples. Pelleting and biomass blending had no significant effects on sugar yields of the AFEX™ pretreated corn stover and switchgrass samples. This results indicate that blending and pelleting the AFEX™ pretreated feedstocks can be a potential and viable option to minimize the logistical issues without affecting the sugar yields.

The impacts of AFEX™ pretreatment, feedstock moisture content, particle size, and extrusion temperature was investigated on pellet bulk density, pellet hardness, and sugar recovery from corn stover, prairie cord grass, and switchgrass. The feedstocks were densified using a laboratory-scale extruder. AFEX™ pretreatment increased subsequent pellet bulk density of corn stover, prairie cord grass, and switchgrass. Maximum pellet hardness was recorded for AFEX™ pretreated feedstocks compared to the pellets made from untreated feedstocks. Glucose yields of the pellets produced from AFEX™ corn stover, AFEX™ prairie cord grass, and AFEX™ switchgrass were 1.6 times, 2.1 times, and 2.3 times higher, respectively, compared to pellets produced from untreated samples. Glucose and xylose yields of AFEX™ pellets were not affected by the extruder barrel temperature and the hammer mill screen size. The results obtained showed that low temperature and large particle size during the extrusion pelleting process can be employed for AFEX™ treated biomass without compromising sugar yields.

Durability of the AFEX™ pretreated corn stover, prairie cord grass, and switchgrass pellets ranged from 94.5% to 99.2%, 94.3% to 98.7, and 90.1% to 97.5% respectively. A significant increase in the pellet durability was noticed for the pellets made from AFEX™ pretreated feedstocks compared to the untreated feedstocks. The impacts of AFEX™ pretreatment and densification were studied on the thermochemical conversion process. Thermal stability of the feedstocks were increased after AFEX™ pretreatment when thermogravimetric analysis was used. It was observed that hammer mill screen size did not have any significant influence on the fast pyrolysis products yield. The yields of bio-oil and bio-char varied from 45.9% to 48% and 22.0 to 24.9%, respectively for the untreated and AFEX™ pretreated feedstocks. No significant difference in the bio-oil and bio-char yields was observed for the untreated and AFEX™ pretreated feedstocks when subjected to fast pyrolysis. Similarly, the extrusion and ComPAK co densified feedstocks had no significant effect on the products yield indicating the feasible option to densify the AFEX™ pretreated feedstocks in the processing depots without affecting the product yields.

7.2. Recommendations

7.2.1. Increase the hammer mill screen size range

In this study, hammer mill screen sizes were varied at 2, 4, and 8 mm. The results obtained showed that hammer mill screen sizes employed had no significant influences on the densified products quality and products yield. Hence, the hammer mill screen size should be expanded beyond 8 mm and the impacts can be studied.

7.2.2. Varying extruder parameters

Extrusion study was conducted only varying the barrel temperature. Literature shows that screw speed and die diameter influences the quality of the densified products and end product yields. Hence different screw speeds and die diameter can be evaluated.

7.2.3. Comparison of different densification methods

In this study, two types of densification method was studied viz. Extrusion pelleting and ComPAK co technique. The quality of the densified products obtained from different methods can be compared to evaluate the best densification method for logistics. This includes comparing the product hardness, bulk density, water resistance, energy requirements, etc.

7.2.4. Determine the effects of different temperature and heating rates on pyrolysis yields

In our study, set temperature of 400°C and heating rate of 30°C per min were used for pyrolyzing the feedstocks. Different combination of pyrolysis temperature and heating rates can be tested to optimize the bio-oil, bio-char, and syngas yields.

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