Natural binders and solid bridge type binding mechanisms in briquettes and pellets made from corn stover and switchgrass

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A B S T R A C T

Corn stover and switchgrass are two important feedstocks considered for producing renewable fuels and energy in the US. Densification of these biomass feedstocks into briquettes/pellets would help reduce the problems and costs of bulk transportation, handling, and storage of biomass feedstocks. In this study, the role of the natural binders in corn stover and switchgrass to make durable particle–particle bonding in briquettes/pellets was investigated by micro-structural analyses. Scanning Electron Microscopy (SEM) images of briquettes made by using a uniaxial piston-cylinder densification apparatus in the laboratory, briquettes made by using a pilot-scale roll-press briquetting machine, and pellets made by using a pilot-scale conventional ring-die pelleting machine were analysed. The SEM images showed that the bonding between particles was created mainly through solid bridges. The solid bridges between particles were made by natural binders in the biomass expressed during the densification process. UV auto-fluorescence images of briquettes and pellets further confirmed that the solid bridges were made mainly by natural binders such as lignin and protein. It was found that activating (softening) the natural binders using moisture and temperature in the range of glass transition is important to make durable particle–particle bonding.

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1. Introduction

Corn stover and switchgrass are potential biomass feedstocks for producing liquid transportation fuels such as ethanol, combined heat and power, and chemicals in the US (Sokhansanj and Turhollow, 2004; Colley et al., 2006; DOE, 2007; Kaliyan et al., 2009). These biomass materials are often handled in baled forms, which involve a lot of handling, transportation and storage costs because of low bulk density of bales. One of the solutions to reducing handling, transportation and storage costs is densification of the biomass materials into briquettes, pellets, or cubes with bulk densities of 450–700 kg m⁻³ (Sokhansanj and Turhollow, 2004; Colley et al., 2006; Kaliyan et al., 2009). Densification (briquetting, pelleting, or cubing) of particulate matter is achieved by forcing the particles together by applying mechanical force to create inter-particle bonding, which makes well-defined shapes and sizes such as briquettes, pellets, and cubes. The bonding of particles in briquettes, pellets, or cubes can be understood at microscopic or macroscopic level.

Chung (1991) presented a microscopic level of interpretation of bonding between particles. Chung (1991) reviewed several prior adhesion theories and derived two criteria for strong adhesion between molecules: intimate molecular contact of closer than 9 Å (necessary condition), and maximum attractive force with minimum potential energy (sufficient condition). The driving force of adhesion is in the electronic interactions between molecules. When the maximum attractive force is near the minimum potential energy, chemical bondings are established. Pressure, heat (above glass transition temperature), and solvent such as water are the industrial techniques to promote adhesion by increasing molecular contact between two sets of molecules (Chung, 1991).

Macroscopically, the binding forces between the particles can act through two binding mechanisms (Rumpf, 1962; Pietsch, 2002): (i) bonding without a solid bridge, and (ii) bonding with a solid bridge between particles. Without a solid bridge, attraction forces between solid particles help bond the particles. Short-range forces such as molecular [valance forces (i.e., free chemical bonds), hydrogen bridges, and van der Waals' forces], electrostatic, and magnetic forces can cause solid particles to adhere to each other if the particles are brought close enough together. Valance forces are effective only if the inter-particle distance is about 10 Å. van der Waals' forces believed to make the most contribution to all intermolecular attractive effects and are partly responsible for the adhesion between particles less than 0.1 μm apart. Electrostatic forces help binding when there is an excess charge or electrical double layer, which may be created during grinding or by inter-particle friction. If magnetic forces exist in the powder...
system, this could contribute to the particle bonding. The effectiveness of short-range forces diminishes dramatically as the size of the particles or inter-particle distance increases (Rumpf, 1962; Pietsch, 2002).

Solid bridge type binding mechanisms can occur in several modes (Rumpf, 1962; Pietsch, 2002). Due to the application of high pressures and temperatures, solid bridges may be developed by diffusion of molecules from one particle to another at the points of contact. Solid bridges may also be formed between particles due to crystallization of some ingredients, chemical reaction, hardening of binders, and solidification of melted components. Solid bridges are mainly formed during cooling/drying of densified products. During the compression process, fibers, flat-shaped particles, and bulky particles can interlock or fold about each other resulting in interlocking bonds. Mechanical interlocking bonds can resist the disruptive forces caused by elastic recovery following compression.

