**Physical characteristics of AFEX-pretreated and densified switchgrass, prairie cord grass,
and corn stover**

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Abstract

The goal of the study was to evaluate and compare the physical properties of control, pretreated and densified corn stover, switchgrass, and prairie cord grass samples. Ammonia Fiber Expansion (AFEX) pretreated switchgrass, corn stover, and prairie cord grass samples were densified by using the comPAKco device developed by Federal Machine Company of Fargo, ND. The densified biomass were referred as “PAKs” in this study. All feedstocks were ground into three different grind size of 2, 4 and 8 mm prior to AFEX pretreatment and the impact of grinding on pellet properties was studied. The results showed that the physical properties of AFEX-PAKed material were not influenced by the initial grind size of the feedstocks. The bulk density of the AFEX-PAKed biomass increased by 1.2 to 6 fold as compared to untreated and AFEX-pretreated materials. The durability of the AFEX-PAKed materials were between 78.25 and 95.2%, indicating that the AFEX-PAKed biomass can be transported easily. To understand the effect of storage on the physical properties of these materials, samples were stored in the ambient condition ($20 \pm 2^{\circ}\text{C}$ and $70 \pm 5\%$ relative humidity) for six months. After storage, thermal properties of the biomass did not change but glass transition temperature decreased. The water absorption index and water solubility index of AFEX-treated and AFEX-PAKed biomass showed mixed trends after storage. Moisture content decreased and durability increased upon storage.

Keywords

Ammonia Fiber Expansion, Densification, Lignocellulosic, Pellet durability, Storage
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1. Introduction:

Lignocellulosic biomass, for example corn stover, switchgrass, and prairie cord grass are widely available and can be converted through wide range of technologies to different forms of energy, chemicals, and materials [1, 2]. Efficient conversion of biomass into bioenergy relies heavily on the effective, consistent, and economical transport of biomass from field to the biorefinery. The high moisture content, irregular shape and size, and low bulk density of biomass (40-200 kg/m³) [3, 4] are significant challenges to the developing bio-economy. These properties can lead to high costs of biomass handling, transport, and storage [5]. To address this problem, biomass materials could be densified in a regional biomass processing facility located near the field and then transported to a centralized biorefinery for final processing to energy products [6-11]. The concept of decentralized Regional Biomass Processing Depots (RBPDs) to feed a larger centralized biorefinery was first introduced by Carolan et al. [6] in 2007. Since then, this model has been extensively studied by various group of researchers. Studies have indicated that implementation of RBPDs in feeding large centralized biorefineries would help advance local economies by generating jobs; reducing the cost of biomass storage, handling, and transportation; and reducing greenhouse gas emissions [7-9, 11-12].

Biomass densification through various types of pelleting process has been found to be effective in increasing the initial bulk density of biomass from 40 to 200 kg/m³ to final bulk density of 600 to 800 kg/m³ [13-14]. The biochemical conversion process of lignocellulosic biomass into ethanol is affected by several factors, primarily by the recalcitrant nature of the lignocellulosic biomass and by the accessible surface area of exposed cellulose [15]. Therefore, pretreatment is needed for cellular disruption and to further enhance the accessibility of carbohydrates to cellulolytic enzymes. Numerous pretreatment techniques have been studied. Pretreatment

technologies can be broadly classified into four major categories: a) physical, b) chemical, c) solvent fractionation, d) biological [16]. Ammonia Fiber Expansion (AFEX), a physio-chemical pretreatment method, increases the surface accessibility, enhances cellulose de-crystallization and hemicellulose de-polymerization, and reduces lignin recalcitrance leading to glucose yields of up to 98% of theoretical [17]. Despite this, the bulk density of the AFEX-pretreated feedstocks remains fairly low and thus such pretreated feedstocks would need to be densified for effective handling, transportation, and storage. Various densification processes and their impact on the pellet characteristics have been studied [5, 18-20]. But the most of the established densification processes are energy-intensive and thus are costly [5, 21]. Therefore, to lower the net cost of feedstock delivery, cost-effective biomass densification processes are critically needed. In this study, a novel densification device referred to as the ComPAKco densification system, developed by Federal Machine (Fargo, ND) was used to compact the AFEX-pretreated switchgrass, corn stover, and prairie cord grass of different grind sizes (2 mm, 4 mm, and 8 mm). Unlike the commercial ring die pelleting units, this system uses a gear and mesh system to compress the biomass [1]. The system operates at relatively low temperatures (ambient to 60°C) and pressures with low energy input (180 HP motor to produce 7-8 tons/hr). Whereas, the traditional ring/die pelleting units uses 400 HP motor to process 4-5 tons/hr and temperature of the feedstock could reach as high as 180-200°C due to high friction [5, 21]. Additionally, no binder is needed during the densification of AFEX-pretreated feedstocks. Hence, RBPD using integrated AFEX-pretreatment and ComPAKco densification could minimize the transportation and processing cost of the feedstocks for large scale bio-refineries. The briquettes/pellets produced by using ComPAKco system post-AFEX pretreatment are referred to as the “PAKs” throughout the article. Rijal et al. [1] studied the effect of densification on biochemical

