FEEDSTOCK AND PROCESS VARIABLES INFLUENCING BIOMASS DENSIFICATION

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ABSTRACT

Densification of biomass is often necessary to combat the negative storage and handling characteristics of these low bulk density materials. A consistent, high-quality densified product is strongly desired, but not always delivered. Within the context of pelleting and briquetting, binding agents are commonly added to comminuted biomass feedstocks to improve the quality of the resulting pellets or briquettes. Many feedstocks naturally possess such binding agents; however, they may not be abundant enough or available in a form or state to significantly contribute to product binding. Also, process parameters (pressure and temperature) and material variables (particle size and moisture content) can be adjusted to improve the quality of the final densified product.

Densification of ground biomass materials is still not a science, as much work is still required to fully understand how the chemical composition and physical properties, along with the process variables, impact product quality. Generating densification and compression data, along with physical and mechanical properties of a variety of biomass materials will allow for a deeper understanding of the densification process. This in turn will result in the design of more efficient densification equipment, thus improving the feasibility of using biomass for chemical and energy production.

Experiments were carried out wherein process (pressure and temperature) and material (particle size and moisture content) variables were studied for their effect on the densification process (compression and relaxation characteristics) and the physical quality of the resulting products (pellets). Two feedstocks were selected for the investigation; namely, poplar wood and wheat straw, two prominent Canadian biomass resources. Steam explosion pretreatment was also investigated as a potential method of

improving the densification characteristics and binding capacity of the two biomass feedstocks.

Compression/densification and relaxation testing was conducted in a closed-end cylindrical die at loads of 1000, 2000, 3000, and 4000 N (31.6, 63.2, 94.7, and 126.3 MPa) and die temperatures of 70 and 100°C. The raw poplar and wheat straw were first ground through a hammer mill fitted with 0.8 and 3.2 mm screens, while the particle size of the pretreated poplar and wheat straw was not adjusted. The four feedstocks (2 raw and 2 pretreated) were also conditioned to moisture contents of 9 and 15% wb prior to densification.

Previously developed empirical compression models fitted to the data elucidated that along with particle rearrangement and deformation, additional compression mechanisms were present during compression. Also, the compressibility and asymptotic modulus of the biomass grinds were increased by increasing the die temperature and decreasing product moisture content. While particle size did not have a significant effect on the compressibility, reducing it increased the resultant asymptotic modulus value. Steam explosion pretreatment served to decrease the compressibility and asymptotic modulus of the grinds.

In terms of physical quality of the resulting product, increasing the applied load naturally increased the initial density of the pellets (immediately after removal from the die). Increasing the die temperature served to increase the initial pellet density, decrease the dimensional (diametral and longitudinal) expansion (after 14 days), and increase the tensile strength of the pellets. Decreasing the raw feedstock particle size allowed for the increase in initial pellet density, decrease in diametral expansion (no effect on longitudinal expansion), and increase in tensile strength of the pellets. Decreasing the

moisture content of the feedstocks allowed for higher initial pellet densities, but also an increased dimensional expansion. The pretreated feedstocks generally had higher initial pellet densities than the raw grinds. Also, the pretreated feedstocks shrank in diameter and length, and had higher tensile strengths than the raw feedstocks. The high performance of the pretreated poplar and wheat straw (as compared to their raw counterparts) was attributed to the disruption of the lignocellulosic structure, and removal/hydrolysis of hemicellulose, during the steam pretreatment process which was verified by chemical and Fourier transform infrared analysis. As a result, a higher relative amount of lignin was present. Also, the removal/hydrolysis of hemicellulose would indicate that this lignin was more readily available for binding, thus producing superior pellets.

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a = constant

A = cross-sectional area (m^2)

b = constant

B = allowable variation

c_1, c_2 = constants (Pa)

C = degree of volume reduction

d = compact diameter (m)

df = degrees of freedom

E_A = asymptotic modulus (Pa)

F = load at fracture (N)

F_0 = initial force (N)

$F(t)$ = force at time t (N)

h_1, h_2 = constants

k_1, k_2 = constants

l = compact thickness (m)

m_1, m_2 = constants; compressibility

MS = Mean square

n = sample size

P = pressure (Pa)

SS = Sum of squares

t = time (s)

t_s = student's t value

v = coefficient of variation

V = volume of compact at pressure P (m^3)

V_0 = volume of compact at zero pressure (m^3)

V_R = volume ratio

V_s = void-free solid material volume (m^3)

wb = wet basis moisture content

z_1, z_2 = constants

ε = strain

ρ = density of compact (packing density)

σ_x = tensile (horizontal) stress (Pa)

1 INTRODUCTION

As the world population increases (along with an increase in consumption and standard of living), so does the demand for chemicals and energy. The net result of this has been that the demand for energy has multiplied manifold and it can no longer be satisfied by the traditional inefficient energy technology which utilizes only a few local resources (Jebaraj and Iniyan 2006). Therefore, there has been considerable interest in biomass feedstocks (along with other renewable resources) for chemical and energy production.

Biomass is any type of organic material that is available on a renewable or reoccurring basis, and includes such things as agricultural crops and waste, wood and wood wastes, animal wastes, aquatic plants, and organic fractions of municipal and industrial waste (BIOCAP and Pollution Probe 2004). Biomass energy (bioenergy) is then the chemical energy stored in organic matter and derived from solar energy via photosynthesis (Hall and Rosillo-Calle 1999). The use of biomass residues (for chemical and energy production) was first seriously investigated during the oil embargo of the 1970s. When oil prices dropped after the embargo, biomass residue lost its competitiveness with fossil fuel (Matsumura et al. 2005).

Crawford (2001) reported that Canada's surplus forestry residues were approximately 5.1 million dry tonnes, while surplus crop residues were roughly 3.6 million tonnes per year (accounting for animal bedding, soil conservation, and soil enhancement). He noted that as Canadians, we should be considering the best ways to use these renewable resources to maximize the benefits experienced by society. In terms of the forestry sector, a prominent Canadian biomass resource is poplar. With the

introduction of hybrid poplar, these hardwood trees grow as much as three meters in height per year (Cates 1998). Poplar is used to produce plywood, pallets, and most notably, pulp for paper production. Poplar is also commonly used in combustion furnaces to supply heat. From an agricultural standpoint, wheat straw is a major agricultural residue which is commonly left in the field after harvest to protect the soil from wind and water erosion; however, not all of the straw must be left in the field and therefore, wheat straw is utilized for animal bedding, strawboard, and alternative forms of energy. More wheat is produced in Canada than any other crop. Also, Saskatchewan alone produces ten percent of the world's total exported wheat (Saskatchewan Agriculture and Food 2007). Harvest reports from the 2006 crop year (Saskatchewan Agriculture and Food 2006) indicate that wheat production was estimated at 12.48 million tonnes, compared to 5.13 million tonnes of coarse grain (barley, oats, and rye), 4.77 million tonnes of oilseed (canola and flax), and 2.98 million tonnes of pulse crops (peas, lentils, and chickpeas). The availability of the two aforementioned biomass species is one of the many reasons they are being investigated as potential feedstocks for bioenergy production.

Due to their heterogeneous nature, biomass materials possess inherently low bulk densities, and thus, it is difficult to efficiently handle large quantities of most feedstocks. Therefore, large expenses are incurred during material handling (transportation, storage, etc.). A detailed study by Kumar and co-workers (2003) examined the cost to produce biomass power from direct combustion in western Canada. Of all the factors considered, transportation had the second highest cost (next to capital recovery) when the biomass power plant was at full capacity (year 3). It was also noted that transportation costs will

increase with increasing power plant size. In order to combat the negative handling aspects of bulk biomass, densification is often required.

In its most general form, the process of agglomeration involves taking discrete, independent particles, bringing them into contact with one another, promoting (or allowing) interparticle adhesion to occur, and then causing structure rearrangement, usually under the action of external forces (Hogg 1992). Densification of biomass is a form of promoted agglomeration wherein pressure (along with other process variables) is utilized to force the smaller particles together. Conventional processes for biomass densification can be classified into three types: extrusion, roll briquetting, and pelletizing (Li and Liu 2000). Extrusion involves forcing material through a heated die by pressure typically exerted on the product by a tapered screw. The process of briquetting employs a roll press to compress a material passing between the two rolls. Depending on the surface geometry of the rolls, various shapes and sizes of compact material can be produced. Generally speaking, pelletizing (pelleting) is a process by which ground material is forced by an internal roller through cylindrical dies in an external ring (Figure 1.1), producing compact pellets of the charge material. Pelleting is the densification process of interest to this study.

Densification of biomass improves its handling characteristics, reduces transportation cost, enhances its volumetric calorific value, and produces a uniform, clean, stable fuel, or an input for further refining processes (Granada et al. 2002). Densifying biomass feedstocks improves the process of feeding the fuel into co-fired power plants (e.g. coal) (Li and Liu 2000). Also, the combustion of dense granulated and uniformly sized biomass can be controlled more precisely than loose, low bulk density biomass and thus reduce emissions (Sokhansanj et al. 2005). With respect to animal

feed, the benefits of pelleting include enhanced handling characteristics of feeds and improved animal performance. Pelleting increases bulk density and flowability and decreases spillage and wind loss (Briggs et al. 1999).

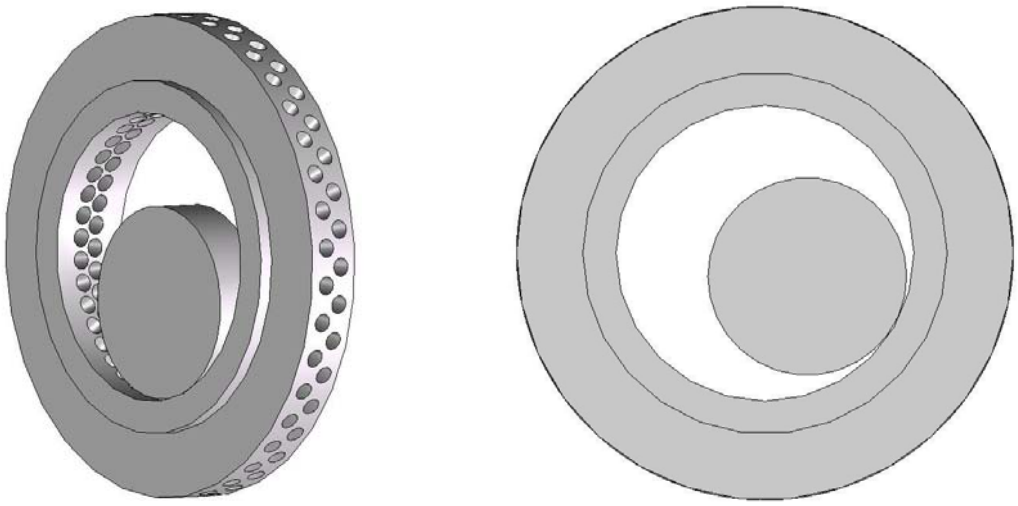

Figure 1.1 Internal roller and external ring (housing cylindrical dies) of a pellet mill.

Producing quality pellets (and most other forms of densified biomass) is largely thought of as an art rather than science by many feed mill operators (Briggs et al. 1999). The effect of the changes in one or more parameters and its effect on pellet quality (durability and hardness) are often a matter of judgement and experience of the operator (Thomas et al. 1997). Producers are constantly searching for ways to produce a consistently high quality densified material.

A high quality densified product is essential to ensure that the positive effects of densification are not mitigated. Therefore, artificial binding agents are often added to the pre-densified biomass to improve pellet quality. Studies have demonstrated that different biomass grinds bind well without the use of artificial binding agents (Shaw and Tabil

2005); such feedstocks possess natural binding agents that allow them to exhibit preferential qualities after densification. The mechanism of how particles bind during compression has been studied; however, knowledge of natural biochemical constituent behavior during densification has enormous potential to provide insight into the complex process of biomass compression. Thomas and co-workers (1998) concluded that more research efforts should be directed towards the effects of individual constituents and their respective properties, since the latter appeared to affect, to a large extent, the final hardness and durability of pellets. It was stated that the effects of raw material constituents, both their level and physico-chemical properties, may provide more information on pelleting characteristics and pellet quality than the ingredient inclusion level.

Studying the compression/compaction behavior of biomass will provide insight into the densification process. This in turn will allow the design of more efficient and cost effective densification systems, thus improving the feasibility of biomass densification for feed, chemical, and energy production.

1.1 Objectives

The main goal of this study was to evaluate pertinent densification and relaxation (viscoelastic) properties of poplar and wheat straw grinds utilizing a heated plunger-die apparatus, as well as characterization of how chemical constituents influence pellet quality. Specifically, the objectives of this study are:

1. to utilize previously developed mathematical models to determine dominant densification mechanisms;

2. to evaluate the effect of temperature, pressure, particle size, moisture content, chemical composition, and steam explosion pretreatment on the densification/relaxation properties of biomass grinds; and
3. to investigate how temperature, pressure, particle size, moisture content, chemical composition, and steam explosion pretreatment influence the physical quality of densified biomass.

2 LITERATURE REVIEW

As it applies to the subject of interest, densification simply refers to the mechanical increase in density of biomass feedstocks via compression. The field of biomass densification is continually evolving. A wealth of literature has emerged, especially in recent years, which examines the many facets of biomass compression/compaction. Denny (2002) concluded that there are over 200 publications per year on compaction alone. Densification of lignocellulosic material is a complex process and no coherent theory exists (Granada et al. 2002). There are numerous methods available to accomplish densification of biomass; conventional processes for biomass densification can be classified into three types: extrusion, roll briquetting, and pelletizing (Li and Liu 2000). This literature review primarily focused on densification via pelletizing and closed-end die compression. In order to fully understand the physical and chemical processes occurring during biomass densification, literature from disciplines such as engineering, food/feed science, as well as pharmaceutical, ceramic, and metallurgical compression/compaction were consulted.

2.1 Previous biomass densification studies

Uni-axial compression via a plunger in a cylindrical die is one of the most common methods reported in literature for studying the force-deformation, relaxation, and subsequent quality characteristics of a variety of powdered and ground materials. This method allows detailed analysis of the compression/relaxation behavior of feedstocks at the laboratory scale. Plunger-die systems have been used to study the compression of alfalfa (Adapa et al. 2002; Hall and Hall 1968; Tabil and Sokhansanj

1996a; Tabil and Sokhansanj 1996b; Tabil and Sokhansanj 1997), straws/grasses (Demirbaş 1999; Kaliyan and Morey 2006; Mani et al. 2004; Mani et al. 2006a; Mani et al. 2006b; Ndiema et al. 2002; Shaw et al. 2006; Singh and Singh 1983; Smith et al. 1977; Wamukonya and Jenkins 1995), palm fiber/shell (Husain et al. 2002), olive cake/refuse (Al-Widyan et al. 2002; Yaman et al. 2000), as well as wood and wood waste (Chin and Siddiqui 2000; Demirbaş et al. 2004; Li and Liu 2000; Rhén et al. 2005). Raw feedstocks are typically milled or comminuted, and conditioned to an appropriate moisture content (either by dehydration or moisture addition) prior to the densification process. The attempt is to simulate conditions of commercial/industrial densification. The resultant products of uni-axial tests are commonly referred to in literature as pellets or briquettes. The name 'pellet' is usually given to materials less than 15 mm in diameter, while 'briquette' is generally the term used for larger units of densified material.

2.2 Variables influencing biomass densification

Drawing from previous biomass densification studies, the following factors were found to influence binderless densification experiments using a plunger-die assembly to produce single pellets/briquettes (Rehkugler and Buchele 1969; Granada et al. 2002):

1. Process variables
    a. Temperature
    b. Pressure and pressure application rate (compression velocity)
    c. Hold time
    d. Die geometry

2. Feedstock/material variables
    a. Moisture content
    b. Particle size, shape, and distribution
    c. Biochemical characteristics
    d. Pretreatment

2.2.1 Process variables

Process variables are those factors which are non-material specific, that is to say that they are a set of conditions (temperature, pressure, etc.) imposed on biomass materials by the mechanical densification equipment.

2.2.1.1 Temperature

Following a review of literature, Mani and co-workers (2003) found that higher process temperatures require less loads to achieve a desired compact density with less power consumption. Hall and Hall (1968) found that for a given moisture content, the pressure required to obtain a certain wafer (alfalfa and Bermuda grass) density was reduced by the addition of heat in the wafering die. Likewise, adding heat increased the moisture content at which a certain pressure was able to produce a specific wafer density. Sokhansanj and co-workers (2005) supported this observation by stating that with an increase in temperature, the resistance of the material decreases against an applied load. In a study investigating briquetting of wheat straw, Smith and co-workers (1977) found that for a given pressure, the higher the temperature (within limits of 60-140°C), the greater the degree of compaction and stability of the briquettes. Also, the length of recovery (expansion) of the briquettes was less when the die temperature was

between 90 and 140°C. The authors observed that wheat straw briquettes were surface charred and slightly discolored at temperatures above 110°C due to chemical degradation. In a study evaluating the densification characteristics of corn stover and switchgrass, Kaliyan and Morey (2006) used the glass transition temperature to determine the temperatures at which to study densification behavior of corn stover and switchgrass. They found that the average glass transition temperature (for moisture contents of 10, 15, and 20% wet basis (wb)) was 75°C. Increasing the moisture content generally decreased the glass transition temperature. The endpoint of the glass transition region was 100°C. Therefore, 75 and 100°C were chosen as processing temperatures for the study, along with 150°C to observe the effect of temperature beyond the glass transition. It was discovered that there was moisture migration at the highest temperature resulting in a lower durability for the 150°C briquettes than the 100°C briquettes. The durability of the 100°C briquettes was also higher than the 75°C briquettes.

2.2.1.2 Pressure

Butler and McColly (1959) observed that the density of chopped alfalfa hay pellets was proportional to the natural logarithm of the applied pressure. There is no doubt that an increase in applied pressure will increase the density; however, the mechanical strength of the pellets is not so easily predicted. Yaman and co-workers (2000) recommended that briquetting pressure should be selected at an optimum value. They explained that as the briquetting pressure increases, the mechanical strength of the briquettes increases as a result of the plastic deformation. However, above an optimum briquetting pressure, fractures may occur in the briquette due to a sudden dilation. For a given die size and storage conditions, there is a maximum die pressure beyond which no

significant gain in cohesion (bonding) of the briquette can be achieved (Ndiema et al. 2002). With respect to pressure application rate, Li and Liu (2000) compressed oak sawdust at pressure application rates varying from 0.24 to 5.0 MPa/s. The dry density of the compacts, measured 2 min after compression, decreased with an increase in compaction speed up to 3 MPa/s. The compaction speed became negligible at rates higher than 3 MPa/s.

2.2.1.3 Hold (dwell) time

The hold time of the material in the die will influence the quality of the pellets. Li and Liu (2000) found that the hold time for oak sawdust had more effect at lower pressures than at higher pressures. At the highest pressure (138 MPa), the effect of holding time became negligible. Holding time had little effect on the expansion rate. It appeared that hold times greater than 40 s had a negligible effect on density. Al-Widyan and co-workers (2002) discovered that hold (dwell) times between 5 and 20 s did not have a significant effect on olive cake briquette durability and stability.