Table 1
Compositions of corn stover and switchgrass grinds.

<table>
<thead>
<tr>
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<tr>
<td></td>
<td>This study (% of dry matter) (n = 1)</td>
<td>Mani et al. (2006) (% of dry matter)</td>
<td>DOE (2007) (range, % of mass)</td>
<td>This study (% of dry matter) (n = 1)</td>
<td>Mani et al. (2006) (% of dry matter)</td>
<td>DOE (2007) (range, % of mass)</td>
</tr>
<tr>
<td>Cellulosea</td>
<td>49.4</td>
<td>31.3</td>
<td>30.6–38.1</td>
<td>43.8</td>
<td>44.3</td>
<td>27.8–37.1</td>
</tr>
<tr>
<td>Hemicelluloseb</td>
<td>26.2</td>
<td>21.1</td>
<td>19.1–25.3</td>
<td>28.8</td>
<td>30.0</td>
<td>22.4–28.6</td>
</tr>
<tr>
<td>Ligninc</td>
<td>8.8</td>
<td>3.1</td>
<td>17.1–21.3</td>
<td>9.2</td>
<td>7.4</td>
<td>13.2–22.5</td>
</tr>
<tr>
<td>Crude protein</td>
<td>3.6</td>
<td>8.7</td>
<td>NAb</td>
<td>3.9</td>
<td>1.6</td>
<td>NA</td>
</tr>
<tr>
<td>Starch</td>
<td>0.4</td>
<td>NA</td>
<td>NA</td>
<td>1.0</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Crude fat</td>
<td>0.7</td>
<td>1.3</td>
<td>NA</td>
<td>0.9</td>
<td>1.9</td>
<td>NA</td>
</tr>
<tr>
<td>Water soluble</td>
<td>7.9</td>
<td>NA</td>
<td>NA</td>
<td>2.2</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>carbohydrates</td>
<td>Moist content</td>
<td>5.4</td>
<td>NA</td>
<td>5.7</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Ash</td>
<td>11.2</td>
<td>7.5</td>
<td>9.8–13.5</td>
<td>5.0</td>
<td>5.5</td>
<td>2.5–7.6</td>
</tr>
</tbody>
</table>

a Cellulose = acid detergent fiber (ADF) – lignin.
b Hemicellulose = neutral detergent fiber (NDF) – acid detergent fiber (ADF).
c Lignin values measured for the biomass materials used in this study and in Mani et al. (2006) were acid insoluble lignin contents, whereas the lignin contents obtained from DOE (2007) were total lignin in the biomass materials.
d NA = data not available.

Fig. 1. Scanning Electron Microscopy (SEM) (magnification at 600 ×) and UV-Auto-Fluorescence (UV-AF) (magnification at 145 ×) images of corn stover (Fig. 1a and b) and switchgrass (Fig. 1c and d) grinds before briquetting or pelleting. The green or yellow-green fluorescence represents protein compounds, and whitish fluorescence represents the cutin (cuticle). (a) SEM image of corn stover grind (particle size = 0.34 mm). (b) UV-AF image of corn stover grind (particle size = 0.34 mm). (c) SEM image of switchgrass grind (particle size = 0.49 mm). (d) UV-AF image of switchgrass grind (particle size = 0.49 mm).
Highly viscous binders (e.g., molasses and tar) adhere to the surfaces of solid particles to generate strong bonds that are very similar to those of solid bridges. Adhesion forces at the interfaces between the solid particles and the viscous binder, and cohesion forces within the viscous binder can bond the solid particles until the weaker of the two fails. Many viscous binders harden after cooling and form solid bridges. Thin adsorption layers (<3-nm thick) are immobile and can form strong bonds between adjacent particles either by smoothing out surface roughness and increasing the inter-particle contact area or by decreasing the inter-particle distance and allowing the intermolecular attractive forces to participate in the bonding mechanism. Presence of liquids such as free moisture between particles causes cohesive forces between particles. If the base powder has appreciable solubility in the liquid binder (e.g., water), the liquid binder wets and spreads in the interstices between primary particles, forming liquid bridges that hold particles together by capillary and viscous forces. Due to the subsequent drying, the liquid evaporates from the bridges to leave solid bridges (necks) between particles. The solid bridges will be formed by recrystallisation (or precipitation) of the base powder. The solid bridges impart mechanical strength to the densified products (Bika et al., 2005).