92 conversion of these PAKs by subjecting to fermentation process and their result showed that
93 densification process did not counteract the effect of original pretreatment. Their study showed
94 that AFEX pretreatment may enable the use of low-pressure, low-temperature densification in
95 producing the biomass pellets. However, it is important to study the physical characteristics of
96 the pellets as they are critical in determining their long term storability and their economic
97 viability when transporting the densified biomass materials. These physical properties, which
98 include moisture content, water activity, bulk density, true density, thermal properties, glass
99 transition temperature, and pellet durability, were measured using 2 mm, 4 mm, and 8 mm grind
100 size control samples as well as, AFEX-pretreated, and AFEX- densified PAKs of switchgrass,
101 corn stover, and prairie cord grass. Switchgrass, corn stover and prairie cord grass are seasonal
102 harvest biomass materials. After harvest, they must be stored, sometimes for long periods, until
103 they are used. Thus, it is important to have biomass with consistent physical and chemical
104 characteristics during long storage periods. Our literature review suggested that only few studies
105 have been reported on the physical characteristics of the AFEX-pretreated and densified
106 feedstocks. Hoover et al. [22] reported that highly dense and durable pellets can be produced
107 from the AFEX-pretreated corn stover and Campbell et al. [23] indicated that low moisture
108 content (<20%) AFEX-pretreated corn stover and wheat straw can produce high-quality pellets.
109 In contrast to our present study, both of the studies have used a flat-die mill for pellet formation.
110 From several studies, it has become apparent that the densification process, feedstocks types, and
111 feedstock composition plays an important role in the quality of densified feedstocks [18]. Hence,
112 the overall objectives of this study were to firstly, evaluate the effect of AFEX pretreatment and
113 the novel densification process by examining and comparing the physical properties of the
114 control (untreated biomass), AFEX-pretreated biomass, and AFEX-PAKed switchgrass, corn

stover, and prairie cord grass. And secondly, to examine the physical properties of AFEX-pretreated and AFEX-PAKed switchgrass, corn stover, and prairie cord grass after storing in ambient condition ($20 \pm 2^\circ\text{C}$ and $70 \pm 5\%$ relative humidity) for six months.

2. Materials and Methods

2.1. Sample Preparation

Switchgrass, corn stover, and prairie cord grass samples were collected from a local farm in Brookings, South Dakota and ground to size of 2, 4, and 8 mm using a hammer mill (Speedy Jr, Winona Attrition Mill Co, MN). Samples were then sent to Michigan State University for AFEX pretreatment using a high pressure stainless steel 5 gallon vessel (Parr Instruments; Moline, IL, USA) in a batch process. Pretreatment parameter for individual feedstocks were optimized (data not shown) according to the previously described method [17]. The optimal AFEX pretreatment conditions used for three different types of biomass are shown in Table 1. Pretreated biomass was dried in a fume hood for overnight to remove residual ammonia left in the biomass after pretreatment. AFEX-pretreated samples were then sent to Federal Machines, Inc, Fargo, ND for densification by using comPAKco system. The term “PAKs” is used here to describe the products resulting from the comPAKco equipment. The device used for compacting the biomass and the resulting densified PAKs (approximately, 1 in x 0.5 in x 4 in) from three different feedstocks are shown in Figure 1 and Figure 2, respectively. The control, AFEX-pretreated and AFEX-PAKed samples were then stored in the refrigerator in a plastic bags until further studies. Five hundred grams of 8 mm AFEX-pretreated and 8 mm AFEX-PAKed switchgrass, corn stover, and prairie cord grass samples were separated and stored in ambient condition ($20 \pm 2^\circ\text{C}$ and $70 \pm 5\%$ relative humidity for 6 months. Preliminary results of physical properties showed

that initial grind size did not have significant impact on the physical properties of the different forms of feedstocks, hence the only 8 mm size feedstocks were selected for the storage study. Physical characteristics of all the samples were studied before and after storage, as described in the section below.

2.2. Moisture Content

Moisture content of the raw, the AFEX-pretreated, and the AFEX-PAKed biomasses were measured according to the NREL procedure (NREL/TP-510-42621) and using a laboratory electric oven (Thelco Precision, Jovan Inc., Winchester, VA) at 105°C for 4 h [24].

2.3. Water Activity

Water activity of the samples was measured by using the water activity meter (Novasina AW sprint TH 500, Switzerland). Depending on the sample, it took about 15 to 45 min for the analysis to complete. All the analyses were done in triplicate.

2.4. Water Absorption and Solubility Indices (WAI & WSI)

Approximately 2.5 g sample was suspended in 30 ml of distilled water in a tarred 50 ml centrifuge tube. The centrifuge tube was placed in a laboratory oven (Thelco Precision, Jovan Inc., Winchester, VA) at 30°C. This tube was stirred intermittently for a period of 30 min and centrifuged at 3,000 rpm for 10 min. The supernatant liquid was transferred into an aluminum dish, placed in the oven for 2 h at 135°C [25], and then desiccated for 20 min before weighing the dry solids of the supernatant. The mass of the remaining gel was weighed, and WAI (-) was calculated as the ratio of gel mass to the original sample mass. WSI (%), on the other hand was determined as the ratio of mass of dry solids in the extract to the original sample mass.

2.5. Aerated Bulk Density (ABD) and Packed Bulk Density (PBD)

ABD and PBD of the biomass were measured by using the Hosokawa Powder Tester (Model PTR, Hosokawa Micron Powder systems, Summit, NJ). The samples were fed into the vibrator on the top of the device which distributes the biomass samples into a cup of known volume and weight. The cup is filled until it overflows. The overflowing material was scraped off and the weight of the cup was measured again. The difference in weight after filling divided by the volume of the empty cup gave the value of aerated bulk density.

A cap was then placed on the cup and the vibration process was repeated until the cap was filled to the top. After vibration, the equipment started tapping at the rate of 1 tap per second. After 30 taps, the cap was removed and the overflowing material was scraped off. The new weight of the samples filled the cup divided by the volume of the empty cup gave the value of packed bulk density.