2.2.1.4 Die geometry

In this context, die geometry refers to the size of the die, and will influence the amount of material which can be pelleted, energy required for compression, etc. Butler and McColly (1959) found that when pelleting a constant mass of material, pellet density was greater for smaller diameter chambers at a given pressure. Also, longer pellets were produced in the smaller chambers (using a constant mass in all chambers), resulting in a smaller percentage of expansion.

2.2.2 Feedstock/material variables

Feedstock/material variables are those factors which are characteristic of a particular biomass feedstock.

2.2.2.1 Moisture content

In the briquetting process, water acts as a film-type binder by strengthening and promoting bonding via van der Waal's forces by increasing the contact area of the particles (Mani et al. 2003). As a general rule, the higher the moisture content, the lower the density of the pellet. Demirbaş (2004) found that increasing the moisture content (7-15%) of pulping rejects and spruce wood sawdust resulted in stronger briquettes. Mani and co-workers (2006a) report that corn stover of a low moisture (5–10%) resulted in denser, more stable and more durable briquettes than high moisture stover (15%). Li and Liu (2000) recommend that the optimum moisture content for compacting wood in a punch-and-die assembly was approximately 8%. Following a study of the compaction of tree bark, sawmill waste, wood shavings, alfalfa hay, fresh alfalfa, and grass, Moshenin and Zaske (1976) reported that materials having lower moisture content and fewer long fibers (more fines) gave more stable wafers, due to limited expansion. Protoplasm, liberated during the compression, acted as a binder and provided fresh alfalfa (19% moisture) with the highest durability. Sokhansanj and co-workers (2005) identified that feed material containing higher proportions of starch and protein will produce higher quality pellets than material high in cellulosic material. The authors also identified that the optimum moisture content for pelleting cellulosic material ranges from 8 to 12% wb, while the optimum moisture content for starch and protein material (most animal feeds) can reach 20% wb. Li and Liu (2000) found that at moisture

contents equal or less than 4% wb, pellets tended to absorb moisture from the air and expand significantly, becoming fragile in a few days. Starch gelatinization, protein denaturation, and fiber solubilization processes are facilitated by the presence of water; however, water added as steam is far superior to conditioning with water alone, since the additional heat modifies physico-chemical properties (gelatinization of starch, denaturation of protein) to such an extent that binding between particles is greatly enhanced resulting in improved physical pellet quality (Thomas et al. 1997). It is evident that the optimum moisture content for densification is different for each individual feedstock and set of process conditions.

Ollett and co-workers (1993) undertook a study to determine the effect of water content on the compaction behavior of food powders. Following the study, they reported that the compaction of the studied food powders and the effects of water content proved to be complex phenomena. Increased water content resulted in a decrease in deformation stresses, as determined by the Heckel (1961) analysis. The authors attributed this to plasticization of amorphous materials. For crystalline materials, this was explained by lubrication effects during particle rearrangement.

In an experiment examining the effect of moisture on the stress relaxation of compacted powders, Peleg and Moreyra (1979) demonstrated that wet powders were more deformable than dry powders, as indicated by the longer time required to reach the preset load (Figure 2.1). This allows more stress relaxation to occur during relaxation.

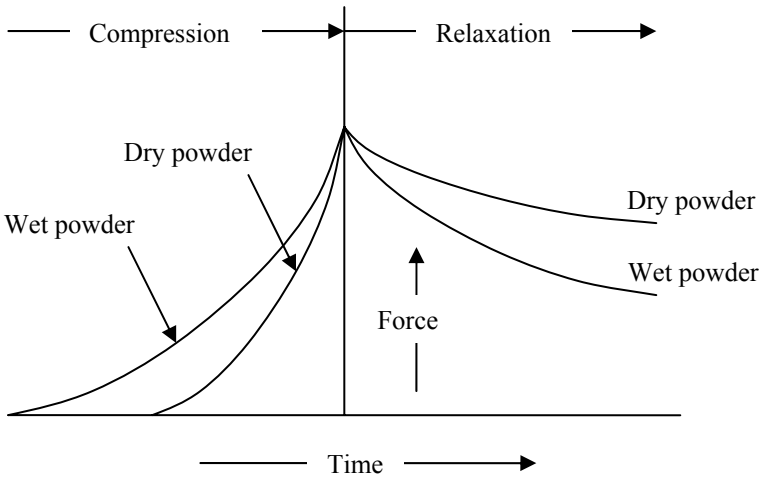

Figure 2.1 Generic compression and relaxation curve of wet and dry powders (Moreyra and Peleg 1980).

2.2.2.2 Particle size, shape, and distribution

Numerous studies report that smaller particle sizes will produce higher density pellets. Generally, the quality of the pellets is inversely proportional to the particle size; however, this is not always the case as conflicting results can be found in literature. Mani and co-workers (2003) alluded to the idea that particle size distribution has an effect on pellet quality. Payne (1978) reported that a proportion of fine to medium particles is required, but pellet quality and the efficiency of commercial pelleters will suffer if coarse material is not present. Table 2.1 shows the particle size distribution (spectrum) for producing quality pellets, which was proposed by Payne (1996). The effect of particle size distribution was listed as an important material property for forage wafering when comparing leaf to stem ratios, as a higher leaf content has been reported to produce a superior densified product; this may also be due to increased protein

content in the leaf. Smith and co-workers (1977) noted that the compaction and stabilization of straw may have a different mechanism than for grass due to the fact that straw is dead material and has a significantly smaller leaf content.

There is a lack of information relating the effect of particle shape (i.e. roundness and surface roughness) to the quality of biomass pellets, and may be an area of future research initiatives.

Table 2.1 Suggested particle size spectrum for quality pellets, reported by Payne (1996).

Sieve (mm)	Material retained on sieve
3.00	$\leq 1\%$
2.00	$\leq 5\%$
1.00	$\approx 20\%$
0.50	$\approx 30\%$
0.25	$\approx 24\%$
<0.25	$\geq 20\%$

2.2.2.3 Biochemical composition

Due to the vast array of biomass materials, the number of chemical constituents and compositions are nearly innumerable. Consequently, it is almost impossible to identify and quantify all of the chemical reactions taking place during the densification process. Therefore, it is wise to focus on those chemical constituents common to the majority, if not all, of the relevant biomass feedstocks, in order to gain an understanding of how these select chemical compounds affect the densified product's quality. Research in this area is primarily carried out for the purpose of manufacturing animal feed and pharmaceutical tablets.

Thomas and co-workers (1998) reported that ingredient constituents (for animal feed pelleting) can be classified as starch, protein, sugar and non-starch-polysaccharides (NSP), fat, fibre, inorganic matter, and water. The processing conditions (temperature,

pressure, shear, steam) induce changes causing individual constituents, or interacting constituents, to positively or negatively affect pellet quality. In the food processing industry, mixtures of food polymers can result in stronger gels, as compared to either polymer alone, owing to synergistic mechanisms (Shim and Mulvaney 2001). What is not known are all the specifics of how the chemical constituents influence pellet quality.

2.2.2.3.1 Starch

Starch is a polymer of D-glucose, made up of either branched (amylopectin) or un-branched (amylose) chains. Next to cellulose, starch is the most abundant carbohydrate in plants (Collado and Corke 2003). Ellis and co-workers (1998) conducted a comprehensive review of starch production and its industrial use. They explained that starch occurs as semi-crystalline granules in the chloroplasts of green leaves and in the amyloplasts of storage organs such as seeds and tubers. Starch granules may also contain non-starch components such as lipids, proteins, and phosphate groups. The crystalline region is an ordered arrangement of double helical amylopectin structures (Atichokudomchai et al. 2001). Starch contributes greatly to the textural properties of many foods and is widely used in food and industrial applications as a thickener, colloidal stabilizer, gelling agent, bulking agent, water retention agent, and adhesive (Singh et al. 2002). Starches are also used in non-food applications as adhesives for board, paper or labels in the paper industry (Thomas et al. 1999). In the pharmaceutical industry, starch is used in tablet formulation as a binder, disintegrant, or filler, due to its suitable physico-chemical properties and relative inertness (Alebiowu and Itiola 2002). Along with acting as a binding or adhesive agent, starch provides a lubricating effect during the pelleting process. The exploitation of these desirable

properties appears to be the successful gelatinization of starch granules. In its native granular form, starch has few uses; therefore, to release the polymer properties, granule disruption and sometimes modification are necessary (Lillford and Morrison 1997). For starch molecules to be used as an adhesive, they must be chemically or thermally hydrated (Kennedy, 1989).

Three starch reactions of interest were discussed by Collado and Corke (2003); namely, gelatinization, pasting, and retrogradation. Gelatinization is an irreversible process wherein the starch granule losses its crystallinity and becomes soluble, the granule also swells and breaks down. Thomas and co-workers (1999) summarized the factors influencing the gelatinization of starch:

- *Water*. Necessary for swelling and weakening of the different bonds in the starch kernel.
- *Heat*. Facilitates entry of water and causes part of the granule (amylose) to solubilize. In the presence of enough water, it induces melting of crystalline regions.
- *Shear*. Physical force is necessary for disruption of the kernel, thereby facilitating the entry of water and aiding in swelling and solubilization of the kernel and starch respectively.
- *Residence time*. A prolonged period of time increases the combined effects of shear, water, and heat on the degree of starch gelatinization.

Hermansson and co-workers (1995) explained that when starch granules are heated, the crystalline portion of the granule melts and part of the starch solubilizes. The authors discussed that if swelling is limited, the solubilized starch (mainly amylose) will

leach out of the granule and become distributed in a continuous starch phase. However, if there is rapid swelling (i.e. faster than solubilized starch leakage), then the swollen granules come into contact and form a closely packed arrangement. These reactions are dictated by the relative amount of amylose to amylopectin, and their degree of separation. Most starches start to swell at about 60 to 70^{o}C, and appear to be reasonably dispersed at 95°C. In order to completely solubilize the starch, a much higher temperature of 150-160°C is required (Kruger and Lacourse, 1990). The low water content during feed processing limits the extent of gelatinization, but gelatinization temperature and extent of gelatinization will be affected by properties of the starch (Svihus et al. 2005). The underlying mechanism of the contribution of gelatinized starch in binding properties in pellets is still not fully elucidated (Thomas et al. 1998).

Pasting follows, which includes a further increase in granule swelling (potentially resulting in total granule breakdown), as well as the loss of granular components. Michel and Autio (2001) define retrogradation as the term used to describe the structural changes that occur when gelatinized starch is cooled to room temperature and stored. Basically, the amylopectin portion of the starch granule recrystallizes, and increases the rigidity of starch gels. Svihus and co-workers (2005) explained that retrogradation is the crystallization of gelatinized starch in an amorphous matrix, and it involves formation and subsequent aggregation of double helices of amylose and amylopectin. Amylose retrogradation occurs much faster (days) than amylopectin retrogradation (weeks or months).

Michel and Autio (2001) claimed that pressure-induced physiochemical changes are similar to those induced during heat treatment, but rheological properties differ

greatly. A supporting example is that of potato starch under pressure, the swelling of starch granules increases, providing high rigidity to pressure treated starch gels.

Collado and Corke (2003) discussed that because of its linear structure, amylose has the ability to change conformations because of high hydrogen bonding capability due to its many hydroxyl groups. Because of its many hydroxyl groups, starch has a high affinity for polar substances such as water or cellulose (Kruger and Lacourse 1990).

Thomas and co-workers (1998) attributed starch binding/adhesion characteristics to the amylose:amylopectin ratio. After gelatinization of the starch granule, amylose immediately forms double helices which may aggregate (hydrogen bonds) to each other and create semi-crystalline regions. From literature, the authors identified that pellet binding occurs most likely by amylopectin due to the double helices formed at the non-reducing ends of this very large branched molecule that may aggregate with compatible starch or fibre surfaces on the different particles present during and after gelatinization.

During steam conditioning prior to commercial pelleting, only between 10 and 200 g starch/kg is usually gelatinized; this low extent of gelatinization implies that steam conditioning and pelleting will not have a marked effect on neither starch digestibility nor physical quality of the feeds (Svihus et al. 2005). At lower moisture contents, a higher temperature is required to induce starch melting or gelatinization.

2.2.2.3.2 Protein

Thomas and co-workers (1998) explained that pellet processing involves the combined effect of shear, heat, residence time and water resulting, among others, in partial denaturation of the protein in pelleted feed. They added that upon cooling, proteins re-associate and so bonds can be established between the different particles.

Studies of thermal processing effects on (soy) proteins have been reported by various researchers, and all show that, following denaturation, the proteins will often interact with either themselves or with other molecules (Nyanzi and Maga 1992). Nyanzi and Maga (1992) reported that binding capacity is likely due to the chemical interaction nature of the individual proteins. The authors also reported that a common protein-protein or protein-polymer interaction is non-covalent binding. Tabil (1996) explained that if sufficient natural protein is available, it will plasticize under heat, improving the quality of the pellets. Briggs and co-workers (1999) found that increasing protein content increased pelleted feed durability. Wood (1987) determined that the physical quality of pellets could be improved by using raw protein (up to 35%) as opposed to denatured protein in the feed mixture.

Aslaksen and co-workers (2006) reported that globular (i.e. soybean) proteins have a higher denaturation temperature (approximately 95°C) than fibrous (i.e. muscular) proteins (50-60°C). The authors explained that this is due to the compact three-dimensional form and highly hydrophobic interior of globular proteins. Lampart-Szczapa and co-workers (2006) suggested that when examining the behavior of proteins in food systems, the primary factors to be taken into account are amino acid composition, sequence, and molecular weight. These factors affect secondary structure of protein, its hydrophobicity, the net charge and charge distribution, flexibility of the molecule, and isoelectric point. Surface hydrophobicity is a unique property of proteins, correlating with their functional properties, such as solubility, water absorption, gelation, emulsifying, and foaming properties (Lampart-Szczapa et al. 2006).

Due to the low and intermediate moisture contents required for optimum biomass densification, the discipline of extrusion can be looked upon for valuable information

relating to the result of high temperature and pressure on low and intermediate moisture products. Extrusion causes protein conformation modification; numerous non-covalent and covalent bonds stabilizing secondary structure are destroyed, and new intermolecular bonds can occur between forming subunits (Lampart-Szczapa et al. 2006). In particular, texturization in extruded food materials is attributed to a combination of fragmentation and aggregation, non-covalent associations, and covalent cross-linking of proteins and starches (Schaich and Rebello 1999). Studies on soy flours and concentrates have attributed texturization to cross-linking of soy proteins, involving both main-chain polypeptide and disulfide bonds, although the relative contributions of the two types of cross-linking have not been distinguished (Rebello and Schaich 1999). Ledward and Tester (1994) provided an overview of protein molecular transformations during extrusion. They stated that hydrogen bonding and hydrophobic interactions generally form upon cooling and are generally thought of as weak interactions helping to stabilize the basic network. Also, at higher temperatures, the heat-unstable bonds of macromolecules will break (i.e. disulphide bonds). From literature, Lampart-Szczapa and co-workers (2006) found that after extrusion, proteins have a more fibrous structure and that is why it is harder to extract them and estimate their contents.

Cysteine bridges are the only non-peptidic covalent bonds in proteins; formed by the oxidation of cysteine–thiol groups, they contribute to the stabilization of the three-dimensional structure of proteins (Rouilly et al. 2006). Ledward and Tester (1994) explained that disulphide bonds will rupture at higher temperatures, and are reformed during cooling. The disulphide bonds will form at higher temperatures than the weaker hydrogen bonds, or even hydrophobic interactions. Disulfide bonds have the lowest

covalent bond energy in proteins, making them the most susceptible for cleavage by mechanical force (Aslaksen et al. 2006).

Electrostatic charges were also listed as a reason for molecular transformations by Ledward and Tester (1994). Proteins can carry a net positive or negative charge, and even at the isoelectric point, the charge is not evenly distributed. They reported that pressure will cause ionization of groups (i.e. carboxylate and amino groups), and the limited degree of water will limit hydration, therefore, the ionized groups are free to interact or repulse. During extrusion (conditions of high temperature and shear) the macromolecules will arrange themselves to minimize electrostatic repulsion. When so aligned and/or at the same time, potentially reactive groups on the protein and other material in the melt will undergo browning reactions. These will involve certain lysine residues and some glutamine/glutamic acid residues (Ledward and Tester 1994).

2.2.2.3.3 Starch-protein interaction

Significant interactions between starch and protein have been found to influence densified biomass quality. Sokhansanj and co-workers (2005) reported that feed material with larger fractions of starch and protein composition produced denser and more stable pellets than biomass with a larger composition of cellulose. Wood (1987) discovered that the functional properties of the protein and starch fractions had a greater effect on feed pellet quality (durability and hardness) than steam conditioning. The study consisted of mixing native or pre-gelatinized tapioca (cassava) starch (0-40%) and raw or denatured soya-bean meal (protein, 0-35%) with a common base of sunflower cake, groundnut oil, molasses, dicalcium phosphate and salt; providing a mixture similar to that of broiler feed. It was stated that pellet durability was protein dependent, due to the

higher rate of development of water absorption and development of cohesive properties by the raw soya protein when blended with pre-gelatinized starch. Maximum pellet durability (93%) was obtained with mixtures containing raw soya protein and pre-gelatinized tapioca starch and minimum durability with mixtures containing denatured soya protein and native tapioca starch. It was noted that native starches behaved similar to many heat-denatured proteins when mixed with cold water; they possess little water-binding, gelling, or cohesive properties.

Ghorpade and co-workers (1997) studied the structure of corn starch amylose extruded with soy protein isolate or wheat gluten (cereal grain proteins). The shear strength of the extrudate increased with an increase in amylose and protein content, indicating that interactions are present, affecting the microstructure of the extrudate. Goel and co-workers (1999) proposed that one potential interaction is the entrapment of alkyl side chains in the proteins and protein hydrolysates by the helical amylose of starch. The researchers emphasized that proteins contain many hydrophilic groups (-OH, $-NH_2$, -COOH, and -SH) in the alkyl side chains, all of which are capable of forming cross-links with starch and are responsible for the high viscosity of the cold paste.

In a study examining the interaction of casein and starch during the extrusion process, Fernández-Gutiérrez and co-workers (2004) discovered that the compressive force required to break the extruded samples was strongly dependent on moisture content and casein proportion in the blend. It was noted that at starch concentrations of 35 to 65% and moisture contents around 28.5% (at 160°C), the biopolymers acquired a dense and rigid structure, which was difficult to break. The authors speculated that this was probably due to the formation of bonds between starch and casein and the structural modification that each polymer underwent during the extrusion process. It was stated

that starch fragmentation as well as protein denaturation cause a stronger interaction between both polymers and formation of inter- and intramolecular bonds. Hydrogen bonds and van der Waals interactions were listed as possible reasons for the increase in mechanical strength.