Back (1987) reviewed the binding mechanisms in wood and wood products. To produce sufficient bonding area, especially in the absence of a binder, the plasticization of wood polymers above their glass transition temperatures is necessary (Back, 1987). Hydrogen bonding at lignin and cellulose surface areas is considered to be responsible for the main type of bonding in the press-drying operation of wood. Covalent bonds are thought to form between the wood polymer chains in the inter-fiber bonding area of hardboard during hot pressing operations. The London-van der Waals dispersion forces are considered to be of some importance. The covalent bonds are the strongest, the hydrogen bonds are intermediate, and the non-polar van der Waals’ forces are the weakest (Back, 1987).

The following three mechanisms were assumed to contribute to the formation of a durable briquette from agricultural biomass materials such as hay (Pickard et al., 1961): (1) complete crushing of the plant stems, (2) adhesion of stems, and (3) interlacing of stem and leaf materials. Pickard et al. (1961) reported that the degree of adhesion increased with increasing moisture content in lucerne hay due to the higher maceration of the stem and leaf materials. Similarly, Rehkugler and Buchele (1969) reported that the percentage of protein and the relative concentration of pectin, together with the percentage of stem material, were important factors affecting the adhesion of biomass particles. Huang and Yoerger (1961) macerated lucerne hay before briquetting to break down the cell structure and release the cell contents so as to provide greater adhesion and less resilience of the material. Thus, briquettes with higher density and strength were formed from macerated material than from unmacerated material.

The objective of this study was to investigate the natural binders and binding mechanisms of corn stover and switchgrass in briquettes and pellets.

2. Methods

The various forms of corn stover and switchgrass samples used in this study for micro-structural analyses were grinds (i.e., particles), briquettes (19.1 mm diameter × 16.0 mm length) made in the laboratory, roll-press briquettes (31.3 mm length × 23.3 mm width × 17.9 mm depth) made using a pilot-scale roll-press briquetting machine (Model CS-25 Compactor/Briquetter; Bepex International LLC, Minneapolis, MN), and pellets (9.8 mm diameter × 24.0 mm length) made using a pilot-scale conventional ring-die pelleting machine (CPM Master Model No. 818806; California Pellet Mill [CPM] Co., San Francisco, CA) (Kaliyan and Morey, 2009a; Kaliyan et al., 2009). In the laboratory, briquettes were made using a uniaxial piston-cylinder densification apparatus at a compression pressure of 150 MPa (Kaliyan and Morey, 2009a).

The details of the laboratory briquetting and roll-press briquetting/pelleting studies can be found in Kaliyan and Morey (2009a) and Kaliyan et al. (2009), respectively. No binding agents (i.e., additives) were used for any of the briquetting or pelleting experiments (Kaliyan and Morey, 2009a; Kaliyan et al., 2009).

Corn stover and switchgrass grind samples were sent to a forage analysis laboratory (Dairy One, Ithaca, NY) to determine the chemical compositions of these two biomass materials using Near Infrared Reflectance (NIR) spectroscopy methods given in AOAC International (AOAC International, 1995).

Using a Light Microscopy (LM) (Nikon SMZ 1500), LM images for the cross-sections (i.e., fractured surfaces) of the lab briquettes, roll-press briquettes, and pellets were obtained to observe the natural binder coatings on the particles, local melting of biomass components, and mechanical interlocking of particles at a magnification of 20×.

Scanning Electron Microscopy (SEM) (Hitachi S3500N) images were taken for corn stover and switchgrass grinds, and cross-sections (i.e., fractured surfaces) of the lab briquettes, roll-press briquettes, and pellets. To prepare the samples for taking the SEM images, the samples were mounted on a stub and sputter coated with gold. The metallization conditions were 0.33 mbar (250 μHg) argon gas pressure and 10 mA coating current. The SEM observation conditions were at acceleration voltages of 5 kV and a dis-
distance of 10 mm. SEM observations were made at a magnification of 600×.