2.6. True Density

Micromeritics Multivolume Pycnometer (No.1305, Micromeritics Instrument Corporation, Norcross, GA) was used to measure the true density of the samples. The biomass sample was filled into an aluminum cup provided together with the pycnometer and then put into the pycnometer. The unit works on the basis of helium gas replacement in the void space of the biomass sample. The values were measured in the form of P_1 when the knob was in the prep position and P_2 when the knob was in test position. True density of the material was calculated by using the equation

$$TD = \frac{M_{sample}}{V_{cell} - \frac{V_{exp}}{\frac{P_1}{P_2} - 1}}$$

Where TD is the true density (kg/m^3), M_{sample} (kg) is the mass of the biomass sample that was used to fill the aluminum cup, V_{cell} is the empty volume of the sample cell with the empty sample cup in place, and V_{exp} is the expansion volume added while measuring the test samples. The V_{cell} and V_{exp} are the two constant numbers that are provided by the instrument manufacturer (Micromeritics multivolume pycnometer).

2.7. Thermal Properties

Thermal properties (conductivity and diffusivity) were determined by using a thermal properties meter (KD2, Decagon Devices, Pullman, WA.) that utilized the line heat source probe technique. Holes with the diameter 1.9 mm were drilled in the AFEX-PAKed samples to insert the probe and measure the thermal properties.

2.8. Glass Transition Temperature (T_g)

Glass transition temperatures of the materials were measured by a differential scanning calorimeter (DSC (Q200, TA Instrument, New Castle, DE). About 2 mg (± 0.2) of biomass sample was hermetically sealed in an aluminum pan and the sample was placed in the DSC machine for the glass transition temperature measurement. The temperature was increased from 10°C to 150°C at the rate of 5°C per minute. The glass transition temperature (T_g) was measured as the temperature at the midpoint of the change in the slope of the DSC thermo-gram.

2.9. Durability

The durability of the AFEX-PAKed sample was measured according to the procedure outlined in ASAE Standard S269.4 [26]. This involved the tumbling of 100 g test sample for 10 min at 50 rpm in a dust-tight enclosure. After tumbling, the sample was sieved through a No. 5 U.S. sieve (opening diameter of 4 mm). Durability was expressed as the ratio of the mass of pellets retained

on the sieve to the initial weight of the pellets before tumbling (100 g) and expressed as a percentage.

2.10. Statistical Analysis

Switchgrass, corn stover and prairie cord grass with three treatments (control, AFEX treated and AFEX-PAKed) and three grind sizes (2 mm, 4 mm and 8 mm) were prepared, resulting in a total of 9 combinations for each kind of biomass in the study. Each grind size and treatment was analyzed for all the properties and the data were analyzed by the SAS 9.0 software (SAS Institute, Cary, NC, USA) using a Type I error rate (α) of 0.05 to find any significant differences between the three treatments.

3. Results and Discussion

3.1. Moisture Content and Water Activity

The effect of AFEX-pretreatment and densification post-AFEX pretreatment on the moisture content and water activity (A_w) of the samples before and after storage are presented in the Table 2. There were no significant differences in moisture content and water activity among the biomass grind sizes (2, 4 and 8 mm) for all three types of biomass. The initial moisture content of all three biomass were in the range of 6.8 to 7.1%, wb. The AFEX pretreatment and densification post-AFEX pretreatment did not have any significant impact on the moisture content of feedstocks. The moisture content of the AFEX-PAKed biomass (6.5 to 7.4% wb) were relatively lower than the moisture content of pellets reported for wood (9.39% wb), willow (13.46% wb), miscanthus (12.17%, wb), wheat straw (10.66%, wb) and barley straw (10.77%, wb) [27]. However, after storage in an ambient conditions for 6 months, the moisture content of the AFEX-pretreated switchgrass, corn stover, and prairie cord grass samples decreased by

21.21, 44.12, and 29%, respectively. Similarly, the AFEX-PAKed samples of switchgrass, corn stover, and prairie cord grass also lost the moisture at same rate as AFEX-pretreated samples did. High moisture pellet could lead to the microbial growth and subsequent pellet degradation during storage [27- 28], hence, low moisture pellets are considered to be good quality pellets.

Water activity is an important indicator in predicting the shelf-life of the biomaterials. By definition, A_w refers to the ratio of the water vapor pressure of the material to the vapor pressure of the pure water at the same temperature and pressure [29]. It is a measurement of freely available water (unbound water) in the material. Although A_w is largely used by food researcher in developing shelf-stable products, it has also been used in predicting the growth of bacteria, yeasts, and molds during long-term storage of biomass [30-31]. Spoilage of corn components due to mold growth has been reported at A_w of ≥ 0.9 by Igathinathane et al. [30]. Hence, it is important to measure the A_w of the biomass in determining the best storage strategy. The A_w of all samples were in the range of 0.189 to 0.376, suggesting that there is less probability of microbial spoilage during storage. However, it was interesting to observe that the A_w of AFEX and AFEX-PAKed samples for all feedstocks were significantly higher than that of control at same moisture content (Table 2). This suggested that there was significant changes in the structural chemistry of the feedstocks during AFEX pretreatment and further densification process. Those changes in the structural chemistry might have affected the interaction between surface and water molecules, leaving the high amount of freely available water in the feedstocks as compared to the control samples. Hence, the A_w of AFEX and AFEX-densified feedstocks was more than that of control. A_w of the material can change if subjected to the different environmental conditions [28-29]. The reduction in A_w and moisture content as observed for AFEX and AFEX-PAKed materials (Table 2) after 6 months of storage in an ambient condition

could be attributed to the possible evaporation of the unbound water molecules to the environment during storage.