2.2.2.3.4 Lignocellulose

Cellulose, hemicellulose, and lignin are the most abundant wood-based polymers, and comprise a group of biopolymers known as lignocellulose. Lignocellulose is characteristic of non-food-related biomass such as trees, grasses, and waste materials. Cellulose comprises 40-60% of the dry weight of plant material, while hemicellulose and lignin make up 20-40% and 10-25% of the dry weight, respectively (United States Department of Energy 2006). In the cell wall, cellulose forms crystalline microfibrils that are surrounded by amorphous cellulose. The amorphous portion of cellulose is much more open and accessible than is the crystalline portion (Chen et al. 2004). Hemicellulose and lignin (in woody plants) form a matrix which reinforces the cellulose microfibrils. The cell wall is then a fiber-reinforced plastic with cellulose fibers (shown in Figure 2.2) embedded in an amorphous matrix of hemicellulose and lignin (Goldstein 1981).

Cellulose, a fibrous, tough, water-insoluble substance, is found in the cell walls of plants, particularly in the stalks, stems, trunks, and all the woody portions of the plant body (Nelson and Cox 2005). It is the most abundant source of carbon in biomass. Cellulose is a polymer of D-glucose residues that are joined by β1→4 glycosidic bonds. It exists as an un-branched chain, and provides structural support and rigidity to plants. Structural integrity is due, in part, to the high degree of hydrogen bonding that occurs

between the glucose monomers. Zandersons and co-workers (2004) reported that binding of wood material during hot pressing is mainly dependent on the transition of cellulose into the amorphous state. In an article on cellulose adhesives, Hon (1989) stated that because of its semi-crystalline structure, highly hydrogen bonded cellulose cannot be dissolved easily in conventional solvents, and it cannot be melted before it burns; hence, cellulose itself is not a suitable adhesive. Hon (1989) added that this can be overcome by breaking the hydrogen bonds, thus making the cellulose molecule more flexible.

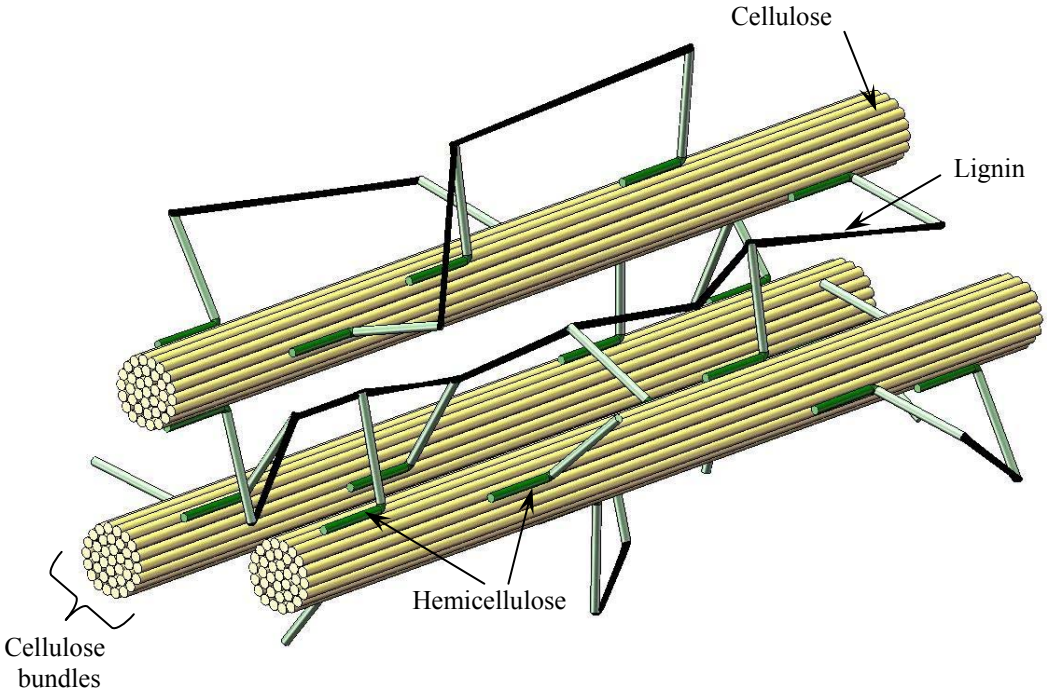

Figure 2.2 Lignocellulose arrangement (adapted from Murphy and McCarthy 2005).

Hemicellulose is also found in the cell wall, but unlike cellulose, it is a heteropolysaccharide that is composed of many other sugars than just glucose. Hemicellulose contains β1→4 bonded D-xylan as the main chain, with branches made

up of L-arabinose, D-glucose, D-galactose, 4-*O*-methyl-D-glucuronic acid, D-mannose, and L-rhamnose (Shambe and Kennedy 1985). Branching in hemicellulose produces an amorphous structure that is more easily hydrolyzed than cellulose. Also, hemicellulose can be dissolved in strong alkali solutions. Hemicellulose provides structural integrity to the cell. Bhattacharya and co-workers (1989) noted that some researchers believe that natural bonding may occur due to the adhesive degradation products of hemicellulose.

In plants, the cell wall may comprise as much as 95% of the plant material, and consists primarily of polysaccharides, and in the case off woody plants, they also contain lignin (Goldstein 1981). Lignin is a random network polymer with a variety of linkages, based on phenyl propane units (Zandersons et al. 2004). While the structure of lignin is complex, it is derived from two amino acids; namely, phenylalanine and tyrosine (Nelson and Cox 2005), both of which contain aromatic rings. There appears to be no distinct configuration for the lignin molecule, however it is a polymer that serves many structural purposes in woody plant material. Lignin acts as glue for the cellulose fibers. van Dam and co-workers (2004) have reported that lignin can be used as an intrinsic resin in binderless board production due to the fact that when lignin melts (temperatures above 140°C) it exhibits thermosetting properties. Lignin is the component that permits adhesion in the wood structure, and is a rigidifying and bulking agent (Anglès et al. 2001). Lehtikangas (2001) stated that the water (8-15%) in pellets will reduce the softening temperature of lignin to 100-135°C by plasticizing the molecule chains. The adhesive properties of thermally softened lignin are thought to contribute considerably to the strength characteristics of briquettes made of lignocellulosic materials (Granada et al. 2002).

2.2.2.3.5 Pectin

Pectins are a family of complex polysaccharides that contain 1,4-linked α-D-galactosyluronic acid (Gal*p*A) residues (Ridley et al. 2001), and are located in the middle lamella of the cell, aiding in cellular binding. They are widely used in food formulations, mainly as gelling agents (Lopes da Silva et al. 1994). While pectin has not been reported by many studies to have contributed significantly to the natural binding of densified biomass, Bhattacharya and co-workers (1989) noted that pectin can be squeezed from the plant cells and act as binding agents. The authors' literature review also uncovered that the application of pressure may transform the chemically bonded water into steam, thus dissolving the pectin holding the cell walls together, and promote natural bonding.

2.2.2.3.6 Lipid/fat

It is generally accepted that fat components will increase pellet product throughput in a pellet mill, due to its lubricating effect in the die. However, the durability and hardness (two quality determinants) of pellets decreases with increasing fat content. Briggs and co-workers (1999) noted that increased oil content produced lower quality pellets. Since most binding of feed particles incorporates water or, when involved, solubilized starches, proteins, and fibers, fat with its hydrophobic nature may interfere with binding properties of water-soluble components in the mixture. Moreover, added fat (and to a lesser extent, fat enclosed in the matrix of cell walls) acts as a lubricant between particles and between the feed mash and the die-wall, resulting in a lower pelleting pressure (Thomas et al. 1998).

York and Pilpel (1973) determined that decreasing the lactose to fatty acid ratio (by adding an increased percentage of fatty acid) during pharmaceutical tableting resulted in a general decrease in tablet strength. This was attributed to an increase in fatty acid – fatty acid bonds which are weaker than lactose – lactose bonds.

2.2.2.4 Pretreatment

Pretreatment of biomass prior to densification is a potential method for altering the physical structure and the structure of the chemical constituents in an attempt to enhance the binding characteristics. Pretreatment can be broken down into two categories: physical/mechanical and chemical.

2.2.2.4.1 Physical/mechanical pretreatment

In chemical production, lignocellulosic materials are commonly milled or comminuted to reduce the particle size; this partially breaks down lignin and allows for increased penetration and attack by acids or enzymes. For densification, milling will provide a larger surface area for binding. This will also increase the porosity of the bulk material. Materials relevant to this study must be ground in order to meet the input requirements of laboratory and commercial densification equipment. For fine powders, the number of contact points between particles is higher than it would be for large particles; furthermore, because the finer the powder, the larger its exposed surface area, the surface energy per unit weight (regardless of its physical-chemical character) also increases with the size reduction of the powder (Peleg 1977). In a study investigating the mechanical properties of pellets from wheat and barley straws, corn stover, and

switchgrass, Mani and co-workers (2006b) concluded that particle size had a significant effect on the pellet density of all feedstocks except for wheat straw.

Compressed hot water or steam is another pretreatment approach which induces lignin removal (Liu and Wyman 2005). Batch, partial flow, and flow-through processing techniques are available. Controlled pH methods have also been investigated (Mosier et al. 2005). It is postulated that by disrupting lignocellulosic biomass materials via steam explosion pretreatment, that the compression and compaction characteristics can be improved. Zandersons and co-workers (2004) stated that activation of lignin and changes in the cellulosic structure during the steam explosion process facilitate the formation of new bonds. Much of the research involving steam explosion pretreatment has focused on the alteration of the lignocellulose matrix in biomass, and subsequent improvement of enzymatic hydrolysis (Ballesteros et al. 2002; Nunes and Pourquie 1996). Steam explosion has also been explored by the flax fiber industry as an upgrading step to produce high quality short fibers for the textile market (Kessler et al. 1998).

Steam explosion pretreatment is a process by which material is introduced into a reactor and heated under steam pressure at elevated temperatures for a few minutes. During the reaction, the hemicelluloses are hydrolyzed and become water soluble, the cellulose is slightly depolymerized, and the lignin melts and is depolymerized (Toussaint et al. 1991). Kaar and co-workers (1998) noted that steam explosion requires little or no chemical input and thus, is environmentally benign relative to other technologies, such as acid hydrolysis.

Anglès and co-workers (2001) explained that hydrolytic depolymerization in aqueous media is catalyzed by acidic species in wood (auto-hydrolysis) or by adding

small amounts of mineral acids (pre-hydrolysis). They further explained the significant chemical reactions taking place in the wood lignocellulose:

- Partial hydrolysis of cellulose and hemicellulose into water soluble sugars and oligomers.
- Partial hydrolysis of lignin to lower molecular weight material.
- At high steam temperatures, some low molecular weight lignin melts, flows, and partially coalesces into droplets.

The latter point was supported by Murray Burke (Vice President & General Manager, SunOpta BioProcess Inc., Brampton, ON) in a personal communication. He explained that his experience demonstrates that during steam pre-treatment, the lignin breaks down and forms 'teardrop' structures. During the pelleting process, the 'teardrop' lignin re-melts and forms an extremely tough outer layer. He added that biomass pellets made after pretreatment with steam auto-hydrolysis will grind the same as coal, and have been utilized to replace 10-15% of the coal in air fired power plants.

2.2.2.4.2 Chemical pretreatment

Due to the fact that lignocellulose is the most abundant chemical constituent in the biomass materials of interest, pretreatment is targeted towards the alteration of the lignocellulosic structure. Pretreated starch (i.e. pre-gelatinized starch) is commonly used in the pharmaceutical industry. However, such starch must be treated independently and then added to the tablet mixture. This study is only concerned with pretreatment of the biomass matrix as a whole.

Several recent studies have been conducted which examined the effect of chemical and hydrothermal pretreatment of lignocellulose materials. However, these

studies investigated the effect of pretreatment on acid or enzymatic hydrolysis of lignocelluloses and subsequent conversion to ethanol. Such studies included the treatment of lignocellulose biomass with alkali solutions, inducing swelling and subsequent delignification. Alkali pretreatment includes aqueous ammonia in a process known as ammonia recycled percolation, or ARP (Kim and Lee 2005). Another alkali pretreatment, known as ammonia fiber explosion (AFEX) involves the use of liquid anhydrous ammonia (Teymouri et al. 2005). Sodium hydroxide (Carrillo et al. 2005) and lime, or calcium hydroxide (Kim and Holtzapple 2006), have also been investigated as pretreatment techniques for alteration of lignocellulose.

Sulfuric acid has been studied as a dilute acid for biomass pretreatment (Lloyd and Wyman 2005; Saha et al. 2005). It has been shown that dilute acid pretreatment is successful in solubilizing the hemicellulose portion of the lignocellulose matrix (Wyman et al. 2005).

While a majority of the aforementioned studies were intended for the pretreatment of lignocellulosic biomass for further acid or enzymatic hydrolysis, they still indicate a definitive alteration of the lignocellulose matrix.

2.3 Agglomeration bonding mechanisms

Compaction of powders or grinds is a form of systematic agglomeration involving pressure. There are a number of processes for systematic agglomeration, for instance, granulation, briquetting, pelletizing, and sintering (Rumpf 1962). Rumpf (1962) discussed the bonding mechanisms involved in size enlargement (agglomeration). He proposed five bonding mechanisms for agglomeration:

2.3.1 Solid bridges

While the other bonding mechanisms primarily contribute to initially bonding particles together during the agglomeration process, it is the solid bridges that will largely determine the strength of the final product (Ghebre-Sellassie 1989). Rumpf (1962) explains that solid bridges between particles in a granule may be formed as follows:

1. *Sintering*. At an elevated temperature, solid bridges may develop by diffusion of molecules from one particle to another at points of contact (Pietsch 1997).
2. *Chemical reactions*. Involves the formation of solid bridges by alteration of chemical structure.
3. *Melting*. Material that is melted during agglomeration will solidify when cooled and form strong bridges between particles (Ghebre-Sellassie 1989). York and Pilpel (1972) attributed an increase in cohesion and tensile strength of pharmaceutical powders to melting at contact points at temperatures below their conventional melting points due to the application of pressure. York and Pilpel (1973) investigated the effects of melting temperature of four fatty acids on the tensile strength of lactose-fatty acid pharmaceutical tablets. They found that a general decrease in strength occurs as the melting point of the fatty acid used increased.
4. *Hardening of bonding agents*. A bridge made up of the binding agent forms between the particles during curing.
5. *Crystallization of dissolved materials*. Following evaporization of solution, dissolved solids will crystallize and form bridges or bonds at contact points.

2.3.2 Interfacial forces and capillary pressure in moveable liquid surfaces

There were three conditions for interfacial forces and capillary pressure in moveable liquid surfaces proposed by Rumpf (1962). The first two binding forces are known as "capillary bonding forces".

1. Void space between particles is only partially filled with liquid
    - This was termed the "pendular state" of the entrapped liquid by Rumpf (1962).
    - The "funicular state", exhibited by a continuous network of liquid rings and entrapment of the air phase, is reached by increasing the liquid content or decreasing the pore volume (Rumpf 1962; Sastry and Fuerstenau 1973).
    - Bridges are formed between individual particles.
    - Surface tension is directed along the liquid surface at the solid-gas contact line.
    - Within the liquid bridge, a negative capillary pressure develops.
2. Void space is completely filled with liquid
    - "Capillary state" (Rumpf 1962; Sastry and Fuerstenau 1973).
    - Bonding forces result from interfacial forces at the surface of the granule.
    - The liquid forms concave surfaces at the edge of the pores.
    - The granule develops tensile strength due to the negative capillary pressure within the liquid.
3. Liquid completely envelops the solid
    - "Droplet state" (Ghebre-Sellassie 1989).
    - The entire granule is surrounded by liquid.

- Most of the grains are still held together in the droplet by the surface tension of the droplet.
- All intergranular capillary bonding forces disappear.

Pietsch (1997) explained that these strong bonds will disappear if the liquid evaporates and no other binding mechanism takes over.

2.3.3 Forces in bonding bridges which are not freely moveable

Adhesion and cohesion forces in bonding bridges which are not freely moveable include the forces introduced by viscous binders or adsorption layers. Pietsch (1997) expanded by stating that highly viscous bonding media (e.g. tar) can form bonds similar to solid bridges, while adsorption layers are immobile and can contribute to the bonding of fine particles. Many viscous binders harden during the agglomeration process, while thin-adsorption layers either smooth out surface roughness and increase particle contact area or decrease the effective interparticle distance and allowing intermolecular forces to participate in the bonding mechanism (Ghebre-Sellassie 1989).

2.3.4 Attraction between solid particles

Solid particles may attract one another through molecular forces (van der Waals and valence), electrostatic charges, or magnetic forces. These are short range forces that are more effective with a smaller particle size. Therefore, the significance of attractive forces in the overall mechanism of agglomerate bonding is not so much that they play a crucial role in the bonding of the final product; it is that they initially hold and orient the particles in a contact region long enough for stronger forces to take over (Ghebre-

Sellassie 1989). van der Waals forces have an effective range of up to 100 Å (Peleg 1977).

2.3.5 Mechanical interlocking (form-closed bonds)

Fibrous, flat or irregularly shaped, and bulky particles mechanically interlock or mat with each other. This form of bonding is no doubt affected by the shape of the particles, as particles with a low surface roughness and high degree of roundness will be less likely to mechanically interlock.

2.4 Powder compression/compaction

As previously mentioned, a great wealth of information can be obtained by studying powder compaction from the pharmaceutical and metallurgical industries. The problem of pelleting granular materials may be considered to have two aspects: the behavior of the particles under pressure so far as density changes are concerned, and the more fundamental problem of the cohesion of the particles to form pellets having considerable mechanical strength (Stewart 1950).

The terms compression and compaction are widely referred to in densification literature; however, their definitions are often confused. Compression is defined as the reduction in volume of a powder bed under a specified pressure (Shivanand and Sprockel 1992). Compressibility, as defined in powder compression studies, is simply the change in bulk density (packed density) of the powder due to pressure (Peleg and Mannheim 1973). Compressibility, adhesion, and cohesion are all powder properties that have been used to evaluate the flow properties of many food and pharmaceutical powders. Typically, compressibility and the cohesiveness of powders are proportional,

and are inversely proportional to the flowability of the powders. Cohesive forces in particular will reduce the flowability of powders. Compression ratio is then the ratio of the compact density obtained at a given pressure to the apparent density of the loose powder (Heckel 1961). Compaction on the other hand, is defined as the increase in mechanical strength of a compact under a specified pressure. This increase in compact physical strength is attributed to bonding between particles which are in close proximity to each other (Shivanand and Sprockel 1992). Compactibility is the minimum pressure needed to produce a given green strength (Heckel 1961).

Once pressure is applied to granular material, a series of events unfold, leading to the eventual agglomeration of particles. Tabil (1996) summarized the stages of particulate compaction:

a. Particle rearrangement occurring at low pressures which disrupts the unstable packing arrangement resulting in a denser packing.
b. Stage A: elastic and plastic deformation occurring at higher pressures results in particle flow into void spaces.