Ultraviolet auto-fluorescence (UV-AF) (Olympus IX70 Inverted Microscope; UV excitation at 330–385 nm; dichroic mirror at 410 nm; emission at 420–700 nm) images of corn stover and switchgrass grinds, and cross-sections (i.e., fractured surfaces) of the lab briquettes, roll-press briquettes, and pellets were obtained to identify the natural binders that coated on the particles. UV auto-fluorescence in plant tissues is caused by the presence of aromatic molecules (e.g., pigments) (Rost, 1995). According to Rost (1995), the color interpretation of UV auto-fluorescence is: green or yellow-green for protein compounds; brilliant blue or bluish-white for lignin; and whitish fluorescence for cutin (cuticle). Also, pure carbohydrates (cellulose, hemicellulose, and starch) and lipid/fat molecules do not fluoresce (Rost, 1995). The UV-AF images were taken at a magnification of 145×, which is a lower magnification than that used for the SEM images. The lower magnification of 145× allowed capturing the distribution of the natural binders on a larger area of the fractured surfaces of the briquettes/pellets.

The LM, SEM, and UV-AF images were taken about one month after making the briquettes and pellets, which were stored in zip-lock plastic bags at room temperature (about 25°C) until used for imaging. Also, the moisture content of the samples (i.e., grinds, briquettes, and pellets) ranged from 5% to 15% wet basis (w.b.). In this article, the densification conditions such as particle size of the grind, grind moisture content, and grind temperature (with or without preheating/steam conditioning) used for making the briquettes/pellets are reported along with the microscopy images.

Fig. 3. Scanning Electron Microscopy (SEM) (magnification at 600×) and UV-Auto-Fluorescence (UV-AF) (magnification at 145×) images of cross-sections (i.e., fractured surfaces) of corn stover briquettes made in the laboratory at a compression pressure of 150 MPa and corn stover grind particle size of 0.66 mm. The green or yellow-green fluorescence represents protein compounds. The brilliant blue or bluish-white fluorescence represents lignin. No fluorescence (i.e., black color) may represent cellulose, hemicellulose, starch, water soluble carbohydrates, and lipid/fat. [MC = grind moisture content; T = grind temperature (with or without preheating); Du = durability of briquettes]. (a) SEM image, MC = 10% w.b., T = 25 °C, and Du = 75%. (b) UV-AF image, MC = 10% w.b., T = 25 °C, and Du = 75%. (c) SEM image, MC = 20% w.b., T = 25 °C, and Du = 96%. (d) UV-AF image, MC = 20% w.b., T = 25 °C, and Du = 96%. (e) SEM image, MC = 10% w.b., T = 75 °C, and Du = 98%. (f) UV-AF image, MC = 10% w.b., T = 75 °C, and Du = 97%. 

Also, the temperature of the roll-press briquettes/pellets measured immediately after making, and the durability of briquettes/pellets measured after one week of making (i.e., after one week of curing) are given along with the microscopy images. The effects of densification process variables such as moisture content and temperature (preheating/steam conditioning) on the binding mechanisms were assessed using the microscopy images and the durability of briquettes/pellets obtained for selected densification conditions. The durability of briquettes/pellets was measured using the tumbling can method given in ASABE Standards (2003). The durability of briquettes is a measure of the ability of the briquettes to withstand the destructive forces such as compression, impact and shear during handling and transportation. The possible amount of fines (dust) generated from the briquettes due to the mechanical handling and transportation can be estimated by 100 minus the percent durability. In addition, the durability values represent the relative strength of the particle–particle bonding in the briquettes/pellets.

3. Results and discussion

3.1. Natural binders

Table 1 gives the compositions of the corn stover and switchgrass grinds (i.e., particles) used for the briquetting and pelleting studies (Kaliyan and Morey, 2009a; Kaliyan et al., 2009). Also, in Table 1, the composition values provided by Mani et al. (2006) and DOE (2007) are compared. The constituents such as lignin, protein, starch, fat, and water soluble carbohydrates are “natural binders” in the biomass materials (Kaliyan, 2008; Kaliyan and Morey, 2009b). These natural binders can be activated (softened or melted locally) either by high moisture or elevated temperature or steam to use their binding functionality (Kaliyan and Morey, 2009b).

The binding functionality of the natural binding components in the corn stover and switchgrass can be enabled (i.e., activated) by the auto-crosslinking reactions by lignin and fat; hydrogen bonding by highly polar components such as cellulose, lignin, starch, and protein; starch gelatinization; protein denaturation; and solubilization and subsequent crystallization of water soluble carbohydrates (Back, 1987; Chung, 1991; Nyanzi and Maga, 1992; Slade and Levine, 1993; Tabil, 1996; Thomas and van der Poel, 1996). Kaliyan and Morey (2009b) discuss the effect of inclusion of different levels of these natural binding components on the strength and durability of densified biomass products with specific data collected from the literature.