3.2. Water Absorption and Solubility Indices (WAI & WSI)

Table 3 showed that the initial grind size of the feedstock had significant impact on the WAI and WSI of all the feedstocks. AFEX pretreatment and densification post the AFEX pretreatment also changed the WAI and WSI values. WAI gives an estimate of amount of water the sample can absorb, on the other hand, WSI is a measurement of the amount of dried solids recovered by evaporating the moisture from the water absorption test. Depending upon the composition of the samples, the WAI and WSI can vary significantly. In this study, among the feedstocks tested, corn stover had the highest WAI (10.9) and lowest WSI (2.1) values (Table 3). Although there was no clear trend, in general, the increase in biomass grind size increased the WAI of switchgrass and corn stover samples, for example, WAI of 6.4 for 2 mm and 7.7 for 8 mm switchgrass, and 9.2 for 2 mm and 10.9 for 8 mm corn stover samples (Table 3). However, WAI of the prairie cord grass samples remained unaffected by the initial grind size. The AFEX-pretreated and AFEX-PAKed samples showed the mixed trends. After AFEX pretreatment the WAI values of switchgrass and corn stover decreased as compared to control, but for the prairie cord grass samples WAI increased from 5.5 to 8.1, and 5.5 to 8.6 for 2 and 4 mm sizes, respectively. Further densification significantly reduced the WAI of all grind size prairie cord grass samples but for switchgrass and corn stover no significant change was observed. Several studies have suggested that the structural changes in macromolecules such as proteins and carbohydrates [32-33] during processing of materials can lead to the change in WAI. WAI and WSI are influenced by the temperature, moisture content, and the pretreatment parameters [34]. Hence, these changes in the WAI values of different feedstocks are attributed to the structural changes that might have occurred during the AFEX pretreatment and densification post AFEX

processes. Additionally, WAI and WSI are inversely related, hence, the increase in WAI corresponds to the decrease in WSI and vice-versa [32, 35]. Accordingly, we also observed the increase in WSI with the decrease in WAI for all feedstocks that were evaluated. In general, the value of WSI of the AFEX-treated biomass was higher than that of the control biomass samples. This could be explained by the fact that the WSI measures the degradation extent of the macromolecule components of the materials. During the AFEX pretreatment WSI is expected to increase due to the combined effect of high temperature, pressure and ammonium hydroxide. Although there are no reports on the WAI and WSI of the lignocellulosic feedstocks, WAI and WSI of distiller's grains based feed have been reported to be in the range of 2.6-3.1 and 16.6-18.3 under different temperatures and moisture contents [32]. After storage for 6 months in an ambient conditions, the WAI of the samples were reduced slightly for all the samples except for the AFEX-PAKed prairie cord grass samples where reduction was significant. This change in WAI could be due to the change in moisture content during storage, as explained in the above section 3.1.

3.3. Aerated Bulk Density (ABD), Packed Bulk Density (PBD), and True Density (TD)

The bulk density is highly influenced by the initial grind size of the material [5, 36]. In our study, we also observed that the ABD and PBD of control samples of switchgrass, corn stover, and prairie cord grass decreased significantly with increase in biomass grind size (Table 4). Likewise, the ABD and PBD of smaller size AFEX-pretreated feedstocks were significantly higher than that of larger grind size AFEX-pretreated samples. Generally, larger size particles tend to occupy more pore volume than smaller size particles and leads to the decrease in bulk densities [37]. These observations were consistent with the previous reports on bulk density of wheat straw, barley straw, corn stover, and switchgrass by Mani et al. [37], dry and wet corn

stover by Zhou et al. [36], and AFEX-pretreated and densified AFEX corn stover by Hoover et al. [22]. However, initial grind size had no significant impact on the ABD and PBD of the densified AFEX-pretreated samples. Similar finding has been reported for the densified AFEX corn stover by Hoover et al. [22]. In our study, the ABD and PBD of densified AFEX corn stover, switchgrass, and prairie cord grass were two to six times greater compared to untreated and AFEX-pretreated samples. Although there are no reports available on the bulk density of densified AFEX switchgrass and prairie cord grass, we noticed that the bulk density of the densified AFEX corn stover (402-443 kg/m³) as obtained in our study was slightly lower than values reported by the Hoover et al. [22] (588-634 kg/m³) and Campbell et al. [23] (505-575 kg/m³) for AFEX-pretreated pellets of corn stover. This difference in bulk densities could probably be due to the different method of densification that is being applied in our study as compared to the studies of Hoover et al. [22] and Campbell et al. [23]. Additionally, for all feedstocks, PAKs generated from different grind sizes had similar ABD and PBD. As expected, true density of all feedstocks of different grind size increased significantly after AFEX pretreatment and subsequent densification (Table 4). AFEX-pretreatment changes the tenacious structure of the biomass and makes them more brittle and friable leading to the increase in densities [22]. Additionally, data indicated that initial grind size of the material did not have significant impact on the TD of raw, AFEX or densified AFEX materials. These observations are in agreement with the reports of Hoover et al. [22] who found despite significant difference in their mean particle size, grind size did not have significant effect on unit density. As shown in the Table 4, the ABD and PBD of the switchgrass and prairie cord grass remained unaffected upon storage for 6 months in an ambient conditions, but the bulk densities

for densified AFEX corn stover decreased significantly after storage. However, there was no change in TD after storage for 6 months.