   Stage B: particle fracture and rearrangement resulting in mechanical interlocking for brittle materials.
c. Stages A and B will continue until the true density is attained. Local melting will occur if the temperature surpasses the constituent melting points.

In the case of biomass and biological materials, pressure acts simultaneously on the tissue's morphology, cell organelles, membranes, and at the molecular level. Plant tissues contain intercellular air spaces; because of the high compressibility of air, the tissue is severely compressed, resulting in cell wall breakage (if the cell wall is not

flexible enough), membrane disruption, loss of compartmentalization, and liberation of cellular compounds (Michel and Autio 2001).

Powder compaction equations/models have been developed to gain insight into the densification process. A compaction equation relates some measure of the state of consolidation of a powder, such as porosity, volume (or relative volume), density, or void ratio, with a function of the compacting pressure (Denny 2002). Certain compaction equations were developed in an attempt to understand and quantify the mechanisms involved during compaction.

Cooper and Eaton (1962) developed a model (Equation 2.1) to describe the compression behavior of ceramic powders. They explained that the compaction of powders occurs via two main processes. The first process involves the filling of large voids of the same size as the original particles. This occurs by particle rearrangement. The second process involves the filling of voids smaller than the original particles, and is accomplished by plastic flow or fragmentation.

$$\frac{V_0 - V}{V_0 - V_s} = h_1 \cdot \exp\left(\frac{-c_1}{P}\right) + h_2 \cdot \exp\left(\frac{-c_2}{P}\right) \tag{2.1}$$

where: V_0 = volume of compact at zero pressure (m^3)

V = volume of compact at pressure P (m^3)

V_s = void-free solid material volume (m^3)

P = pressure (Pa)

h_1, h_2 = model constants

c_1, c_2 = model constants (Pa)

Constant values derived from the Cooper-Eaton model can be used to determine which of the two mechanisms of compression is most prominent. If h_1 is larger than h_2, then the sample compresses mainly by particle rearrangement. Conversely, if h_2 is larger than h_1, then compression proceeds mainly by deformation. Shivanand and Sprockel (1992) reported that the constant c_1 represents the pressure required to induce densification by particle rearrangement, and c_2 is representative of the pressure required to induce densification by deformation. Cooper and Eaton (1962) explained that when the sum of h_1 and h_2 is equal to unity (1), compaction can be completely explained by the two separate processes. They added that, if the sum of h_1 and h_2 is less than unity, other processes must become operative before complete compaction is achieved.

Walker (1923) proposed a model (Equation 2.2) which described the compression of powders such as precipitated calcium carbonate and tetranitro-methylaniline.

$$V_R = m_1 \cdot \ln P + z_1 \tag{2.2}$$

where: V_R = volume ratio = $\frac{V}{V_s}$

m_1 = model constant; compressibility

z_1 = model constant

Another linear model (Equation 2.3) was put forward by Jones (1960) which examined the compressed powder density as a function of the pressure applied.

$$\ln \rho = m_2 \cdot \ln P + z_2 \tag{2.3}$$

where: ρ = density of compact (packing density)

m_2 = model constant; compressibility

z_2 = model constant

Kawakita (1971) developed an equation intended to express the relationship between pressure and volume change in the compression of metallic and medical powders (Equation 2.4).

$$\frac{P}{C} = \frac{1}{ab} + \frac{P}{a} \tag{2.4}$$

where: C = degree of volume reduction = $\frac{V_0 - V}{V_0}$

a, b = model constants

2.5 Relaxation and viscoelastic properties

Since stress relaxation is a reflection of physical changes that occur under constant strain, the phenomenon may be interpreted as due to internal flow and rearrangement of liquid bridges or plasticizing of the particle's texture itself (Peleg and Moreyra 1979). Relaxation testing of compacted powders generally involves logging force-time data at a fixed strain. Peleg (1979) presented a method for normalizing relaxation data from solid foods, which was applied to powder compaction by Peleg and

Moreyra (1979). Moreyra and Peleg (1980) provided further explanation of the normalization equation proposed by Peleg (1979) (Equation 2.5):

$$\frac{F_0 \cdot t}{F_0 - F(t)} = k_1 + k_2 \cdot t \tag{2.5}$$

where: F_0 = initial force (N)

t = time (s)

$F(t)$ = force at time t (N)

k_1, k_2 = model constants

Moreyra and Peleg (1980) explained that the slope of Equation 2.5 (k_2) can be considered an index of how 'solid' the compacted specimen is on a short time scale. Liquids would have a slope of unity ($k_2 = 1$) indicating that the stresses will eventually relax to zero. Therefore the value of k_2 for solid materials must be greater than 1. It was further noted that any larger value of the slope indicates that there are stresses that will eventually remain un-relaxed (a solid state property). The constant k_2 was used to calculate an asymptotic modulus in Equation 2.6, proposed by Scoville and Peleg (1981) and used by Moreyra and Peleg (1981) on food powders.

$$E_A = \frac{F_0}{A\varepsilon}\left(1 - \frac{1}{k_2}\right) \tag{2.6}$$

where: E_A = asymptotic modulus (Pa)

A = cross-sectional area (m^2)

ε = strain

The asymptotic modulus is representative of the ability of a compressed powder to sustain un-relaxed stresses (Scoville and Peleg 1981). It is also a relatively clear indication of compact solidity since it reflects the stresses that the compact can support without dissipation through plastic flow of the solid matrix or flow and reorientation of the interparticle bridges (Moreyra and Peleg 1981).

The viscoelastic (relaxation) properties of powdered materials are highly dependent on moisture and cohesiveness of the particles. Moreyra and Peleg (1980) stated that if the particles are wet or cohesive, then there are two mechanisms by which stress can relax:

1. Reorientation by flow of liquid bridges; and
2. Relaxation of the solid material itself due to the viscoelastic properties of the particle materials, especially when plasticized by water absorption. This mechanism may also apply to any "soft" powder or particles that have liquid or semi-liquid ingredients such as fat.

In the case of dry or cohesionless particles, the stress is mainly supported by a solid matrix and therefore has little tendency to relax (Moreyra and Peleg 1980). Upon decompression, cohesive powders remain compacted while non-cohesive powders return to a free flowing state (Moreyra and Peleg 1980).

The parameters obtained from compression/compaction modeling (e.g. compressibility, relaxation) provide numerical scales for powder quality or properties.

Though the parameters themselves are derived from empirical relationships and therefore cannot be considered as universal properties, they are still meaningful from a physical point of view since they are directly related to the fundamental properties of powders (Moreyra and Peleg 1980).

2.6 Diametral compression test

Evaluation of the densified products' physical properties can be achieved in a number of ways; however, a method commonly used on pharmaceutical tablets is the diametral-compression test. Also referred to as the Brazilian test or the indirect tension test, the diametral-compression test in its simplest form, diametrically compresses a right circular cylindrical specimen between two flat platens (Rudnick et al. 1963). The determination of the tensile strength is highly dependent on the identification of the correct mode of failure. Rudnick and co-workers (1963) identified three modes of failure that can occur during the diametral-compression test: i) compression and shear failure, ii) normal tension failure, and iii) triple-cleft failure. Newton and co-workers (1971) expounded by proposing that pharmaceutical tablets will fracture in any of the five ways shown in Figure 2.3.

The most accurate determination of tensile strength is found when the specimen fails via ideal tensile failure. When the failure of tablets occurs in tension, irrespective of test conditions, there is always a low variance of the value of the load at which the tablet breaks (Fell and Newton 1970). Normal (ideal) tensile fracture occurs when the specimen fractures into two equal hemispherical halves along the loading axis. Rudnick and co-workers (1963) argued that triple-cleft fracture is a variation of normal tensile fracture, and therefore they reason that triple-cleft failure can be used to compute tensile

strength. Newton and co-workers (1971), however, contend that fracture by any other mechanism (Figure 2.3, a-d) will produce a higher variability than normal tensile fracture.

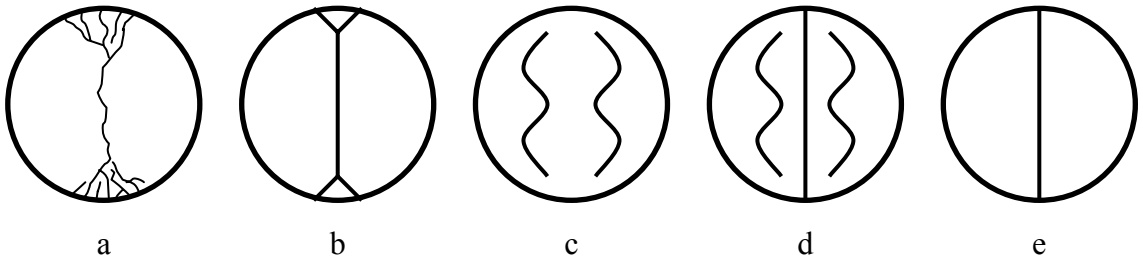

Figure 2.3 Failure of pharmaceutical tablets subjected to diametral compression: a) compression failure locally at the loading points, b) failure under local shear at and near the loading points, c) failure along the maximum shear loci when point loading is applied, d) triple-cleft fracture due to transfer of load to each half disc after breakage along the vertical diameter, and e) ideal tensile failure (adapted from Newton et al. 1971).

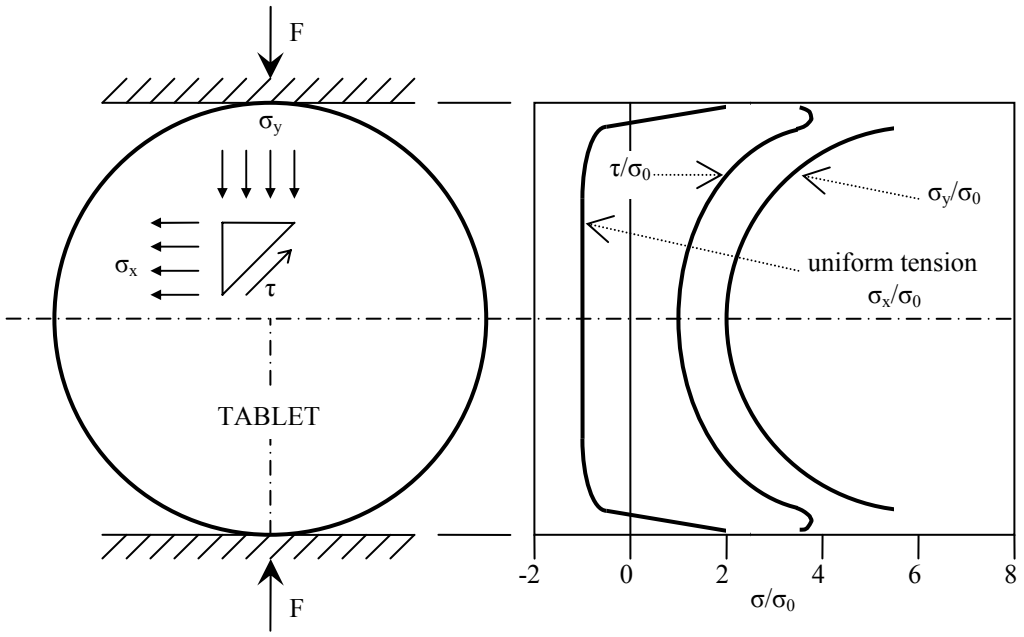

Figure 2.4 Diametral-compression test and corresponding horizontal (tensile), vertical, and shear stress distribution (Newton et al. 1971).

The tensile (horizontal) stress can be calculated using Equation 2.7.

$$\sigma_x = \frac{2F}{\pi d l} \tag{2.7}$$

where: σ_x = tensile (horizontal) stress (Pa)

F = load at fracture (N)

d = compact diameter (m)

l = compact thickness (m)

It can be seen in Figure 2.4 that the horizontal tensile stress component is nearly constant along the loading diameter, causing compact fracture into two equal halves. Obtaining an appropriate load distribution during the diametral-compression test is essential to produce normal tensile fracture. Generally, a padding material is placed between the compact material and the loading platens. The pad should be soft enough to allow distribution of the load over a reasonable area and yet narrow or thin enough to prevent the contact area to become excessive (Rudnick et al. 1963). The conditions of each test must be identical to compare the results of tensile strength.

2.7 Fourier transform infrared photoacoustic spectroscopy (FT-IR PAS)

Spectroscopy is a branch of science which studies the interaction between radiation (typically electromagnetic radiation) and matter. The region of the electromagnetic spectrum interacting with a particular material or substance will dictate which properties of the matter may be elucidated. For example, x-ray spectroscopy

allows the identification of the presence of a particular element in a sample via the interaction between the incident x-rays and the electronic composition (i.e. electrons) of a substance. Nuclear magnetic resonance (NMR) spectroscopy utilizes a magnetic field and radio frequency waves to identify the type (i.e. chemical bonding characteristic) and number of a particular element (isotopes of H, C, F, and P). It is commonly used to determine the chemical structure of organic molecules.

As its name suggests, infrared (IR) spectroscopy is the branch of spectroscopic analysis that utilizes the infrared region of the electromagnetic spectrum, and is of particular interest when examining differences in the chemical structure of untreated and pretreated feedstocks. Infrared electromagnetic radiation is characterized by wavelengths ranging from 7.8×10^{-5} to 1×10^{-1} cm. Wavelength is strictly a property of the electromagnetic radiation; however, energy and frequency are common properties between the radiation and matter (Colthup et al. 1975). The term wavenumber, with units of cm^{-1}, is used to represent segments of the infrared spectrum. The wavenumber is proportional to frequency and is the reciprocal of the radiation wavelength (Colthup et al. 1975). The region of particular interest, deemed mid-infrared, ranges from 4000 to 400 cm^{-1} (wavenumbers). When mid-infrared radiation is absorbed by a molecule it is converted to energy in the form of molecular vibrations (rotational energy changes may also be induced) (Silverstein et al. 2005). The particular frequency (or wavenumber) at which absorption occurs is different for each molecule, and also depends on any bonding present.

Sample preparation can pose many challenges (time, complexity, sample alteration, etc.) in spectroscopic analysis. Photoacoustic spectroscopy (PAS) is one technique which is able to bypass the need for sample preparation and alteration in many

cases. Upon absorbing incident infrared radiation, heat is generated within a sample, diffuses to the sample surface and into the surrounding ambient gas; this results in thermal expansion of the gas (known as the photoacoustic signal) which is detected by a microphone (McClelland et al. 1992).

Fourier transform infrared spectroscopy involves passing the incident infrared beam through a beam splitter resulting in two beams. One beam is reflected off a mirror at a fixed position while the other is reflected of a moveable mirror. Moving the one mirror and recombining the two beams produces interferences (constructive and destructive) in the reconstituted beam, known as an interferogram. Application of the Fourier transform to the interferogram converts the signal from the time domain to the frequency domain, making spectral analysis possible. Due to the fact that a monochromator is not used, the entire infrared radiation range is passed through the material simultaneously, thus saving time (Silverstein et al. 2005). Combining Fourier transform infrared spectroscopy with the photoacoustic detection technique yields Fourier transform infrared photoacoustic spectroscopy (FT-IR PAS).

2.8 Economics

While the objective of this investigation is not to address the economic concerns of biomass utilization for chemicals and energy, the results will hopefully indirectly help to reduce the cost of biomass densification, thus, increasing the feasibility of the overall process. It is well known that transport and handling operations are complex and expensive (Caputo et al. 2005); however, they can be improved through densification processes (as previously mentioned).

Three decades ago, Reed and Bryant (1978) noted that densified biomass mainly consisted of food and feed selling for US$55-110/tonne. Samson and co-workers (2000) conducted a preliminary economic analysis of pelleting bioenergy crops based on previously reported data; the results can be found in Table 2.2. It was stated that prices would drop if higher throughputs were realized. It was emphasized that a more thorough analysis of commercial pelleting operations was required to verify these results.

Table 2.2 Preliminary pelleting costs of wood, switchgrass, and short-rotation forestry (SRF) willow (CAD$/tonne); adapted from Samson and co-workers (2000).

	Wood pellets	Switchgrass pellets	SRF willow pellets
Feedstock	$34.35	$46.00-68.00	$58.00-85.00
Drying	$11.93	$0.00	$15.00
Direct pelleting cost	$59.00	$25.29-39.33	$39.33-50.57
Bagging	$19.25	$19.25	$19.25
Total cost	$124.53	$90.54-126.58	$131.25-169.82

In a study conducted in Spain, Tabarés and co-workers (2000), reported that the cost of forestry and industrial waste briquette production ranged from CAD$38-57/tonne (based on the 1999 average Euro/Canadian dollar exchange rate; Bank of Canada 2007). The bulk sale price at a pelleting plant was reported as US$85-133/tonne, while the public retail price was listed between US$286-476/tonne. Tabarés and co-workers (2000) identified two premises that heavily influence the alternate use of densified biomass over fossil fuels: firstly, raw material cost; second, distance to the point of consumption (transportation costs).

In a study focused on identifying the potential for growing biomass for paper and energy production in Ontario, Jannasch and co-workers (2001) estimated that the delivered fuel value of bagged wood pellets was CAD$215/tonne, while the delivered fuel value of bagged switchgrass pellets was CAD$210/tonne (CAD$70/tonne feedstock

cost, CAD$60/tonne pelleting cost, CAD$20/tonne transportation cost, and a 40% retail mark-up). It was noted that the cost of switchgrass pellets could be reduced to as low as CAD$175/tonne if bulk pellets were used, as bagging costs were CAD$20-25/tonne.

Samson and co-workers (2005) reported that in 2005, retail wood pellet prices reached approximately US$200/tonne in North America and US$250-300/tonne in Europe.

2.9 Summary

It is evident that research into biomass grind pelletization is a multi-discipline effort. Studies from pharmaceutics, food science, metallurgy, animal science, and engineering must be consulted to understand what happens when biomass grinds are subjected to elevated temperatures, pressure, and other process variables (i.e. steam). Much of the literature available on the influence of individual chemical constituents on pellet quality, and their subsequent binding mechanisms resulting from densification conditions, is generated from experimentation with purified compounds. In the case of biomass grinds, these compounds are dispersed in a complex matrix. The studies (generally from animal science and nutrition) investigating chemical interactions of constituents dispersed in a mixture typically only speculate as to how individual constituents help or hinder pellet quality. Therefore, there exists a need to investigate further the binding mechanisms of the pertinent chemical constituents, while evaluating how they influence pellet quality.

3 MATERIALS AND EXPERIMENTAL METHODS

The experimental methodology consisted of four distinct segments. Firstly, feedstocks were procured and their pertinent physical and chemical properties were evaluated. The second segment involved preparing (particle size reduction, moisture conditioning, etc.) the feedstocks for subsequent compression and relaxation studies; which constituted the third segment of the experimental methodology. Finally, infrared spectroscopic analysis was utilized to infer how chemical composition and availability influenced the behaviour and quality of the materials of interest.

3.1 Feedstock procurement and characterization

Following procurement of the biomass feedstocks of interest, an appropriate analysis of physical and chemical properties were required to identify which properties had to be altered (particle size and moisture content) to conform with the pre-established experimental methodology.