Water as moisture in the biomass is one of the most useful agents that is employed as a binder and lubricant. Moore (1965) reported that water is particularly suitable as an aid in briquetting mixtures containing water soluble constituents such as starches, sugars, soda ash, sodium phosphate, potassium salts, and calcium chloride. Water acts as a film type binder by strengthening and promoting bonding via van der Waals’ forces by increasing the contact area of the particles (Pietsch, 2002). A thin film of water around the particles would exhibit bonds via capillary sorption between particles (Pietsch, 2002). With the help of heat, water induces a wide range of physical and chemical changes such as thermal softening of biomass, denaturation of proteins, gelatinization of starch, and solubilization and consecutive recrystallisation.
of sugars and salts (Thomas et al., 1998). These physico-chemical changes affect binding properties of the biomass particles. The optimum moisture content for biomass densification may range from 8% to 20% (w.b.) (Kaliyan and Morey, 2009b). At high moisture (>20% w.b.), coherent biomass briquettes/pellets may not be produced because the cell structure remains largely intact at high moisture levels due to the incompressibility of high moisture biomass particles (Pickard et al., 1961).

In corn stover and switchgrass, the glass transition (i.e., softening) occurs from 50 to 113 °C (Kaliyan and Morey, 2009a). The mean glass transition temperature for both corn stover and switchgrass is 75 °C for the moisture content range of 10–20% (w.b.) (Kaliyan and Morey, 2009a). During glass transition, amorphous materials change their state from a hard glassy to a soft rubbery state (Roos, 1995). Within the glass transition region, many macroscopic properties of the materials such as viscosity and mechanical properties (e.g., modulus of elasticity) would change their values dramatically (Irvine, 1984). Lignin and hemicellulose were found to be amorphous thermoplastic materials which would undergo plastic deformation at low compaction pressures for temperatures in the range of their glass transition temperatures (Back and Salmen, 1982). Irvine (1984) found that the glass transition temperature of lignin ranged from 60 to 90 °C. Therefore, the briquetting/pelletling conditions causing glass transition in biomass particles may activate (soften) the biomass cell contents/natural binders. Also, the glass transition conditions can help plastic deformation of particles, and can reduce the viscosity and increase the mobility of natural binding components. Thus, diffusion of polymer chains and chain ends from one fiber into the proximity of an adjacent fiber is greatly facilitated, promoting bonding area, especially under applied pressure. On cooling, these bonds are consolidated (Back, 1987).

3.2. Binding mechanisms

A macroscopic interpretation of bonding between particles given by Rumpf (1962) and Pietsch (2002) was used to describe the binding mechanisms of corn stover and switchgrass in briquettes and pellets. Thus, the bonding between particles in the briquettes/pellets could take place through a solid bridge or through inter-particle attraction forces when there is no solid bridge (Rumpf, 1962; Pietsch, 2002).

In the laboratory, briquettes were made at 150 MPa pressure. In the roll-press briquetting and pelleting machines, corn stover and switchgrass particles could have experienced pressures of 100–200 MPa (Dec, 2002; Kaliyan and Morey, 2009b). Because of the application of high pressures, particles were brought close together causing inter-particle attraction forces, and the natural binding components in the corn stover and switchgrass were squeezed out of the biomass cells, which made solid bridges between the particles. After cooling, these solid bridges hardened (i.e., curing process). This caused the briquettes and pellets to become strong and durable. This postulate on the binding mechanisms was verified through the micro-structural analyses (i.e., LM, SEM and UV-AF imaging) of briquettes and pellets made from corn stover and switchgrass.