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3.4. Thermal Properties

Thermal properties for different biomass samples (switchgrass, corn stover, and prairie cord grass) were measured in terms of thermal conductivity and thermal diffusivity values (Table 5). Neither grind size of the feedstocks nor AFEX pretreatment affected the thermal conductivity values. However, thermal conductivity values of AFEX-densified samples were increased for all the feedstocks when compared to their respective controls. Hoover et al. [22] investigated the effect of AFEX pretreatment and densification on the cellular structure of corn stover samples by analyzing the micrographs of AFEX-pretreated and AFEX-pelletized corn stover. They observed a slight deformation in the cell-wall structure of the AFEX-pretreated corn stover however, a severe disruption of the cellular structure of the pelletized corn stover was reported. Similarly, difference in microstructure of wood particle [38] and wood pellets [39] were reported. Hence, increase in thermal conductivity values as obtained for the densified PAKs could be attributed to the structural difference between the ground biomass, AFEX-pretreated biomass, and AFEX-densified biomass. Thermal conductivity is one of the critical parameter which controls the rate of heat dissipation during bulk storage [40] while thermal diffusivity indicates the heat storing capability of the material [41]. Thermal diffusivity of the feedstocks were also unaffected by the initial grind size of the feedstocks (Table 5). However AFEX pretreatment and AFEX-densification of corn stover significantly decreased the thermal diffusivity values when

compared to control corn stover. Likewise, the thermal diffusivity of the AFEX-densified switchgrass and prairie cord grass were also reduced significantly as compared to their respective control samples. Thermal diffusivity is the thermal conductivity divided by density and specific heat capacity at constant pressure. Hence, this reduction in the thermal diffusivity of the AFEX-densified feedstock is attributed to the higher bulk density of the PAKs [430 vs 70 kg/m³, 420 vs 75 kg/m³, and 408 vs 108 kg/m³, respectively for the switchgrass, corn stover and prairie cord grass samples (Table 4)] as compared to the control samples. Thermal properties of all the feedstocks remained unchanged after 6 months of storage at an ambient condition. Knowledge of thermal properties of the biomass pellets can be beneficial in understanding the instantaneous thermal environment within the bulk pellets and thus may help in preventing the possible fire accidents during bulk storage of pellets for longer period of time [40].

3.5. Glass Transition Temperature (T_g)

Glass transition temperature is defined as the temperature at which the material transform from brittle, metastable amorphous solid to a rubbery plastic unstable state [42]. In the lignocellulosic biomass, lignin and hemicellulose are the two major components that undergo plastic deformation at their glass transition temperature [43]. The glass transition occurred from 79.2 to 82.7°C for switchgrass, corn stover, and prairie cord grass samples (Table 6). The initial grind size of the biomass did not have any impact on the T_g . Switchgrass, corn stover, and prairie cord grass (2 mm) had glass transition temperature of 82.7, 79.3, and 80.7°C, respectively, and these values were in close agreement with the glass transition temperature reported for corn stover, switchgrass, and prairie cord grass by Karunanithy et al. [43] and average T_g of 75°C for corn stover and switchgrass by Kaliyan and Morey [44]. The AFEX-pretreatment of the switchgrass, corn stover, and prairie cord grass did not alter the T_g of the biomass. One possible explanation

for no change in T_g after AFEX pretreatment could be the fact that during the AFEX pretreatment lignin is not removed from the biomass but it is redistributed on the outer cell wall creating highly porous structure and thus promoting the enzyme accessibility to cellulose [45]. It has been also reported that depending on the biomass source and lignin composition, T_g of lignin can vary between 100 to 160°C [46, 47] and in our study all the biomass were AFEX-pretreated at 100°C (Table 1). We found that the densification of the AFEX-pretreated biomass also did not have any significant impact on the T_g of the biomass tested. Except for the 8 mm AFEX-densified switchgrass, T_g of the AFEX and AFEX-PAKed corn stover, and prairie cord grass were decreased significantly after 6 months of storage. No logical explanation could be found for this observation. According to the Kalyan and Morey [44], reduction in T_g could occur if there is an increase in moisture content of biomass which will act as an plasticizer and thus decrease the T_g , however; in contrast to this, the moisture content of the biomass was decreased during storage period (Table 2). Thus, more detailed study on lignin or hemicellulose chemistry of stored biomass might provide the explanation for the T_g reduction during storage as observed in this study.

3.6. Durability

Durability is one of the most important characteristics of the pellet. It depends on several factors such as chemical and physical properties of the feedstocks, process variables such as pretreatment, grinding, milling, pelleting etc. [2, 48]. The pellet durability of the AFEX-pretreated switchgrass ranged from 78.2 to 91.1% (Table 7). While pellet durability was above 92% for AFEX-densified corn stover and in the range of 87.1 to 92.1% for AFEX-densified prairie cord grass samples. Initial grind size of 2, 4 and 8 mm did not have any significant impact on the durability except for the 4 mm switchgrass samples. Four mm switchgrass gave the

387 maximum durability of 91.1% as compared to 78.2% for 8 mm and 80.3% for 2 mm. In the
388 literature, there are two different explanations available, according the Payne [49] medium or
389 finely ground materials produces the highly durable pellets, whereas Tabil et al. [50] postulated
390 that the mechanical interlocking of the larger particles during pelleting might give the highly
391 durable pellets. This shows that there is a knowledge gap in understanding the relationship
392 between the raw materials, pelleting variables and ultimate effect on pellet durability [48], thus
393 more studies focusing on the effect of the raw material composition and process variables will
394 possibly be helpful in explaining these observations. We presented the durability results (Table
395 7) only on the AFEX-densified biomass, primarily due to the fact that the densification of the
396 AFEX pretreatment process eliminates the addition of the external binders whereas, external
397 binders are needed during the PAKs formation of non-pretreated feedstocks. Thus, the PAKs
398 formed from AFEX-pretreated and non-pretreated feedstock would not be same, hence the
399 comparison would not be fair. However, we did our preliminary study on the PAKs of AFEX-
400 pretreated and un-pretreated feedstocks and results showed that untreated biomass pellets were
401 much less durable than the AFEX-densified biomass (Data not shown). Karunanithy et al. [2]
402 reported the durability of the briquettes of corn stover and prairie cord grass as 97% and 61%,
403 respectively. While comparing the durability of AFEX-densified corn stover and prairie cord
404 grass as obtained in this study with those of Karunanithy et al. [2], the AFEX-densified prairie
405 cord grass had significantly higher durability whereas, the AFEX-densified corn stover had
406 similar durability. Durability of the agricultural biomass has been divided into three different
407 classes of high (>80%), medium (70-80%), and low (<70%) [51]. According to these
408 classification, novel ComPAKco densification process resulted in highly durable pellets from all
409 three AFEX-pretreated feedstocks. After storage, slight increase in durability was observed and

this increase in durability is possibly due to the decrease in moisture content as observed during storage (as discussed in above section 3.1, Table 2). Similar results were found for olive tree pruning residues pellets [52].