3.1.1 Materials

Two biomass feedstocks, poplar wood and wheat straw, were sourced from SunOpta BioProcess Inc. (Brampton, ON). The poplar wood was procured by SunOpta near Oshawa, ON, and was subsequently processed through a wood chipper. The raw poplar was therefore received at the University of Saskatchewan as chips. A portion of the poplar wood was subjected to steam explosion pretreatment by SunOpta, utilizing a temperature of 205°C, a steam pressure ranging between 1.66 and 1.73 MPa (gauge) (241-251 psig), and a retention time of 5.5 min. A hammer mill fitted with a 6.35 mm (0.25 in.) screen was used to grind the wheat straw by SunOpta prior to shipment. Also,

a temperature of 200°C, a steam pressure of 1.45 to 1.50 MPa (gauge) (211-218 psig), and a retention time of 4 min, was used to steam pretreat a portion of the wheat straw. Additional information could not be provided as it was proprietary at the time of the study. Both raw (untreated) and steam exploded (pretreated) portions of the two feedstocks (Figure 3.1) were received at the University of Saskatchewan.

Figure 3.1 Image of (i) poplar wood chips, (ii) pretreated poplar, (iii) wheat straw, and (iv) pretreated wheat straw.

3.1.2 Moisture content

The moisture content of the wheat straw and pretreated feedstocks received from SunOpta was evaluated via ASAE Standard S358.2 (ASABE 2006a). Poplar chip initial moisture content was evaluated via ASTM Standard D4442-92 (ASTM 2003a). The poplar chips and pretreated poplar were received at a moisture content of 21 and 56% wet basis (wb), respectively; while the wheat straw and pretreated wheat straw had a moisture of 12 and 60% wb, respectively. Three replicates of moisture analysis were performed for each sample. Due to their high moisture contents, the pretreated samples were dehydrated to less than 20% wb within 48 h of receiving them.

3.1.3 Particle size

ASAE Standard S424.1 (ASABE 2006b) was used to evaluate the particle size of the two untreated feedstocks, replicating each material three times. The geometric mean diameter (d_{gw}) of the sample and geometric standard deviation of particle diameter (S_{gw}) were calculated and reported. An initial particle size determination of the pretreated materials was not conducted, as no further particle size reduction was necessary.

3.1.4 Bulk density

The bulk density of each of the four initial feedstocks was determined by passing the material through a funnel which sat above a standard 0.5 L steel cup (SWA951, Superior Scale Co. Ltd., Winnipeg, MB). Blockages in the funnel were avoided by using a thin steel wire during biomass flow. Once the cup had filled, the excess was removed by moving a steel roller in a zig-zag pattern across the top of the cup. The mass within the cup was then determined. Three replicates were performed for each feedstock.

3.1.5 Chemical composition

A chemical analysis of the four biomass samples was conducted by SunWest Food Laboratory Ltd. (Saskatoon, SK). The analysis included the determination of protein, ash, fat, crude fiber, neutral detergent fiber (NDF), and acid detergent fiber (ADF). Lignin and starch were determined at the Crop Quality Laboratory of the Crop Development Center (University of Saskatchewan). AOAC method 2001.11 (AOAC International 2005a) was used to determine protein content, while AOAC method 967.04 (AOAC International 2005b) was followed to evaluate ash content. Fat (ether extract) content was found using AOAC method 920.39 (AOAC International 2005c), and the crude fiber was determined by AOAC method 962.09 (AOAC International 2005d). AOAC method 992.16 (AOAC International 2005e) was used to determine NDF content. Lignin and ADF content were found via AOAC method 973.18 (AOAC International 2005f). Starch content was enumerated using the method of Holm and co-workers (1986). Cellulose was calculated in the same manner as Mani and co-workers (2006a), using ADF and lignin composition (ADF–lignin). Hemicellulose was calculated using NDF and ADF, in the same manner as Mani and co-workers (2006a) (NDF–ADF).

3.1.6 Calorific (heating) value

The calorific (heating) value of biomass feedstocks are indicative of the energy they possess as potential fuels. The gross calorific value (higher heating value, HHV) and the net calorific value (lower heating value, LHV) at constant pressure measures the enthalpy change of combustion with and without water condensed, respectively (Demirbaş 2007). A Parr 1281 automatic isoperibol oxygen bomb calorimeter (Parr Instrument Company, Moline, IL) was used to determine the gross calorific value of the

pretreated and raw feedstocks. Pellets created from 15% wb feedstock (Chapter 3.3) were placed in a stainless steel crucible, and a cotton fuse was used to ignite the material in the vessel (bomb). The vessel was filled with oxygen, and was surrounded by a water jacket. Upon ignition, the released heat is transferred to the water jacket. The temperature rise in the water jacket was used by the calorimeter to calculate the heating value of the sample. Tests on each sample were replicated three times. ASTM Standard D5865-03 (ASTM 2003b) test method for gross calorific value of coal and coke, was used as a guideline for heating value testing.

3.2 Feedstock preparation and characterization

After an initial characterization of the four feedstocks, alteration of their particle size and moisture content (and subsequent physical characterization) was performed.

3.2.1 Grinding/particle size reduction

Grinding of the raw (untreated) feedstocks to the pre-determined particle sizes required for compression/relaxation testing was carried out prior to moisture conditioning, as moisture is lost during the grinding process. The grinding test apparatus (Figure 3.2) was used by Mani and co-workers (2004) to study the grinding performance of wheat straw, barley straw, corn stover, and switchgrass. It consists of a hammer mill (Glen Mills Inc., Clifton, NJ) powered by a 1.5 kW electric motor. Screen sizes of 0.8 and 3.2 mm were used; however, as the poplar wood was received as chips, they had to first be ground through a 6.4 mm screen. A known mass of material (either raw poplar chips or wheat straw) was passed through the mill, while the power consumption of the hammer mill was measured using a wattmeter (Ohio Semitronics International, OH). As

reported in the aforementioned study, the data logging system (LABMATE Data Acquisition and Control System, Sciemetric Instruments, ON) was connected to a computer, on which the data was recorded and stored at a rate of 2 points per second. The material passing through the hammer mill was pneumatically transferred to a cyclone where it was separated from the exhaust stream, passing through an air-lock at the bottom of the cyclone for efficient collection. This procedure was replicated three times for each combination of feedstock and screen size. The total energy was determined by integrating, using the trapezoid rule (Cheney and Kincaid 1980), the area under the power-time curve. The net energy was calculated by subtracting the energy required to run the hammer mill empty from the total energy. The net specific energy was then determined utilizing the pre-measured mass of material.

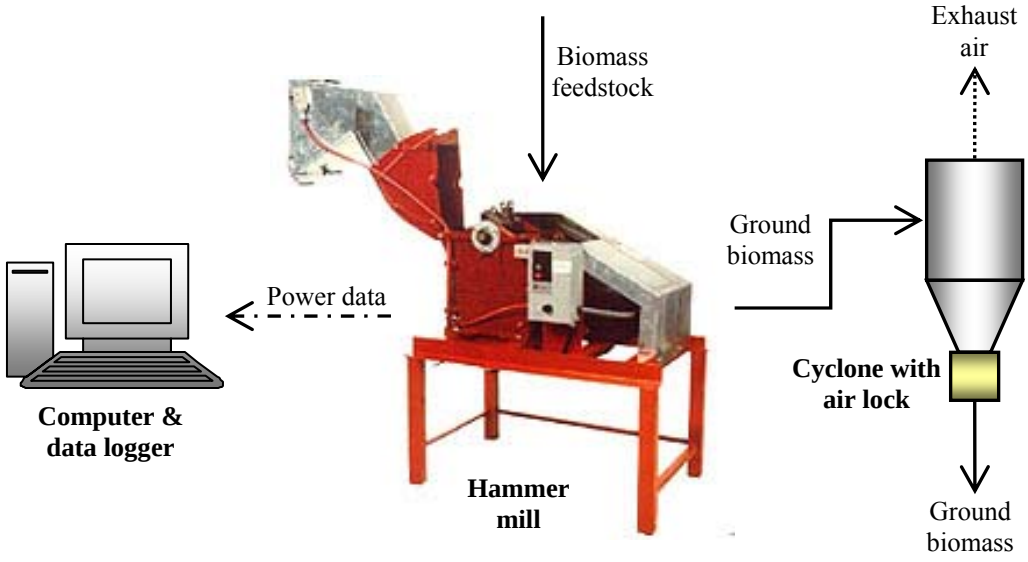

Figure 3.2 Schematic diagram of equipment used to grind the biomass feedstocks.

3.2.2 Moisture conditioning

Moisture content of the grinds and pretreated material was determined via ASTM Standard D3173-03 (ASTM 2003c). Both the grinds and the steam pretreated feedstocks were conditioned to moisture contents of 9 and 15% wb. In the case where the material was too dry, a calculated quantity of water was sprayed on the material and mixed thoroughly. Material that was too high in moisture was dehydrated in a conditioning chamber set to 80°C. Freshly conditioned materials were stored in sealed plastic bags in a conditioned room at 5°C for 48 hours prior to moisture content confirmation and subsequent usage.

3.2.3 Particle size

Particle size analysis was performed on the moisture conditioned grinds and pretreated feedstocks following ASAE Standard S319.3 (ASABE 2006c). A Ro-Tap sieve shaker (W. S. Tyler Inc., Mentor, OH) was used to separate the material through U.S. sieve numbers 4, 6, 8, 12, 14, 20, 40, 60, 80, 100, 140, and 200 (sieve opening sizes: 4.76, 3.36, 2.38, 1.70, 1.41, 0.840, 0.425, 0.250, 0.177, 0.150, 0.106, and 0.0754 mm, respectively). The geometric mean diameter (d_{gw}) of the sample and geometric standard deviation of particle diameter (S_{gw}) were calculated according to the aforementioned standard using three replicates for each feedstock.

3.2.4 Density

Bulk density measurement of the conditioned feedstocks followed the same methodology used for the bulk density measurement of the original feedstocks received from SunOpta, outlined in Chapter 3.1.4.

A gas multi-pycnometer (QuantaChrome, Boynton Beach, FL) was used to determine the particle density of the feedstocks by calculating the displaced volume of nitrogen gas by a known mass of material, following the method reported by Mani and co-workers (2004). Three replicate tests were performed on each sample.

3.3 Feedstock compression, relaxation, and quality evaluation

Following preparation and characterization of the four biomass feedstocks, the compression and relaxation characteristics were evaluated to satisfy the objectives presented in Chapter 1. Also, the quality of the compacted material (pellets) was evaluated by examining pellet density, dimensional expansion, and tensile strength.

3.3.1 Experimental design

Table 3.1 outlines the levels of the experimental factors selected for densification testing. A full factorial treatment design was employed. A preliminary study (Shaw and Tabil 2007) using flax shives, oat hulls, and wheat straw investigated the effect of particle size, moisture content, and temperature on the quality of pellets produced in an identical set-up. The results were used to identify which experimental factor levels to use in this full-scale study.

Table 3.1 Experimental variables, and their respective levels, for compression and relaxation testing.

Feedstock	Pressure (MPa)**	Process Temperature (°C)	Hammer mill screen size (mm)	Moisture content (% wb)
Poplar wood Wheat straw	31.6 (1000 N) 63.2 (2000 N)	70	0.8	9
Pretreated poplar wood* Pretreated wheat straw*	94.7 (3000 N) 126.3 (4000 N)	100	3.2	15

* Pretreatment refers to steam explosion

** Numbers in parentheses are the corresponding pre-set forces.

Sitkei (1986) reported typical pressures within commercial pellet mills range from 50 to 150 MPa. Therefore, pre-set loads of 1000, 2000, 3000, and 4000 N were selected, as they correspond to pressures of 31.6, 63.2, 94.7, 126.3 MPa, respectively. The pressures used during testing were near, or within, the range of those generated in a commercial pellet mill.

The upper process (cylinder die) temperature of 100°C was selected to approximate conditions during commercial pelleting. The lower limit of 70°C represented the temperature experienced in a commercial pellet mill, without the addition of steam.

A 3.2 mm hammer mill screen was selected because this was the upper limit for particle size at which relatively cohesive pellets could be formed in the plunger-cylinder apparatus under the conditions of the study. The lower limit of 0.8 mm was selected for contrast purposes. Also, some spectroscopic quality assessment methods (Chapter 3.4) required powdered material.

As mentioned in Chapter 2.2.2.1, Sokhansanj and co-workers (2005) identified that the optimum moisture content for pelleting cellulosic material ranges from 8 to 12% wb, and the optimum moisture content for starch and protein material (most animal feeds) can reach 20% wb. The purpose of selecting 9 and 15% wb as the two moisture contents for this set of experiments was to be able to significantly observe the effect of moisture on the quality of the pellets, specifically during spectroscopic analysis. Also, it was desired to see the effect of moisture on the compression and viscoelastic data.

3.3.2 Compression

Compression of the biomass feedstocks was carried out in a single-pelleter (plunger-cylindrical die) assembly (Figures 3.3 i and ii) modeled after the apparatus used by Adapa and co-workers (2002), Mani and co-workers (2006a), as well as Tabil and Sokhansanj (1996a, 1996b, and 1997). The steel apparatus has a 6.35 mm internal diameter and a 125 mm internal chamber height. Thermal compound (Wakefield Engineering Inc., Wakefield, MA) was coated on the outer surface of the die prior to wrapping the outer surface with copper shim stock. A dual element heating tape (Cole-Parmer Instrument Company, Vernon Hills, IL) was then wound evenly around the shim stock to provide the necessary heat. One type-T thermocouple, connected to the outer surface of the cylinder, was linked to a temperature controller which regulated the power input to the heater, thus allowing temperature control of the cylinder. Another type-T thermocouple, also connected to the outer cylinder wall, allowed verification of the cylinder temperature via a digital thermocouple reader.

A 6.35 mm plunger/piston cut from drill rod was fitted via a chuck attachment to an Instron Model 1011 (Instron Corp., Canton, MA) universal testing machine, which provided the means to compress the biomass. The cylindrical die slip-fit into a steel base upon which the materials were compressed. The Instron was equipped with a 5000 N load cell, and was linked to a computer which recorded the force-displacement data.

Approximately 0.5 g of the selected grind or pretreated feedstock was loaded into the die cylinder. The test commenced immediately upon filling the die with material. Pre-set loads of 1000, 2000, 3000, and 4000 N (31.6, 63.2, 94.7, and 126.3 MPa) were used to compress the charge material. The Instron was set to lower the plunger (and

compress the biomass) at a rate of 50 mm/min. No lubricant was used in the die, and the plunger-cylinder fit was such that it was assumed that there was negligible friction between the two components. Once the pre-set load was achieved, the plunger was stopped and held in position for 60 s, constituting the relaxation test. The material was retained in the die for approximately 4 min.

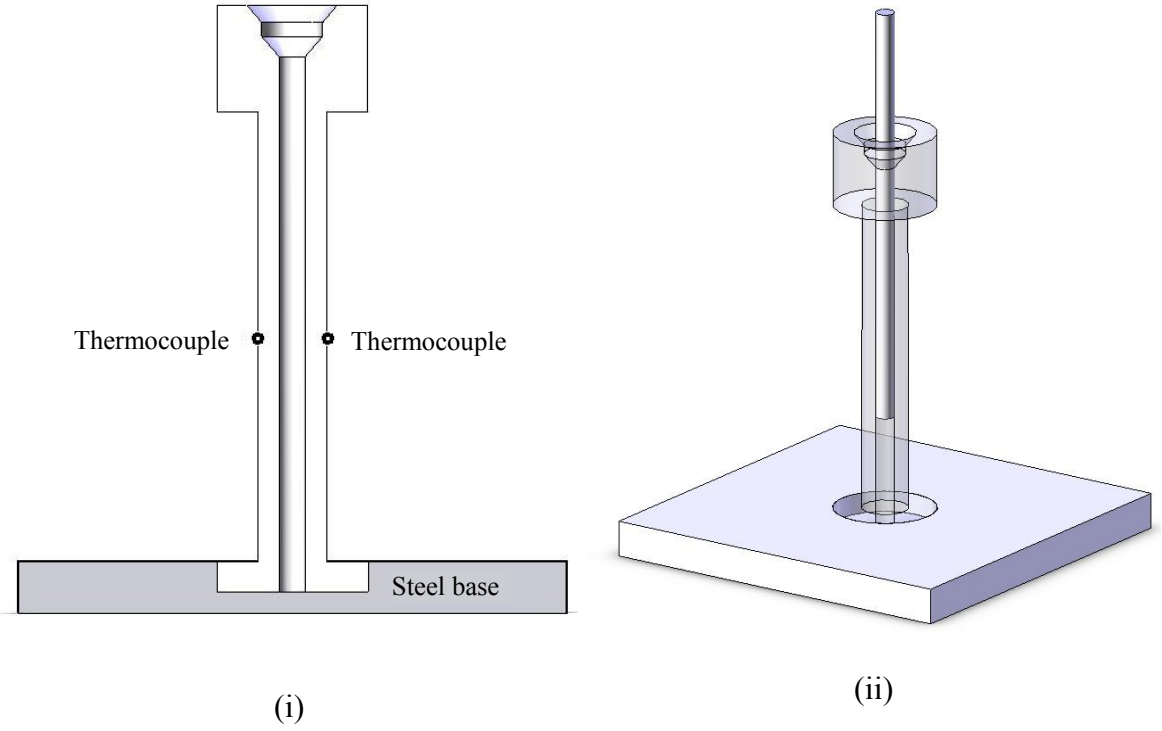

Figure 3.3 Sectional (i) and transparent (ii) views of the single-pelleter (plunger-die) apparatus.

Empirically derived compaction models by Walker (1923), Jones (1960), Cooper and Eaton (1962), and Kawakita (1971) (Chapter 2.4) were fitted to the transformed force-displacement data. Linear regression was used to fit the Walker (1923), Jones (1960), and Kawakita (1971) models to the data. The Cooper-Eaton (1962) model was

fitted to the data using TableCurve 2D (SYSTAT Software Inc., San Jose, CA) due to its non-linear nature. The Solver tool in Microsoft Excel (Microsoft Corporation, Redmond WA) was also used to verify the numeric values of the parameters in the Cooper-Eaton (1962) model.

Following the method of Mani and co-workers (2006b), the area under the force-displacement curve was integrated using the trapezoid rule (Cheney and Kincaid 1980) to determine the energy required for compression. The mass of the pellet allowed the determination of the specific energy of compression. For each combination of material and process variables, the compression test was replicated ten times.

3.3.3 Relaxation (viscoelastic properties)

As stated in the previous section, a 60 s relaxation test was carried out wherein the plunger was held at a constant strain, immediately after the pre-set compression load was attained. Force-time data was logged, and used to determine the asymptotic modulus (Chapter 2.5) values of the grinds and pretreated feedstocks. Peleg and Moreyra (1979) reported that the relative ease, with which relaxation data could be obtained, made it useful complementary information with respect to the properties of powders (grinds).