![Fig. 5. Scanning Electron Microscopy (SEM) (magnification at 600×) and UV-Auto-Fluorescence (UV-AF) (magnification at 145×) images of cross-sections (i.e., fractured surfaces) of roll-press briquettes and pellets made from corn stover. The green or yellow-green fluorescence represents protein compounds. The brilliant blue or bluish-white fluorescence represents lignin. No fluorescence (i.e., black color) may represent cellulose, hemicellulose, starch, water soluble carbohydrates, and lipid/fat. [PS = particle size of the grind; MC = grind moisture content; T = grind temperature (without steam conditioning); L/D = pellet mill-die length (L) to diameter (D) ratio; TP = temperature of briquettes/pellets immediately after making; Du = durability of briquettes or pellets]. (a) SEM image of a roll-press briquette made at PS = 0.34 mm, MC = 15% w.b., and T = 20 °C. TP = 51 °C and Du = 87%. (b) UV-AF image of a roll-press briquette made at PS = 0.34 mm, MC = 15% w.b., and T = 20 °C. TP = 51 °C and Du = 87%. (c) SEM image of a pellet made at PS = 0.34 mm, MC = 19% w.b., T = 11 °C, and L/D = 6. TP = 76 °C and Du = 96%. (d) UV-AF image of a pellet made at PS = 0.34 mm, MC = 19% w.b., T = 11 °C, and L/D = 6. TP = 76 °C and Du = 96%.](image-url)
To prepare biomass samples for briquetting or pelleting, corn stover and switchgrass were ground in a hammer mill to particle sizes of 0.34–0.66 mm. Fig. 1a–d presents the SEM and UV-AF images of corn stover and switchgrass grinds. Fig. 1a shows that most of the corn stover particles appear to be bare without any sign of coating of natural binding components; however, on the switchgrass particles (Fig. 1c), expression of some natural binding components (due to size reduction) can be observed. Fig. 1b and d indicates that size reduction may cause very light expression of natural binders such as protein compounds on the surface of the particles.

The LM images of the cross-sections of the lab briquettes showed that the natural binders were expressed as a glassy layer of coating on the particles (Fig. 2). The natural binders were squeezed out of the biomass cells due to the application of pressure during the densification process. The glassy coating connected the particles as solid bridges (Fig. 2). Fig. 2 illustrates the possible local melting of binding components as white patches at the junction of particles, and mechanical interlocking of particles as meeting of two or more particles at one point. Solid bridges due to the local melting may have been caused by plastic deformation or by actual melting followed by resolidification of natural binding components or the asperitic points of contact between particles where friction may momentarily generate localized temperatures as high as 100–200 °C (Pilpel et al., 1991). Tabil (1996) reported that melting of asperities of the alfalfa particles would form solid bridges upon cooling, thus creating strong pellets. Biomass materials have highly porous structure, and thus, mechanical interlocking of particles by diffusion of particles/molecules from one particle to another can occur, which leads to solid bridges between particles.

The SEM images of the lab briquettes (Figs. 3a, c, e, 4a and c), roll-press briquettes (Figs. 5a and 6a), and pellets (Figs. 5c and 6c) showed that the particles were covered with a layer of natural binders. When viewed with a light microscopy, these coatings appeared as glassy/white sugar-like coatings on the particles, and at the junction of particles, high accumulation of these binding components was observed. The UV-AF images of the lab briquettes (Figs. 3b, d, f, 4b and d), roll-press briquettes (Figs. 5b and 6b), and pellets (Figs. 5d and 6d) indicated that the natural binders that were coated on the particles in the briquettes or pellets were primarily lignin and protein compounds. The molecules that did not fluoresce (i.e., black color) could be carbohydrates (cellulose, hemicellulose, water soluble carbohydrates, and starch) and fat. In addition, the SEM and UV-AF images of briquettes/pellets revealed that the natural binder coating acted as solid bridges which connected (i.e., bind) particles in the briquettes/pellets.

The SEM and UV-AF images of lab briquettes made for the conditions that resulted in both lower and higher durability values had coatings of natural binding components (Figs. 3 and 4). This is because the expression of natural binders on the particles was due to the application of high pressure during the densification process. Fig. 7 shows that for the roll-press briquettes with low durability, the degree of expression of natural binders is lower, and vice versa. Higher moisture contents such as 15–20% (w.b.) can plastically de-
form the particles at room temperature because of lower glass transition temperature at higher moistures. Due to the presence of higher amounts of water soluble carbohydrates in corn stover (Table 1), the expression or activation of water soluble carbohydrates may be higher at higher moisture levels. The durability of corn stover briquettes made in the laboratory at a grind moisture content of 10% (w.b.) was 75% whereas the durability of corn stover briquettes at a grind moisture content of 20% (w.b.) was 96% (Fig. 3a and c). Similarly, corn stover produced more durable roll-press briquettes at 15% (w.b.) moisture content than at 7% (w.b.) moisture content (Fig. 7a and b). Preheating to a temperature close to the glass transition temperature can activate the natural binders (e.g., lignin, protein, starch, and fat) that require heat for activation. The durabilities of switchgrass briquettes made in the laboratory at grind temperatures of 25 °C and 75 °C were 0% and 63%, respectively (Fig. 4a and c). Also, the switchgrass briquettes produced at 68 °C (i.e., steam conditioning) had higher durability than those produced at 19 °C (i.e., no steam conditioning) (Fig. 7c and d). The lower durability of switchgrass briquettes when there was no preheating/steam conditioning may have been due to the lower percentage of water soluble carbohydrates in switchgrass (Table 1). Although corn stover has a higher amount of water soluble carbohydrates than switchgrass, at a moisture content of 10% (w.b.), preheating of corn stover from 25 to 75 °C increased the briquette durability from 75% to 97% (Fig. 3a and e). Thus, preheating/steam conditioning of corn stover and switchgrass may have activated the natural binders (e.g., lignin, protein, starch, and fat) that require heat for activation.