4. Conclusions

The ComPAKco novel densification process resulted in the production of highly densified pellets (bulk densities increased by 1.2 to 6.2 times depending on grind size and the type of biomass) of switchgrass, corn stover, and prairie cord grass. The study showed that the AFEX-pretreated and AFEX-densified switchgrass, corn stover, and prairie cord grass can be stored for long period of time without having any alterations in major physical properties. Desirable characteristics such as low moisture content, low water activity, and low thermal properties, and improved durability during storage of AFEX-densified feedstocks was observed. Initial grind size of the feedstocks did not influence the physical properties of the biomass. The low temperature, low pressure densification process used in this study resulted in fairly high durability pellets. These results suggested that there is a possibility to further increase the durability and bulk densities of AFEX-pretreated biomass by using different pelleting process. Overall, this study showed that the AFEX-PAKed process leads to the formation of pellets with desirable characteristics and has potential to reduce the transportation cost of biomass from the field to biorefinery. The study also showed that type of pretreatment used may affect some important properties of biomass pellets such as water activity and glass transition temperature, which ultimately will have an impact on storability of the pellets in an ambient conditions. Hence, it is important to study the pellet characteristics pretreated biomass. Compacting the biomass will have significant impact on

reducing the processing cost of biofuels and also has potential to reduce greenhouse gas emissions because of more favorable transportation properties.

5. Acknowledgement

We would like to acknowledge the valuable suggestions given by Dr. Farzaneh Teymouri, MBI International regarding procedures to characterize the compacted biomass. We also thank Mr. Charles Donald for doing the AFEX pretreatment for this project. This study was funding through US Department of Energy, Golden, CO, Grant number DE-FG36-08GO88073.

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Figure 1: ComPAKco Single Station Test Device

Figure 2: Untreated, AFEX-pretreated and PAKed samples; a) switchgrass; b) corn stover; c) prairie cord grass

Table 1: AFEX pretreatment parameters of switchgrass, corn stover, and prairie cord grass

Samples	Ammonia loading (dry biomass : ammonia)	Moisture content (% db)	Treatment time (min)
Switchgrass	1:2	50	30
Corn stover	1:1	60	15
Prairie cord grass	1:2	40	30

Pretreatment temperature of 100°C was used for all the samples.

Table 2: Moisture content (MC) and water activity (A_w) of control, AFEX treated, and AFEX-PAKed switchgrass, corn stover, and prairie cord grass before and after storage

			Switchgrass		Corn stover		Prairie cord grass	
			MC (% , db)	A_w	MC (% , db)	A_w	MC (% , db)	A_w
Before storage	Control	2 mm	7.1 ^{a,1}	0.219 ^{a,2}	6.8 ^{a,1}	0.217 ^{a,2}	6.8 ^{a,1}	0.214 ^{a,2}
		4 mm	7.0 ^{a,1}	0.207 ^{a,2}	7.0 ^{a,1}	0.247 ^{a,2}	7.2 ^{a,1}	0.261 ^{a,2}
		8 mm	6.9 ^{a,1}	0.189 ^{a,2}	6.8 ^{a,1}	0.216 ^{a,2}	7.1 ^{a,1}	0.249 ^{a,2}
	AFEX	2 mm	6.9 ^{a,1}	0.345 ^{a,1}	7.0 ^{a,1}	0.377 ^{a,1}	7.1 ^{a,1}	0.382 ^{a,1}
		4 mm	7.0 ^{a,1}	0.341 ^{a,1}	6.7 ^{a,1}	0.323 ^{a,1}	6.8 ^{a,1}	0.327 ^{a,1}
		8 mm	6.6 ^{a,1,A}	0.323 ^{a,1,A}	6.8 ^{a,1,A}	0.359 ^{a,1,A}	6.9 ^{a,1,A}	0.368 ^{a,1,A}
	AFEX -	2 mm	6.6 ^{a,1}	0.307 ^{a,1}	6.6 ^{a,1}	0.307 ^{a,1}	7.0 ^{a,1}	0.344 ^{a,1}
		4 mm	7.2 ^{a,1}	0.343 ^{a,1}	7.0 ^{a,1}	0.340 ^{a,1}	6.7 ^{a,1}	0.318 ^{a,1}
	PAKed	8 mm	6.5 ^{a,1,A}	0.312 ^{a,1,A}	7.4 ^{a,1,A}	0.376 ^{a,1,A}	6.8 ^{a,1,A}	0.329 ^{a,1,A}
After storage	AFEX	8 mm	5.2 ^{1,B}	0.201 ^{1,B}	3.8 ^{1,B}	0.192 ^{1,B}	4.9 ^{1,B}	0.198 ^{1,B}
	AFEX -	8 mm	5.1 ^{1,B}	0.197 ^{1,B}	4.4 ^{1,B}	0.191 ^{1,B}	4.3 ^{1,B}	0.189 ^{1,B}
	PAKed							

Different letters within the same column indicates that means are statistically different ($P < 0.05$)

Small letters: Comparing the significance of biomass grind sizes

Numbers: Comparing the significance of different treatments

Capital letters: Comparing the significance of biomass storage

Table 3: Water absorption index (WAI) and water solubility index (WSI) of control, AFEX treated, and AFEX-PAKed switchgrass, corn stover, and prairie cord grass before and after storage