The viscoelastic properties of the feedstocks were characterized by asymptotic modulus, which is found by normalizing relaxation data, as opposed to the Maxwell model (or some variation of it). Peleg (1979) reported that the number of terms in a Maxwell-type model is between 2 and 4, and the constants can vary independently; therefore, the Maxwell model does not provide a significant advantage for comparing data obtained under different straining conditions, or for different materials. Peleg

(1979) justified the normalization of relaxation data as a mathematical representation of the physical phenomenon due to the fact that the number of constants is maintained at a minimum, the constants carry meaningful physical information, the equation is sensitive to physical changes in the system but insensitive to arbitrary parameters, and the mathematical form of the equation is simple. Similar to the compression test, the relaxation test was replicated ten times for each combination of material and process variables.

3.3.4 Pellet extrusion

Following relaxation test completion, the steel base was removed, and a steel plate with a centrally located hole was inserted under the cylinder for support. The newly formed pellet (or briquette) was ejected from the cylinder at 50 mm/min via load application using the plunger (Figure 3.4). During this time, the force-displacement data was recorded. Specific extrusion energy was calculated following the methodology of Mani and co-workers (2006b). The area under the force-displacement curve was integrated using the trapezoid rule (Cheney and Kincaid 1980); when combined with the pellet mass, it yielded the specific energy required for extrusion. For each combination of material and process variables, the extrusion test was replicated five times due to time constraints. Also, the study by Mani and co-workers (2006b) indicated 5 replicates for this particular measurement.

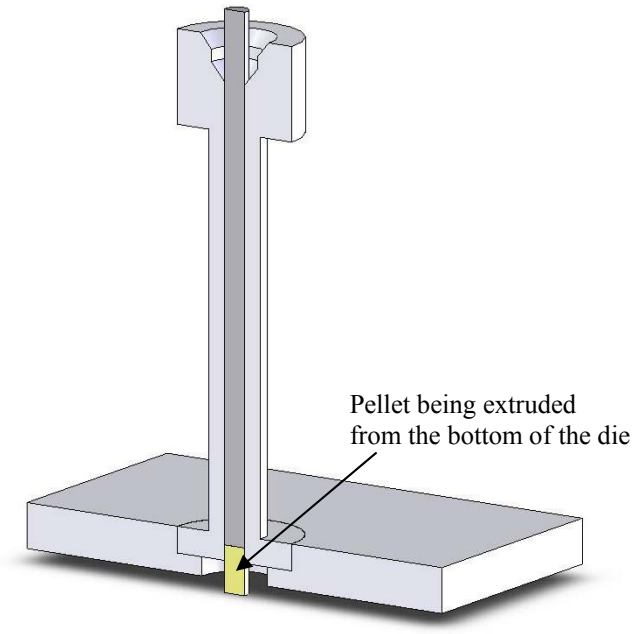

Figure 3.4 Sectional view of the plunder-die apparatus depicting pellet extrusion from the die.

3.3.5 Pellet density and dimensional expansion

Immediately after extrusion from the cylinder, the pellet diameter and length were measured using digital calipers. Pellet mass was also determined with a digital scale. Therefore, the (initial) density of each and every newly formed pellet was evaluated for each combination of material and process variables.

Additionally, the dimensions of each pellet formed using the highest load (4000 N) were measured again after a 14 day period to determine the diametral and longitudinal expansion, along with the relaxed pellet density. During the 14 day holding period, the pellets were stored in individually sealed plastic bags at ambient conditions (approximately 22°C).

3.3.6 Diametral compression

The tensile strength of the pellets created at the highest pressure was evaluated via the diametral compression test (Chapter 2.6). Pellets were first cut diametrally into 2 mm thick tablets. Pretreated feedstock pellets, due to their high strength, were cut using a diamond cutting wheel bit attached to a Dremel rotary tool (Robert Bosch Tool Corporation, Racine, WI). Pellets formed from raw feedstock were cut to the appropriate thickness using a scalpel.

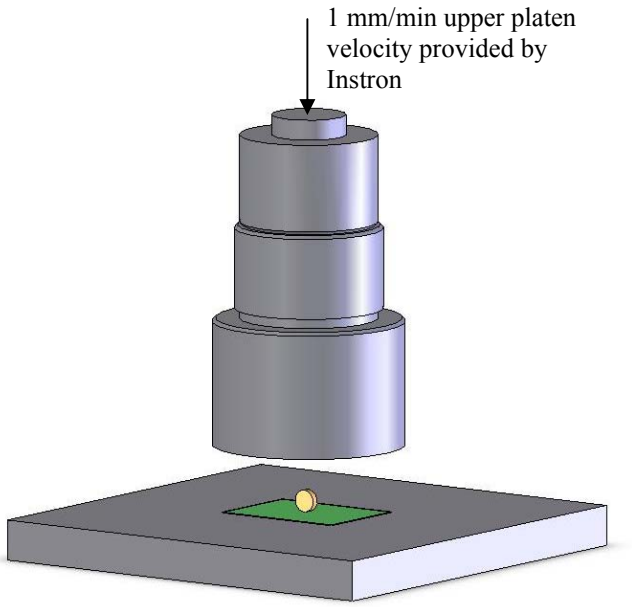

Figure 3.5 Diametral compression test apparatus depicting the upper platen, which is lowered to compress the tablets resting on cardboard fastened to the lower platen.

Figure 3.5 depicts the experimental set-up used in the diametral compression test. Two layers of 'business-card' paper/cardboard were fastened to the lower steel plate and the upper steel plunger. An individual tablet was positioned, on edge, on the lower plate. The upper plunger compressed the tablet at a speed of 1 mm/min until failure was

observed. The fracture force was recorded, and used to determine the tensile strength of the tablet, providing that tensile failure was observed. Only pellets produced by compression at the 4000 N load were analyzed in this study.

Tabil and Sokhansanj (1996b) reported a high variability in breaking force when evaluating the tensile strength of alfalfa pellets. Therefore, the equation used by Patil and co-workers (1996) (Equation 3.1) was used to determine an appropriate sample size.

$$n = \frac{(t_s v)^2}{B^2} \tag{3.1}$$

where: n = sample size (number of replicates)

t_s = value of student's t for two sided limits at 95% probability level and infinite degrees of freedom, 1.96 for population

v = estimate of the coefficient of variation

B = the value of allowable variation

The coefficient of variation (v) of tensile strength was taken from diametral compression data (alfalfa pellets) reported by Tabil and Sokhansaj (1996b). The highest coefficient of variation (0.146 for alfalfa pellets made from intermediate quality grinds) of the pellets compressed to 4000 N was used in order to provide a worst case scenario estimate. The sample size (n) yielded 8 when the value of allowable variation (B) was allowed to slightly exceed 10% (Patil and co-workers (1996) used 15%). This was considered acceptable, as there were only a maximum of ten pellets that could be used for each combination of variables. Therefore, the diametral compression test was

replicated eight times for each combination of material variables and pelleting temperature, which left two extra pellets incase tensile failure was not observed in any of eight used in this test.

3.4 Fourier transform infrared photoacoustic spectroscopy

Fourier transform infrared photoacoustic spectroscopy (FT-IR PAS) was used as a means of identifying the chemical composition differences of the untreated and pretreated feedstocks. The infrared spectra of the raw and pretreated, ground and pelleted, feedstocks were measured using a Bruker Optics IFS66vs unit (Bruker Optiks Inc., Billerica, MA) and a MTEC Model 300 photoacoustic detector (MTEC Photoacoustics Inc., Ames, IA) located at the Canadian Light Source – Synchrotron at the University of Saskatchewan. Feedstocks conditioned to 9% wb were analyzed due to the fact that moisture in the 15% wb materials provided too much interference at the H_2O absorption band. The spectra for each sample (~5 mg) were recorded from 4000 to 400 cm^{-1}, with a resolution of 4 cm^{-1}. OPUS 4.2 (Bruker Optiks Inc., Billerica, MA) computer software was used to obtain and analyze the FT-IR PAS data. The 'Peak Picking' tool was used with a 3% threshold to identify the major peaks and resolve their relative intensities.

4 RESULTS AND DISCUSSION

Results from the experimentation outlined in the previous chapter are presented in this chapter. The received materials (poplar, pretreated poplar, wheat straw, and pretreated wheat straw) had physical property and chemical compositional analyses performed on them. The untreated materials were then ground, and the specific energy for grinding was measured. Further physical characterization of the ground untreated and pretreated feedstocks were undertaken prior to compression/relaxation testing in a closed-end cylindrical plunger-die assembly. Previously reported compression models were fitted to compression data, the relaxation behaviour of the grinds in the die was characterized, and the specific energy required to compress the grinds and extrude the resultant pellet was evaluated. A dimensional expansion test and diametral compression test were used to evaluate the quality of the pellets. Fourier transform infrared photoacoustic spectroscopy was utilized to identify differences between the untreated and pretreated feedstocks.

4.1 Feedstock physical properties and chemical composition

Table 4.1 lists the physical properties of the feedstocks received from SunOpta Inc. Poplar chips had a geometric mean diameter of 32.50 mm, and a geometric standard deviation of 1.61 mm. A 1.85 mm geometric mean diameter was found for the raw wheat straw, along with a 2.23 mm geometric standard deviation. The bulk density of the poplar and pretreated poplar were 192 and 147 kg/m^3, respectively; while the wheat straw and pretreated wheat straw had bulk densities of 69 and 257 kg/m^3, respectively.

Table 4.1 Physical properties of poplar (untreated and pretreated) and wheat straw (untreated and pretreated), as received.

Feedstock	Initial moisture content (% wb)	Geometric mean particle diameter, d_{gw} (mm)*	Bulk density (kg/m^3)**
Poplar	21.1	32.50 (1.61)	192.2 (0.9)
Pretreated poplar	55.6	-	146.7 (2.8)
Wheat straw	11.7	1.85 (2.23)	68.6 (3.7)
Pretreated wheat straw	60.3	-	257.3 (4.3)

* Numbers in parenthesis are geometric standard deviations of particle diameter, S_{gw} (n = 3)
** Numbers in parentheses are standard deviations (n = 6)

The chemical composition of the four feedstocks is shown in Table 4.2. Although the amount is low, the wheat straw feedstocks have six to seven times more protein than the poplar feedstocks; along with a significantly higher ash content. Perhaps the most notable difference was the hemicellulose content following pretreatment. The chemical constituents reported account for a higher percentage of the composition of the untreated feedstocks, as opposed to the pretreated feedstocks. This is most likely due to the hemicellulose hydrolysis that occurs during pretreatment. The evidence suggests that simple sugars may be present in the pretreated samples that were not tested for. The steam pretreatment process evidently removed/converted a significant portion of the hemicellulose from both the poplar and wheat straw. This conforms with reports in literature, as Toussaint and co-workers (1991) reported that during the steam explosion process, the hemicellulose is hydrolysed and becomes water-soluble, thus facilitating removal. Also, the relative amount of lignin was increased in the pretreated feedstocks due to the removal/loss of other chemical constituents during the pretreatment process. The steam explosion process melts and depolymerizes the lignin (Toussaint et al. 1991). Both the poplar and the wheat straw feedstocks were therefore classified as lignocellulosic materials due to the fact that cellulose, hemicellulose (in the untreated

materials), and lignin made up the most significant portion of their chemical composition.

Table 4.2 Chemical composition of poplar (untreated and pretreated) and wheat straw (untreated and pretreated).

Composition (% dry mater)	Poplar	Pretreated poplar	Wheat straw	Pretreated wheat straw
Starch	2.28	1.95	2.30	2.29
Protein	0.51	0.54	3.22	3.59
Fat (ether extract)	1.08	1.63	1.20	1.01
Ash	0.20	0.54	4.63	4.02
Cellulose	66.71	55.37	52.04	47.31
Hemicellulose	24.52	3.14	30.12	2.64
Lignin	8.43	13.04	7.79	11.67

Table 4.3 shows the gross calorific values of the four feedstocks. The raw and pretreated poplar feedstocks had higher gross calorific values (17.76 and 18.95 MJ/kg, respectively) than the raw and pretreated wheat straw feedstocks (17.04 and 17.67 MJ/kg, respectively). This difference was no doubt due to the chemical composition of the two feedstocks; specifically, the ash content. Sheng and Azevedo (2005) proposed a model (from proximate analysis) to predict the gross calorific value of biomass fuels based on the ash content, in which the calorific value of a biomass fuel decreases with increasing ash content. The poplar feedstocks had significantly less ash than the wheat straw feedstocks, thus they have a higher gross calorific value. Also, steam pretreatment of the materials increased the gross calorific value of both biomass materials, potentially due to the higher lignin content of the pretreated materials. Demirbaş (2001) found that the heating value of biomass fuels increased linearly with lignin content.

Table 4.3 Gross calorific values of poplar (untreated and pretreated) and wheat straw (untreated and pretreated).

Feedstock	Moisture content (% wb)	Gross calorific value (MJ/kg)*
Poplar	8.2	17.76 (0.20)
Pretreated poplar	6.7	18.95 (0.08)
Wheat straw	8.0	17.04 (0.11)
Pretreated wheat straw	8.1	17.67 (0.14)

* Numbers in parentheses are standard deviations (n = 3)

Mani et al. (2004) reported that the heating value of wheat straw at 6.2% wb was 16.81 MJ/kg, slightly lower than the 17.04 MJ/kg measured in this study. Hale (1933) reported that the calorific value of common Canadian hardwoods were approximately 19.5 MJ/kg oven-dry. The moisture content will significantly influence the higher heating value of biomass, and was considered a source of variation. Pellets created from 15% wb moisture feedstocks (Chapter 3.3) were used to determine the higher heating values. As shown in Table 4.3 the feedstocks lost a small amount of moisture throughout the compression process, conceptually due to the heat added during the process. Demirbaş (2007) reported that as moisture content increases in a biomass fuel, the gross calorific value decreases. The high gross calorific value of pretreated poplar may be due, in part, to its lower moisture at the time of calorific value testing relative to the other three feedstocks.

4.2 Specific energy required for grinding

The grinding process is an important unit operation prior to densification. Quantification of the specific energy required to grind biomass materials is important in the overall energy requirement for pelleting. Outlined in Table 4.4 are the mean specific energy requirements required to grind the two untreated feedstocks. Due to the differing initial feedstock conditions (moisture and particle size) and two stage grinding required

for poplar, it is difficult to compare the specific energy requirements for grinding the two materials. However, the specific energy consumption during grinding of poplar through 0.8 and 3.2 mm screens was 120.7 kW h t^{-1} and 188.5 kW h t^{-1}, respectively. These values include the specific energy required to grind the poplar chips using a 6.4 mm screen (73.0 kW h t^{-1}). Specific energies of 78.8 and 11.3 kW h t^{-1} were required to grind the wheat straw through screen openings of 0.8 and 3.2 mm, respectively. The hammer mill required significantly more energy to reduce the particle size of the poplar chips to the appropriate size, than wheat straw, which is intuitive for a number of reasons. First, and perhaps most significant, the initial particle size of the poplar chips were considerably higher than wheat straw. Also, the initial moisture content of the poplar chips were higher than wheat straw. Annoussamy and co-workers (2000) found that an increase in moisture content also increased the shear strength of wheat straw. Mani and co-workers (2004) confirmed this, as they found that a higher moisture content increased the specific energy consumption required for grinding. As the hammer mill screen opening size decreased, the specific energy consumption increased. This is intuitive, as more energy is required to further reduce feedstock particle size.

Table 4.4 Specific energy required for grinding raw poplar and wheat straw in a hammer mill.

Feedstock	Initial moisture content (% wb)	Initial geometric mean particle diameter (mm)	Hammer mill screen size (mm)	Mean specific energy req'd for grinding (kW h t^{-1})*	Post-grinding moisture content (% wb)
Poplar	21.1	32.50	0.8 (+ 6.4)	188.54 (5.23)	4.3
			3.2 (+ 6.4)	120.66 (2.87)	7.3
			6.4	72.95 (4.26)	-
Wheat straw	11.7	1.85	0.8	78.77 (0.62)	5.2
			3.2	11.33 (0.86)	7.4

* Numbers in parentheses are standard deviations (n = 3)

Moisture loss occurred during the grinding process. Poplar incurred higher moisture losses than wheat straw due to the fact that a two stage grinding process was required. Also, increased moisture losses resulted from using a smaller screen size opening, due to an increased material retention time in the grinder and increased particle surface area.

Conditioning material between 10 and 15% wb, Esteban and Carrasco (2006) determined that the specific energy requirements to grind poplar chips in a primary hammer mill were 82.6, 37.7, 27.5, 12.9, and 11.7 kW h t^{-1} (oven dry) using 1.5, 4, 6, 8, and 10 mm screen openings, respectively. Holtzapple and co-workers (1989) reported equipment manufacturer estimates of the energy requirements for mechanical particle size reduction. It was reported that 0.18 MJ/kg (50 kW h t^{-1}) of energy was required by a two-stage hammer mill to reduce the particle size of poplar chips 25.4 x 6.4 mm to 2 mm in length (passing through a U.S. number 10 standard mesh). However, no indication of moisture content was given. Mani and co-workers (2004) evaluated the specific energy requirements required to grind wheat straw, among three other feedstocks. At 12% wb, the specific grinding energy was 45.3 and 24.7 kW h t^{-1} for hammer mill screen openings of 0.8 and 3.2 mm, respectively. It is possible that the feeding rates into the hammer mill were different.

4.3 Physical properties of ground and conditioned feedstocks

The physical properties of the feedstocks ground and conditioned for compression and relaxation analysis are presented in Table 4.5. The bulk density of the raw feedstocks decreased with an increase in moisture content and screen size; however, the bulk density increased with moisture content for the pretreated feedstocks. Poplar

had a higher bulk density than wheat straw; however, pretreated wheat straw had a higher bulk density than pretreated poplar. Pretreated poplar had lower bulk density values than untreated poplar, while pretreated wheat straw had higher bulk density values than untreated wheat straw. Particle density of the feedstocks decreased with and increase in moisture content and screen size in all instances.

Table 4.5 Physical properties of poplar (untreated and pretreated) and wheat straw (untreated and pretreated) prepared for compression and relaxation testing.

Feedstock	Screen size (mm)	Moisture content (% wb)	Bulk density (kg/m^3)*	Particle density (kg/m^3)**	Geometric mean particle diameter, d_{gw} (mm)***
Poplar	0.8	9	151.57 (1.01)	1428.69 (3.77)	0.29 (0.23)
		15	142.14 (1.25)	1350.33 (21.06)	0.30 (0.24)
	3.2	9	120.35 (3.35)	1370.98 (21.91)	0.69 (0.57)
		15	116.59 (2.02)	1353.08 (21.87)	0.77 (0.55)
Pretreated poplar	-	9	94.82 (1.48)	1324.64 (4.02)	0.76 (0.89)
		15	101.71 (1.68)	1313.42 (18.36)	0.84 (0.85)
Wheat straw	0.8	9	117.57 (0.90)	1382.79 (19.10)	0.29 (0.22)
		15	113.11 (0.64)	1333.41 (18.62)	0.30 (0.23)
	3.2	9	88.00 (1.67)	1224.18 (27.58)	0.58 (0.35)
		15	90.80 (1.91)	1169.32 (23.68)	0.60 (0.38)
Pretreated wheat straw	-	9	125.21 (1.43)	1372.90 (7.70)	1.37 (0.93)
		15	131.49 (1.18)	1350.47 (17.51)	1.33 (0.88)

* Numbers in parentheses are standard deviations (n = 6)
** Numbers in parentheses are standard deviations (n =3)
*** Numbers in parentheses are geometric standard deviations of particle diameter, S_{gw} (n = 3)

Increasing the moisture content served to increase the geometric mean particle diameter of the feedstocks, except for the pretreated wheat straw. Both the untreated feedstocks had identical geometric mean diameters after passing through the hammer mill fitted with the 0.8 mm screen. The poplar however, had a higher geometric mean diameter than wheat straw after passing the 3.2 mm screen. Larger particle sizes were found for the pretreated feedstocks, with pretreated wheat straw having the highest.