Therefore, the SEM and UV-AF images can only explain the squeezing of natural binders from the particles due to the application of high pressures during the densification process, but not the differences in the durability values. The differences in the durability values can be explained by the extent of activation of the natural binders through moisture or temperature or both. The amount of required moisture depends on the amount of natural binder (e.g., water soluble carbohydrates) available that requires moisture for activation. At high moistures (15–20% w.b.), corn stover resulted in stronger and more durable briquettes than switchgrass because of the presence of a higher amount of water soluble carbohydrates than switchgrass (Kaliyan et al., 2009) (Table 1).

The glass transition in corn stover and switchgrass starts at 50 °C (Kaliyan and Morey, 2009a). It appears that glass transition temperature is the minimum temperature required for activation of natural binders to produce durable densified products. The measured temperatures of roll-press briquettes and pellets ranged from 51 to 81 °C, which is well within the range of glass transition temperatures of corn stover and switchgrass (i.e., 50–113 °C). Therefore, by providing enough moisture and a temperature in the range of the glass transition for the biomass materials, the natural binding components could be fully activated to express higher amounts of natural binders from the biomass cells and to enhance the binding functionality of the natural binders.

Fig. 8 reveals that the shiny appearance of pellets is due to the lignin coating on the outer surface of the pellets. Because lignin is hydrophobic in nature, the lignin coating on the outer surfaces of

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**Fig. 7.** Scanning Electron Microscopy (SEM) (magnification at 600×) images of cross-sections (i.e., fractured surfaces) of roll-press briquettes made from corn stover (Fig. 7a and b) and switchgrass (Fig. 7c and d). The SEM images compare the degree of coating of natural binders on both low and high durability briquettes. [PS = particle size of the grind; MC = grind moisture content; T = grind temperature (with or without steam conditioning); TB = temperature of briquettes immediately after making; Du = durability of briquettes].

(a) Corn stover briquette made at PS = 0.34 mm, MC = 7% w.b., and T = 22 °C. TB = 57 °C and Du = 67%. (b) Corn stover briquette made at PS = 0.34 mm, MC = 15% w.b., and T = 20 °C. TB = 51 °C and Du = 87%. (c) Switchgrass briquette made at PS = 0.49 mm, MC = 9% w.b., and T = 19 °C. TB = 58 °C and Du = 40%. (d) Switchgrass briquette made at PS = 0.49 mm, MC = 12% w.b., and T = 68 °C. TB = 75 °C and Du = 70%.

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the briquettes/pellets can make them water resistant (Anglés et al., 2001).

4. Conclusions

The micro-structural analyses (i.e., light microscopy, scanning electron microscopy, and UV auto-fluorescence imaging) of corn stover and switchgrass briquettes and pellets showed that the natural binders in these biomass materials created “solid bridge” type bonding between particles in the briquettes and pellets. The potential natural binding components in these biomass materials are water soluble carbohydrates (2.2–7.9% d.b.), lignin (8.8–9.2% d.b.), protein (3.6–3.9% d.b.), starch (0.4–1.0% d.b.), and fat (0.7–0.9% d.b.). The natural binders in the biomass can be expressed or activated (softened) under high pressures in the presence of moisture (e.g., water soluble carbohydrates) and in some cases increased temperature (e.g., lignin, protein, starch, and fat). When pressure is removed and the binder cools, it hardens or “sets up” forming bridges or bonds between particles, which has the effect of binding them together and making the resulting product more durable. Furthermore, activating (softening) the natural binding components through moisture and temperature in the range of glass transition is essential to produce highly durable briquettes and pellets.

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References