			Switchgrass		Corn stover		Prairie cord grass	
			WAI	WSI	WAI	WSI	WAI	WSI
Before storage	Control	2 mm	6.4 ^{b,1}	7.1 ^{b,2}	9.2 ^{b,1}	6.8 ^{b,2}	5.5 ^{a,2}	9.3 ^{a,2}
		4 mm	6.6 ^{b,1}	9.1 ^{a,1}	9.8 ^{b,1}	4.7 ^{b,3}	5.5 ^{a,2}	10.4 ^{a,3}
		8 mm	7.7 ^{a,1}	4.4 ^{c,2}	10.9 ^{a,1}	2.1 ^{c,2}	5.8 ^{a,1}	7.1 ^{c,3}
	AFEX	2 mm	5.8 ^{a,1}	8.9 ^{a,1}	5.8 ^{a,2}	8.9 ^{c,1}	8.1 ^{a,1}	14.9 ^{a,1}
		4 mm	6.0 ^{a,1}	9.5 ^{a,1}	5.7 ^{a,2}	10.1 ^{b,1}	8.6 ^{a,1}	15.1 ^{a,1}
		8 mm	5.1 ^{a,2,A}	10.1 ^{a,1,A}	4.6 ^{a,2,A}	11.2 ^{a,1,A}	5.0 ^{b,1,A}	16.9 ^{a,1,A}
	AFEX - PAKed	2 mm	5.1 ^{a,2}	9.4 ^{a,2}	5.0 ^{ab,2}	8.0 ^{b,1}	5.1 ^{ab,2}	11.8 ^{a,2}
		4 mm	5.6 ^{a,2}	8.3 ^{a,2}	4.6 ^{b,3}	7.6 ^{b,2}	6.2 ^{a,2}	12.7 ^{a,2}
		8 mm	5.4 ^{a,2,A}	10.9 ^{a,1,A}	5.6 ^{a,2,A}	8.6 ^{a,2,A}	3.7 ^{b,2,A}	9.3 ^{b,2,A}
After storage	AFEX	8 mm	4.6 ^{1,A}	9.1 ^{1,A}	4.1 ^{1,A}	9.1 ^{1,B}	4.9 ^{1,A}	16.5 ^{1,A}
	AFEX - PAKed	8 mm	5.2 ^{1,A}	8.0 ^{1,B}	4.6 ^{1,B}	9.4 ^{1,A}	2.4 ^{2,B}	4.8 ^{2,B}

Different letters within the same column indicates that means are statistically different ($P < 0.05$)

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Table 4: Aerated Bulk Density of AFEX treated, and AFEX-PAKed switchgrass, corn stover, and prairie cord grass before and after storage

			Switchgrass			Corn stover			Prairie cord grass		
			ABD (kg/m ³)	PBD (kg/m ³)	TD (kg/m ³)	ABD (kg/m ³)	PBD (kg/m ³)	TD (kg/m ³)	ABD (kg/m ³)	PBD (kg/m ³)	TD (kg/m ³)
Before storage	Control	2 mm	143 ^{a,3}	172 ^{a,3}	886 ^{a,2}	111 ^{a,3}	123 ^{b,3}	942 ^{a,2}	213 ^{a,3}	123 ^{a,3}	1062 ^{a,2}
		4 mm	97 ^{b,3}	136 ^{b,3}	828 ^{a,3}	95 ^{b,3}	117 ^{b,3}	954 ^{a,2}	154 ^{b,3}	117 ^{a,3}	943 ^{a,2}
		8 mm	70 ^{c,3}	106 ^{c,3}	773 ^{a,2}	75 ^{c,3}	89 ^{c,3}	832 ^{a,2}	108 ^{c,3}	89 ^{b,3}	957 ^{a,2}
	AFEX	2 mm	194 ^{a,2}	225 ^{a,2}	1287 ^{a,1}	141 ^{b,2}	160 ^{b,2}	1337 ^{a,1}	252 ^{a,2}	280 ^{a,2}	1409 ^{a,1}
		4 mm	157 ^{b,2}	184 ^{b,1}	1303 ^{a,2}	134 ^{b,2}	153 ^{b,2}	1341 ^{a,1}	166 ^{b,2}	191 ^{b,2}	1464 ^{a,1}
		8 mm	131 ^{c,2,A}	159 ^{c,2,A}	1363 ^{a,1,A}	180 ^{a,2,A}	196 ^{a,2,A}	1329 ^{a,1,A}	133 ^{c,2,A}	156 ^{c,2,A}	1401 ^{a,1,A}
	AFEX PAKed	2 mm	462 ^{a,1}	493 ^{a,1}	1441 ^{a,1}	429 ^{a,1}	429 ^{a,1}	1495 ^{a,1}	414 ^{a,1}	433 ^{a,1}	1561 ^{a,1}
		4 mm	408 ^{a,1}	434 ^{a,1}	1458 ^{a,1}	406 ^{a,1}	430 ^{a,1}	1585 ^{a,1}	408 ^{a,1}	425 ^{a,1}	1541 ^{a,1}
		8 mm	430 ^{a,1,A}	460 ^{a,1,A}	1434 ^{a,1,A}	420 ^{a,1,A}	443 ^{a,1,A}	1429 ^{a,1,A}	408 ^{a,1,A}	427 ^{a,1,A}	1545 ^{a,1,A}
After storage	AFEX	8 mm	131 ^{2,A}	159 ^{2,A}	1293 ^{1,A}	173 ^{2,A}	191 ^{2,A}	1282 ^{1,A}	121 ^{2,A}	137 ^{2,A}	1309 ^{1,A}
	AFEX PAKed	8 mm	414 ^{1,A}	451 ^{1,A}	1403 ^{1,A}	357 ^{1,B}	383 ^{1,B}	1424 ^{1,A}	397 ^{1,A}	424 ^{1,A}	1460 ^{1,A}