4.4 Compression and relaxation behaviour of biomass feedstocks

Results from compression testing, compression modeling, relaxation testing, and the calculation of specific energy required for compression and extrusion from the die are presented and discussed in this section.

4.4.1 Compression behaviour and modeling

Typical force-time relationships for compression/relaxation testing of each of the four pre-set loads are depicted in Figure 4.1. The compression force increases gradually and spikes just prior to achieving the pre-set maximum load for each test. The maximum load achieved was always slightly higher than the pre-set value due to momentum effects of the Instron crosshead. Following the peak compressive load, the force relaxed (constant strain test) to an asymptotic value. Typical force-time plots for the four feedstocks are shown in Figure 4.2.

Table 4.6 outlines the model constants obtained by fitting the Walker (1923) model to the compression data. Figures A.1 and A.2 illustrate typical Walker (1923) plots for the poplar and wheat straw feedstocks, respectively. Coefficient of determination (R^2) values for the model ranged from 0.61 (pretreated wheat straw, 100°C, and 15% wb) to 0.97 (poplar, 70°C, 0.8 mm, and 9% wb), and standard errors ranged between 0.02 and 0.07. The model constant m_1, which happens to be the slope, is indicative of a material's compressibility, which is to say, the change in density of a powder due to pressure (Peleg 1973). Therefore, a higher magnitude of the absolute value of m_1 signifies a higher compressibility. The absolute values of compressibility ranged from 0.1093 (pretreated wheat straw, 70°C, and 15% wb) to 0.2945 (wheat straw, 70°C, 0.8 mm, and 9% wb).

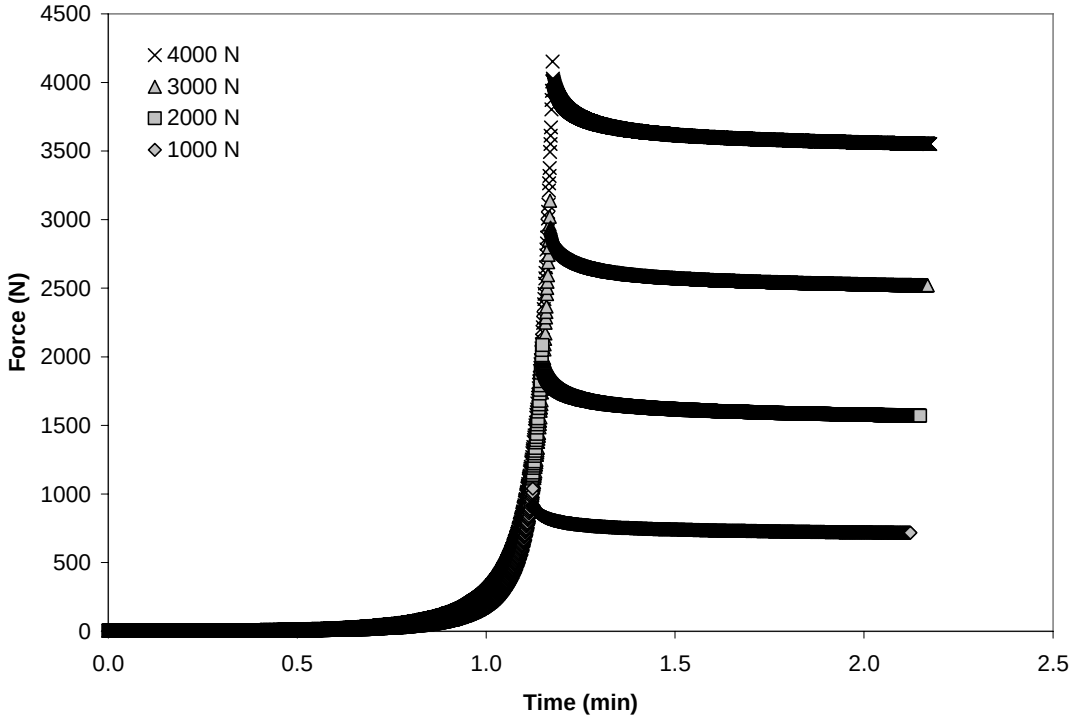

Figure 4.1 Typical force-time curves of the four pre-set loads resulting from compression (and relaxation) testing.

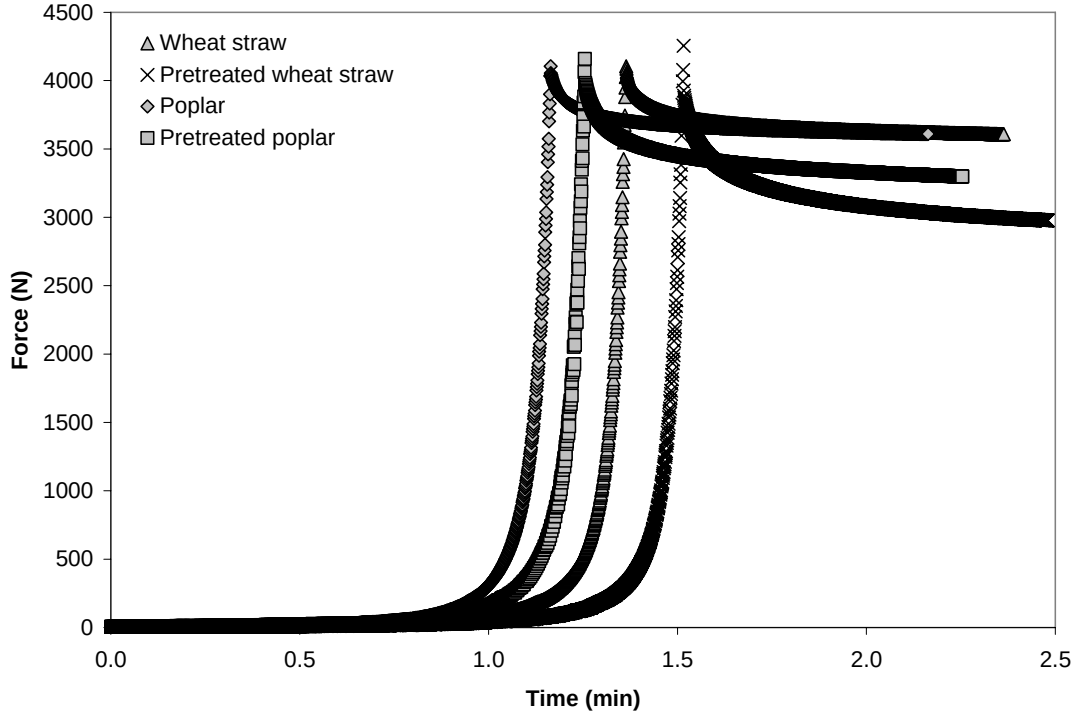

Figure 4.2 Typical force-time curves of the four biomass feedstocks during compression (and relaxation) testing at the highest pre-set load (4000 N).

Table 4.6 Walker (1923) empirical compression model constants [$V_R = m_1 \cdot \ln P + z_1$].

Feedstock	Temperature (°C)	Screen size (mm)	Moisture (% wb)	m_1	z_1	R^2	Standard error
Poplar	70	0.8	9	-0.2289	5.2133	0.97	0.02
			15	-0.1849	4.3251	0.94	0.03
		3.2	9	-0.2325	5.2551	0.95	0.03
			15	-0.1976	4.5850	0.91	0.03
	100	0.8	9	-0.2611	5.7955	0.83	0.06
			15	-0.2227	5.0075	0.81	0.06
		3.2	9	-0.2603	5.7574	0.82	0.07
			15	-0.2371	5.3073	0.86	0.05
Pretreated poplar	70	-	9	-0.2309	5.2034	0.94	0.03
			15	-0.1480	3.5859	0.84	0.04
	100	-	9	-0.2010	4.6402	0.71	0.07
			15	-0.1324	3.2916	0.72	0.05
Wheat straw	70	0.8	9	-0.2945	6.3904	0.94	0.04
			15	-0.1922	4.4400	0.91	0.03
		3.2	9	-0.2592	5.6426	0.95	0.03
			15	-0.1931	4.3648	0.89	0.04
	100	0.8	9	-0.2842	6.1926	0.85	0.06
			15	-0.2677	5.8312	0.80	0.07
		3.2	9	-0.2846	6.1100	0.83	0.07
			15	-0.2528	5.4547	0.80	0.07
Pretreated wheat straw	70	-	9	-0.2277	5.1481	0.91	0.04
			15	-0.1093	2.8855	0.66	0.05
	100	-	9	-0.1769	4.1695	0.73	0.06
			15	-0.1110	2.9075	0.61	0.05

The Walker (1923) empirical model indicated that increasing the cylinder temperature served to increase the compressibility of the untreated feedstocks. Compressibility was not affected by the particle size of the materials. Compressibility decreases with an increase in moisture content. Peleg and Mannheim (1973) reported that the cohesion of sucrose powders increased with moisture content, and that cohesive powders have higher compressibilities. However, the loads in that study ranged from 0.004 to 0.059 MPa; significantly lower than the loads used in this study. It is speculated that the influence of moisture on compressibility in this study (higher loads) can be explained by the fact that moisture increased the packing density of the feedstocks at lower pressures (Figures A.1 to A.4). This may have been due to increased plasticization of the particles and molecular chains, allowing for increased deformation. At higher

pressures, this effect was mitigated, thus resulting in higher compressibilities for the feedstocks with higher moisture contents. Pretreatment decreased the compressibility of both feedstocks. Wheat straw was more compressible than poplar; however, pretreated poplar was more compressible than pretreated wheat straw.

Model constants obtained from fitting the Jones (1960) model to the compression data is listed in Table 4.7. Typical Jones (1960) model plots can be found for the poplar and wheat straw feedstocks in Figures A.3 and A.4, respectively. Just as in the Walker (1923) model, the slope m_2 is representative of compressibility. Coefficient of determination (R^2) values ranged from 0.58 (pretreated wheat straw, 100°C, and 15% wb) to 0.96 (poplar, 70°C, 0.8 mm, and 9% wb) and standard errors ranged from 0.02 to 0.07. Compressibility (m_2) values ranged from 0.1131 (pretreated wheat straw, 70°C, and 15% wb) to 0.2834 (wheat straw, 100°C, 3.2 mm, and 9% wb).

The Jones (1960) model demonstrated that temperature had more of an effect on the untreated feedstocks (as opposed to the pretreated feedstocks) to increase the compressibility. This may be due to an increased moisture loss at the higher temperature. The effect of temperature on the compressibility of the pretreated feedstocks is less clear. Particle size shows no appreciable effect on compressibility. Decreasing the sample moisture content increased compressibility. Wheat straw had a higher compressibility than poplar. Again, pretreatment of the feedstocks yielded lower compressibilities. The pretreated poplar had higher compressibility values than the pretreated wheat straw.

The results from the Walker (1923) and Jones (1960) models are, for the most part, in agreement, despite minor discrepancies between the relative compressibility in a few cases. There appears to be no chemical explanation for the compressibility of the

feedstocks. A potential reason could be the relative particle sizes of the four feedstocks, wheat straw had the lowest geometric mean diameters (at each combination of hammer mill screen size and moisture), followed by poplar, pretreated poplar, and wheat straw (identical to the order of relative compressibilities). However, no significant difference in compressibility was found between the material ground through a 0.8 mm hammer mill screen and those ground through a 3.2 mm screen.

Table 4.7 Jones (1960) empirical compression model constants [$\ln \rho = m_2 \cdot \ln P + z_2$].

Feedstock	Temperature (°C)	Screen size (mm)	Moisture (% wb)	m_2	z_2	R^2	Standard error
Poplar	70	0.8	9	0.2108	3.3872	0.96	0.02
			15	0.1875	3.8425	0.93	0.03
		3.2	9	0.2192	3.2159	0.95	0.03
			15	0.1947	3.6848	0.90	0.03
	100	0.8	9	0.2339	2.9727	0.82	0.06
			15	0.2226	3.2130	0.80	0.06
		3.2	9	0.2362	2.9116	0.81	0.06
			15	0.2272	3.0909	0.85	0.05
Pretreated poplar	70	-	9	0.2218	3.1577	0.93	0.03
			15	0.1614	4.3624	0.85	0.04
	100	-	9	0.1937	3.6869	0.69	0.07
			15	0.1482	4.6142	0.70	0.06
Wheat straw	70	0.8	9	0.2683	2.3275	0.95	0.03
			15	0.1986	3.6470	0.91	0.03
		3.2	9	0.2663	2.3508	0.95	0.03
			15	0.2202	3.2257	0.88	0.04
	100	0.8	9	0.2618	2.4572	0.84	0.06
			15	0.2624	2.4727	0.80	0.07
		3.2	9	0.2834	2.0357	0.82	0.07
			15	0.2745	2.2378	0.79	0.07
Pretreated wheat straw	70	-	9	0.2168	3.2824	0.92	0.04
			15	0.1131	5.2750	0.88	0.02
	100	-	9	0.1791	4.0234	0.72	0.06
			15	0.1261	5.0369	0.58	0.06

Constant values for the Kawakita (1971) model are shown in Table 4.8. Representative Kawakita model graphs are located in Figures A.5 and A.6 for the poplar and wheat straw feedstocks, respectively. Coefficient of determination (R^2) values were 1.00 in all cases but one, and standard errors ranged from 0.92 to 3.48 MPa. The

constant *a* in the Kawakita (1972) equation was first reported to be equal to the initial porosity of the powder; however, this is not always the case in practice, due to the nonlinearity of the plots (Denny 2002). Figure A.7 is a scatter plot showing the relationship between the constant *a* and the theoretical initial porosity. It can be seen that there is a weak relationship; however, the constant *a* consistently overestimated the theoretical initial porosity of the biomass grinds.

Table 4.8 Kawakita (1971) empirical compression model constants [$P/C = 1/ab + P/a$].

Feedstock	Temperature (°C)	Screen size (mm)	Moisture (% wb)	*a*	Initial porosity	1/*b* (MPa)	R^2	Standard error
Poplar	70	0.8	9	0.8701	0.8576	1.7191	0.99	3.48
			15	0.8674	0.8442	1.4138	1.00	2.32
		3.2	9	0.8918	0.8738	1.7029	1.00	1.41
			15	0.8948	0.8768	1.3469	1.00	1.30
	100	0.8	9	0.8584	0.8663	-0.0311	1.00	2.41
			15	0.8884	0.8566	2.1950	1.00	2.93
		3.2	9	0.8938	0.8780	1.5073	1.00	1.71
			15	0.8954	0.8834	0.9346	1.00	1.38
Pretreated poplar	70	-	9	0.8838	0.8723	0.9232	1.00	1.38
			15	0.8942	0.8730	0.5078	1.00	1.94
	100	-	9	0.8918	0.8740	1.4043	1.00	1.63
			15	0.8954	0.8766	0.2434	1.00	2.13
Wheat straw	70	0.8	9	0.8995	0.8811	1.8215	1.00	0.92
			15	0.9017	0.8801	1.1690	1.00	0.98
		3.2	9	0.9286	0.8869	2.6693	1.00	1.08
			15	0.9235	0.8789	2.1945	1.00	1.20
	100	0.8	9	0.9022	0.8851	1.5478	1.00	1.07
			15	0.9167	0.8872	1.9736	1.00	1.18
		3.2	9	0.9239	0.8802	3.0502	1.00	2.02
			15	0.9334	0.8773	3.0257	1.00	1.00
Pretreated wheat straw	70	-	9	0.8845	0.8702	1.2060	1.00	0.95
			15	0.8942	0.8737	0.4956	1.00	1.91
	100	-	9	0.8855	0.8715	0.5774	1.00	1.67
			15	0.8980	0.8729	0.8156	1.00	2.34

The constant 1/*b* (with units of MPa) was also reported by Kawakita (1977) to represent, or be related to, the yield strength of the powder particle. Sonnergaard (2001) however, did not observe this phenomenon when evaluating the compression of

pharmaceutical powders. The author did note that high values of this parameter indicated a high degree of compressibility for pharmaceutical powders. This is in agreement with the compressibility values defined by the Walker (1923) and Jones (1960) models.

Wheat straw had higher *a* values than the other three feedstocks. Pretreatment served to decrease the value of 1/*b*, and as a general trend, wheat straw had higher 1/*b* values than poplar. Temperature did not appear to have any correlation to the model constants. Higher *a* values were found by increasing the hammer mill screen size, thus supporting that this constant coefficient is related to the initial porosity of the grind. As a general rule, the value of 1/*b* decreases with an increase in moisture content. More work should be done to evaluate the Kawakita (1971) coefficients for compression of biomass grinds.

Table 4.9 shows that the numerical values for the Cooper-Eaton (1962) model. Coefficient of determination (R^2) values ranged from 0.45 (pretreated wheat straw, 100°C, and 15% wb) to 0.98 (wheat straw, 70°C, 0.8 mm, and 15% wb), and the standard errors were between 0.0023 and 0.0111. Typical Cooper-Eaton (1962) plots for the poplar and wheat straw feedstocks are depicted in Figures A.8 and A.9, respectively. The authors explained that the dimensionless constants h_1 and h_2 indicate the fraction of theoretical compaction that is achieved by particle rearrangement and fractionation/deformation, respectively. Tabil and Sokhansanj (1996a) observed greater h_1 values during compression studies of alfalfa grinds. This was attributed to the fact that h_2 may have included elastic deformation, which occurs at lower pressures than plastic deformation. There appeared to be no correlation between the coefficients h_1 and h_2, and the independent experimental variables. Also, no clear trends were identified between the coefficients and the feedstocks.

Table 4.9 Cooper-Eaton (1962) empirical compression model constants [$(V_0\text{-}V)/(V_0\text{-}V_s) = h_1 \cdot \exp(-c_1/P) + h_2 \cdot \exp(-c_2/P)$].