Different letters within the same column indicates that means are statistically different ($P < 0.05$)

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Table 5: Thermal conductivity and thermal diffusivity of control, AFEX treated, and AFEX-PAKed switchgrass, corn stover, and prairie cord grass before and after storage

			Switchgrass		Corn stover		Prairie cord grass	
			Thermal conductivity	Thermal diffusivity	Thermal conductivity	Thermal diffusivity	Thermal conductivity	Thermal diffusivity
			(W/m ^o C)	(m ² /s)	(W/m ^o C)	(m ² /s)	(W/m ^o C)	(m ² /s)
Before storage	Control	2 mm	0.05 ^{a,2}	0.19 ^{b,1}	0.04 ^{a,2}	0.24 ^{a,1}	0.05 ^{a,2}	0.20 ^{a,1}
		4 mm	0.05 ^{a,2}	0.21 ^{a,1}	0.04 ^{a,2}	0.23 ^{a,1}	0.05 ^{a,2}	0.20 ^{a,1}
		8 mm	0.04 ^{a,2}	0.22 ^{a,1}	0.04 ^{a,2}	0.22 ^{a,1}	0.04 ^{a,2}	0.23 ^{a,1}
	AFEX	2 mm	0.05 ^{a,2}	0.19 ^{a,1}	0.05 ^{a,2}	0.17 ^{a,2}	0.05 ^{a,2}	0.22 ^{b,1}
		4 mm	0.05 ^{a,2}	0.18 ^{a,2}	0.05 ^{a,2}	0.17 ^{a,2}	0.05 ^{a,2}	0.19 ^{c,1}
		8 mm	0.04 ^{a,2,A}	0.19 ^{a,2,B}	0.04 ^{a,2,A}	0.18 ^{a,2,B}	0.04 ^{a,2,A}	0.26 ^{a,1,A}
	PAKed	2 mm	0.10 ^{a,1}	0.10 ^{a,2}	0.09 ^{a,1}	0.11 ^{a,3}	0.11 ^{a,1}	0.11 ^{a,2}
		4 mm	0.11 ^{a,1}	0.10 ^{a,3}	0.09 ^{a,1}	0.10 ^{a,3}	0.11 ^{a,1}	0.10 ^{a,2}
		8 mm	0.09 ^{a,1,A}	0.12 ^{a,3,A}	0.09 ^{a,1,A}	0.10 ^{a,3,A}	0.11 ^{a,1,A}	0.10 ^{a,2,A}
After storage	AFEX	8 mm	0.04 ^{2,A}	0.25 ^{1,A}	0.04 ^{2,A}	0.25 ^{1,A}	0.04 ^{2,A}	0.25 ^{1,A}
	PAKed	8 mm	0.09 ^{1,A}	0.11 ^{2,A}	0.09 ^{1,A}	0.11 ^{2,A}	0.10 ^{1,A}	0.10 ^{2,A}

Different letters within the same column indicates that means are statistically different (P<0.05)

Small letters: Comparing the significance of biomass grind sizes

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Table 6: Glass transition temperature of control, AFEX treated, and AFEX-PAKed switchgrass, corn stover, and prairie cord grass before and after storage

			Glass transition temperature (T _g , °C)		
			Switchgrass	Corn stover	Prairie cord grass
Before storage	Control	2 mm	82.7 ^{a,1}	79.3 ^{a,1}	80.7 ^{a,1}
		4 mm	80.8 ^{a,1}	79.9 ^{a,1}	81.9 ^{a,1}
		8 mm	82.5 ^{a,1}	79.2 ^{a,1}	80.1 ^{a,1}
	AFEX	2 mm	82.7 ^{a,1}	79.0 ^{a,1}	72.7 ^{a,2}
		4 mm	80.7 ^{a,1}	78.6 ^{a,1}	72.6 ^{a,2}
		8 mm	78.2 ^{a,1,A}	79.4 ^{a,1,A}	74.2 ^{a,2,A}
	AFEX PAKed	2 mm	69.8 ^{a,2}	73.7 ^{a,1}	73.4 ^{a,2}
		4 mm	72.4 ^{a,2}	75.4 ^{a,1}	73.8 ^{a,2}
		8 mm	69.6 ^{a,2,A}	73.5 ^{a,1,A}	75.6 ^{a,2,A}
After storage	AFEX	8 mm	69.3 ^{1,B}	66.2 ^{1,B}	66.1 ^{1,B}
	AFEX PAKed	8 mm	68.5 ^{1,A}	66.9 ^{1,B}	66.4 ^{1,B}

Different letters within the same column indicates that means are statistically different ($P < 0.05$)

Small letters: Comparing the significance of biomass grind sizes

Numbers: Comparing the significance of different treatments

Capital letters: Comparing the significance of biomass storage

Table 7: Durability of AFEX-PAKed switchgrass, corn stover, and prairie cord grass before and after storage

Durability (%)		Switchgrass	Corn stover	Prairie cord grass
Before storage	2 mm	80.3 ^b	95.2 ^a	92.1 ^a
	4 mm	91.1 ^a	92.6 ^a	87.1 ^a
	8 mm	78.2 ^{b,A}	92.8 ^{a,A}	91.3 ^{a,A}
After storage	8 mm	81.7 ^{1,A}	93.9 ^{1,A}	97.1 ^{1,A}

Different letters within the same column indicates that means are statistically different ($P < 0.05$)

Small letters: Comparing the significance of biomass grind sizes

Numbers: Comparing the significance of different treatments

Capital letters: Comparing the significance of biomass storage