Feedstock	Temperature (°C)	Screen size (mm)	Moisture (% wb)	h_1	h_2	c_1 (MPa)	c_2 (MPa)	$h_1 + h_2$	R^2	Standard error
Poplar	70	0.8	9	0.9355	0.1228	10.707	-27.501	1.0582	0.94	0.0056
			15	0.1035	0.9699	-31.569	10.357	1.0734	0.95	0.0045
		3.2	9	0.5125	0.5125	3.956	-0.023	1.0250	0.89	0.0064
			15	0.9366	0.1222	10.111	-28.384	1.0588	0.96	0.0031
	100	0.8	9	0.5128	0.5128	2.101	2.101	1.0256	0.82	0.0092
			15	0.5197	0.5197	2.043	2.043	1.0395	0.76	0.0110
		3.2	9	0.5142	0.5142	2.074	2.074	1.0284	0.86	0.0080
			15	0.9629	0.0775	0.393	41.803	1.0403	0.85	0.0075
Pretreated poplar	70	-	9	0.6842	0.3756	15.919	12.479	1.0598	0.97	0.0036
			15	0.9514	0.1217	-1.178	74.007	1.0731	0.83	0.0057
	100	-	9	0.5138	0.5138	1.660	1.660	1.0275	0.72	0.0099
			15	0.9961	0.0585	0.036	78.434	1.0546	0.61	0.0096
Wheat straw	70	0.8	9	0.5143	0.5143	1.235	3.227	1.0287	0.92	0.0063
			15	0.1129	0.9472	-28.318	9.057	1.0601	0.98	0.0023
		3.2	9	0.9861	0.0703	6.682	-30.188	1.0564	0.95	0.0043
			15	0.9622	0.1109	9.050	-28.980	1.0731	0.88	0.0056
	100	0.8	9	0.5144	0.5144	2.071	2.098	1.0288	0.85	0.0082
			15	0.5171	0.5171	1.924	1.924	1.0342	0.78	0.0095
		3.2	9	0.5213	0.5213	2.272	2.272	1.0426	0.82	0.0103
			15	0.5250	0.5250	2.021	2.021	1.0500	0.79	0.0099
Pretreated wheat straw	70	-	9	0.1161	0.9414	60.214	-0.342	1.0575	0.91	0.0062
			15	0.9433	0.1228	-1.652	72.192	1.0661	0.88	0.0037
	100	-	9	0.5158	0.5158	1.557	1.547	1.0317	0.69	0.0099
			15	0.5165	0.5165	0.371	1.679	1.0329	0.45	0.0111

The sum of h_1 and h_2 equals unity (1) when the compaction process can be explained by the two aforementioned processes. If the sum is less than unity, compaction cannot be explained by these two processes exclusively (i.e., there are other processes present). The summation of h_1 and h_2 yielded a value greater than unity in all cases. As Sonnergaard (2001) noted, Cooper and Eaton (1962) did not comment on the physical meaning of the cases wherein the summation of the two coefficients was greater than one. The evidence is however, supportive of the fact that there are other physical processes occurring.

The values of c_1 and c_2 represent the pressure required to induce particle rearrangement and deformation, respectively. Upon observation of the results, it can be seen that negative values were calculated for some of the c_1 and c_2 constants. This is counter-intuitive as these values are reported to indicate a compressive pressure. All of the values were greater than zero for the 100°C process temperature; however, in 10 of 12 of these cases, the h_1 and h_2 coefficients had identical numerical values. Also, the R^2 values in each of these 12 cases was less than or equal to 0.86.

Negative coefficient values were not encountered in any of the pharmaceutical powder compression literature surveyed. Tabil and Sokhansanj (1996a) however, encountered negative values when compressing alfalfa grinds. The validity of the model constants for these biomass feedstocks to represent their physical definition must be called into question, and further work may be needed to verify application of this model to other feedstocks.

4.4.2 Relaxation behaviour

Tables B.1 and B.2 present the analysis of variance (ANOVA) of the factors affecting the asymptotic modulus (E_A) of the poplar and wheat straw feedstocks, respectively. Asymptotic modulus values calculated from relaxation testing of poplar and wheat straw feedstocks can be found in Tables C.1 and C.2, respectively. Mean values of asymptotic modulus ranged from 16.7 (pretreated wheat straw, 1000 N, 100°C, and 15% wb) to 148.3 MPa (pretreated poplar, 4000 N, 100°C, and 15%) with standard deviations between 0.3 and 30.8 MPa.

The applied load had a significant effect on the E_A values of the four feedstocks. As the load was increased, the resulting E_A value increased as well. This behaviour has been predicted by empirical power models (Tabil and Sokhansanj 1997) and linear relationships (Mani et al. 2006a). Process temperature did not have a significant effect on the asymptotic modulus of the wheat straw feedstocks, which was consistent with the findings of Shaw and Tabil (2007). Temperature had a significant effect on the E_A values of the two poplar feedstocks, as an increase in process temperature served to increase the E_A values. This may potentially be due to the fact that a larger moisture loss occurs at the higher die temperature, and a decrease in moisture significantly increased the E_A values of the two untreated feedstocks. This is due to the fact that moisture increases the plasticization of molecular chains, and would appear to facilitate deformation. There is however, a significant interaction effect between the pre-set load and moisture content, which became prevalent upon examination of the data for the pretreated feedstocks. As previously mentioned, the asymptotic modulus of the untreated feedstocks will decrease with an increase in moisture content; however, this is only true

for the pretreated feedstocks at the lower pre-set loads. As the pre-set load was increased, the E_A values became higher at the larger moisture content. Reducing the particle (screen) size of the two untreated feedstocks significantly increased the E_A values. The significant interaction between pre-set load and screen size resulted in the screen size effect being minimized, or even vaguely reversed (in the case of wheat straw), at lower loads.

From Figure 4.2, it is evident that the pretreated feedstocks relax to a greater extent than the untreated feedstocks. As a general rule, the untreated feedstocks had higher E_A values than the pretreated feedstocks; however, the aforementioned interaction between pre-set load and moisture content yields higher E_A values for the 15% wb pretreated feedstocks at higher loads. This phenomenon can be explained by examining the actual maximum compressive loads. In all cases, the maximum load was higher than the pre-set load due to momentum effects of the Instron cross-head. At the higher moisture content, this effect was compounded, thus resulting in these materials experiencing a higher load than the low moisture materials. The higher loads, in turn, yielded higher E_A values. The higher degree of relaxation (lower E_A values) of the pretreated materials (as opposed to the untreated materials) could be attributed to the cohesiveness of the feedstocks. Moreyra and Peleg (1980) stated that cohesionless particles have little tendency to relax, whereas cohesive particles will relax similar to wet particles. It is possible that the pretreated feedstocks were much more cohesive than their untreated counterparts. Moreyra and Peleg (1980) reported that a higher degree of stress relaxation would indicate that particles deformed, whereas a lower degree of stress relaxation indicated that stresses were supported by a solid matrix, and thus less

deformation occurred. The authors attributed this to the fact that relaxation is an indication of internal processes within the compacted specimen.

4.4.3 Specific energy required for compression and extrusion

Results from the ANOVA of the experimental factors affecting the specific energy required for compression of the poplar and wheat straw feedstocks are shown in Tables B.3 and B.4, respectively. The ANOVA for the specific energy required to extrude the poplar and wheat straw feedstocks (untreated and pretreated) are shown in Tables B.5 and B.6, respectively. The specific energy required to compress and extrude the poplar and wheat straw feedstocks are shown in Tables C.3 and C.4, respectively.

More specific energy was required to compress the feedstocks than to extrude them. Quantitatively, between 95 and 99% of the total specific energy was required to compress the grinds, whereas between 1 and 5% of the total specific energy was required to extrude the pellet. Mean values of specific compression energy ranged from 7.2 (pretreated wheat straw, 1000 N, 100°C, and 15% wb) to 39.1 MJ/t (wheat straw, 4000 N, 70°C, 3.2 mm, and 9% wb), with standard deviations between 0.36 and 6.81 MJ/t. Intuitively, increasing the pre-set load significantly increased the specific energy required for compression. Temperature did not have as significant of an influence on specific compression energy of the untreated feedstocks as it did on the pretreated feedstocks; in fact, temperature did not have a significant effect on the wheat straw. Generally, increasing the process temperature resulted in a decrease in the specific energy required to compress the feedstocks. This supports the statement by Sokhansanj and co-workers (2005); the resistance of the material to an applied load decreases with an increase in temperature. Moisture also significantly affected the specific compression

energy of the four feedstocks. Increasing feedstock moisture content decreased the specific energy required for compression. Increasing the particle (screen) size significantly increased the specific compression energy presumably due to the increased plastic deformation which these large particles must undergo.

Wheat straw (12.7-39.1 MJ/t) required more energy to compress than poplar (10.6-29.4 MJ/t), while pretreated wheat straw (7.2-26.1 MJ/t) required less energy to compress than the pretreated poplar (9.0-28.8 MJ/t). Therefore, less energy was required to compress the feedstocks with higher bulk and particle densities. Less specific energy was required to compress the pretreated wheat straw, than the untreated wheat straw. Specific energy patterns for compression of the pretreated poplar compared to its untreated counterpart were a little more complicated. No clear trend existed for the pretreated and untreated poplar.

There was no correlation between the specific energy required for compression and extrusion. Mean values for the specific energy required to extrude the pellets from the cylindrical die fell between 0.25 (wheat straw, 1000 N, 70°C, 0.8 mm, and 9% wb) and 0.84 MJ/t (poplar, 2000 N, 70°C, 3.2 mm, and 9% wb). Standard deviation values ranged from 0.02 to 0.61 MJ/t. Pre-set load had a significant effect on the specific extrusion energy required to extrude pellets of the four feedstocks, although an unambiguous pattern of this effect could not be elucidated. Process temperature only had a significant effect on the pretreated poplar feedstock, with higher energy required to extrude the material at the lower temperature. Increasing the particle (screen) size significantly increased the specific energy required to extrude the untreated feedstocks from the die. Increasing the moisture content significantly decreased the specific extrusion energy required for the two pretreated feedstocks; however, moisture had no

significant effect on the untreated feedstocks. The additional moisture presumably acted as a lubricant between the biomass and the die, reducing frictional forces.

The significant main effects made it difficult to rank the four feedstocks in terms of their specific energy requirements for extrusion. Mean values for poplar fell between 0.33 and 0.84 MJ/t, while mean values for pretreated poplar ranged from 0.29 to 0.78 MJ/t. Mean specific energy required for extrusion ranged from 0.25 to 0.79 MJ/t for wheat straw, and 0.34 to 0.71 MJ/t for pretreated wheat straw.

Mani and co-workers (2006b) reported that 8.1 and 7.3 MJ/t were required to compress corn stover to 5 MPa at 10 and 15% wb, respectively. It was also reported that 14.0 and 15.8 MJ/t were required to compress the corn stover to 15 MPa at 10 and 15 % wb, respectively. The total specific energy required to compress the corn stover ranged between 12 and 30 MJ/t, which included the specific extrusion energy. The diameter of the die used by Mani and co-workers (2006b) was 30 mm. Kaliyan and Morey (2006) reported that the specific energy required to compress corn stover (3.0 mm hammer mill grind) to 150 MPa was 38.6 MJ/t at 10% wb, while the specific compression energy for switchgrass under identical conditions was 37.5 MJ/t. The authors reported that the specific extrusion (ejection) energy at the aforementioned conditions was 1.0 and 0.2 MJ/t for corn stover and switchgrass, respectively. The diameter of the die used in the study by Kaliyan and Morey (2006) was 18.8 mm. The specific compression energy of the poplar and wheat straw feedstocks is comparable to that reported by the two aforementioned studies (corn stover and switchgrass), while the specific compression energy is in agreement with those values reported by Kaliyan and Morey (2006).

4.5 Pellet density and dimensional expansion

The maximum density achieved during compression by each feedstock (packing density), along with the initial pellet density (measured immediately after extrusion) are shown in Tables C.5 and C.6 for the poplar and wheat straw feedstocks, respectively. The ANOVA of the effect of experimental variables on poplar and wheat straw initial pellet density are shown in Tables B.7 and B.8.

Table 4.10 Relaxed density, diametral and longitudinal expansion of poplar and wheat straw (untreated and pretreated) pellets compressed to a pre-set load of 4000 N.

Feedstock	Temperature (°C)	Screen size (mm)	Moisture (% wb)	Relaxed pellet density (kg/m^3)*	Diametral expansion (%)*	Longitudinal expansion (%)*
Poplar	70	0.8	9	1013 (44)	0.47 (0.27)	6.30 (2.29)
			15	1069 (23)	-0.02 (0.28)	0.25 (1.41)
		3.2	9	961 (35)	0.85(0.46)	6.85 (2.23)
			15	997 (27)	0.46 (0.56)	1.97 (2.06)
	100	0.8	9	1050 (20)	0.38 (0.22)	3.61 (1.47)
			15	1100 (13)	-0.11 (0.22)	-2.44 (2.21)
		3.2	9	1031 (31)	0.40 (0.39)	1.62 (1.21)
			15	1032 (47)	0.22 (0.53)	-0.72 (1.52)
Pretreated poplar	70	-	9	1219 (22)	0.03 (0.16)	0.58 (0.80)
			15	1291 (33)	-0.31 (0.31)	-1.07 (1.12)
	100	-	9	1231 (74)	-0.02 (0.33)	0.01 (0.95)
			15	1341 (8)	-0.49 (0.27)	-2.41 (0.93)
Wheat straw	70	0.8	9	912 (73)	0.67 (0.33)	8.54 (6.65)
			15	979 (19)	0.09 (0.18)	1.93 (1.74)
		3.2	9	835 (55)	1.14 (0.37)	8.62 (5.31)
			15	915 (21)	0.37 (0.45)	0.33 (1.23)
	100	0.8	9	1005 (34)	0.26 (0.25)	1.87 (2.03)
			15	1004 (18)	0.17 (0.15)	-0.34 (1.44)
		3.2	9	937 (43)	0.54 (0.45)	2.48 (2.29)
			15	930 (45)	0.36 (0.56)	2.31 (2.12)
Pretreated wheat straw	70	-	9	1272 (22)	-0.34 (0.19)	-0.47 (1.17)
			15	1283 (87)	-0.51 (0.57)	-1.64 (2.42)
	100	-	9	1324 (45)	-0.62 (0.32)	-1.65 (0.95)
			15	1318 (20)	-0.53 (0.37)	-1.95 (1.32)

* Numbers in parentheses are standard deviations (n = 10)

The relaxed (14 day) density, diametral expansion, and longitudinal expansion of the poplar and wheat straw (untreated and pretreated) pellets are shown in Table 4.10.

Analysis of variance for the factors affecting diametral expansion of poplar and wheat straw pellets (untreated and pretreated) are shown in Table B.9. Similarly, the ANOVA for the factors affecting longitudinal expansion of poplar and wheat straw pellets (untreated and pretreated) are shown in Table B.10.

Lower initial pellet densities (than packing densities) indicates that the pellets expanded once the load was removed. In some instances (at higher loads) the packing density of the feedstocks exceeded the particle density. This was most likely due to voids present within the particles that were not exposed during conditioning and grinding.

Pellet diameters (measured immediately after extrusion) ranged between 6.39 and 6.55 mm, indicating that all the pellets expanded immediately following extrusion, as the die was 6.35 mm in diameter. The length of the pellets ranged from 10.94 to 16.92 mm, and varied with the mass of the material initially placed in the die.

Pretreated feedstocks had higher initial pellet densities than the untreated feedstocks, with pretreated wheat straw pellets ranging from 997 to 1286 kg/m^3, and pretreated poplar pellet initial densities ranging from 966 to 1296 kg/m^3. Poplar pellets (initially) had a higher density (788-1096 kg/m^3) than wheat straw pellets (654-1026 kg/m^3), while pretreated wheat straw pellets generally had a higher initial densities than pretreated poplar pellets. Therefore, the initial pellet densities were inversely proportional to the compressibility of the feedstocks.

Increasing the pre-set load and temperature significantly increased the initial density of the pellets. The initial density of the pellets was also significantly increased by decreasing the particle (screen) size. There is a significant interaction between the pre-set load and moisture content of the material. At lower loads (and the lower

temperature in the case of wheat straw), the initial pellet density is higher at 15% wb; however, as the load is increased, the untreated feedstock pellets made from 9% wb were the densest. All the pellets made of 15% wb pretreated poplar had higher initial pellet densities than those made from 9% wb material. At higher loads, the pretreated wheat straw pellets made from 9% wb feedstock had an initial density higher than those made from 15% wb material. In nearly every instance, feedstocks conditioned to 15% wb experienced a higher maximum load than the material conditioned to 9% wb due to the momentum effects of the Instron. This would explain why the higher moisture pellets had higher initial pellet densities in some cases. Shaw and Tabil (2007), along with many other researchers, have concluded that lower moisture materials produce denser pellets.

Pellets made from untreated feedstocks generally expanded in the diametral and longitudinal axes, while the pretreated pellets generally decreased in diameter and length, increasing in density. Theoretically, the increase in available lignin caused by steam explosion is responsible for the excellent performance of the pretreated pellets in the dimensional expansion test. The lignin is made available for binding by the disruption of the lignocellulosic structure. For the most part, the poplar pellets expanded slightly less than the wheat straw pellets both diametrally (poplar, -0.11 to 0.85%; wheat straw, 0.09 to 1.14%) and longitudinally (poplar, -2.44 to 6.85%; wheat straw, -0.34 to 8.62%); however, the pretreated wheat straw pellets decreased in size diametrally (pretreated poplar, -0.49 to 0.03%; pretreated wheat straw, -0.62 to -0.34%) and longitudinally (pretreated poplar, -2.41 to 0.58%; pretreated wheat straw, -1.95 to -0.47%) to a greater extent than pretreated poplar pellets.

Temperature only had statistically significant effect on the diametral and longitudinal expansion for the pellets made from the untreated feedstocks. For the most part, increasing the process temperature served to decrease the diametral and longitudinal expansion (or increased the dimensional reduction), and while the statistical significance was not always present, the trend is evident for all feedstocks. Increasing the moisture content significantly decreased the diametral and longitudinal expansion of all feedstocks except pretreated wheat straw; however, this trend still exists. Decreasing the particle (screen) size significantly decreased the dimensional expansion of the raw feedstocks but had no effect on the longitudinal expansion.

Li and Liu (2000) reported that the length elongation of logs (briquettes) made from oak sawdust (~10 to 16% wb) was less than 5%, while pine sawdust briquettes (~10 to 16% wb) expanded between approximately 5 and 15%. The briquettes were produced by compression at a pressure of 138 MPa and elongation measurements were made on the pellets after three days. Shaw and co-workers (2005) reported that peat moss, wheat straw, oat hulls, and flax shive grinds expanded 0.52, 2.59, 1.80, and 1.27% longitudinally when compressed at 126 MPa. The authors also reported diametral expansions of 0.02, 0.61, 0.31, and 0.33% for peat moss, wheat straw, oat hulls, and flax shive grinds, respectively. The pretreated feedstocks performed better in the dimensional expansion test than any material surveyed in literature. The dimensional expansion of the untreated feedstocks was similar to studies utilizing similar feedstocks and experimental set-ups.

4.6 Diametral compression (tensile strength) of pellets

Typically, durability and hardness are used as indicators of pellet quality; however, the durability test requires 100 g of pellets and hardness testing requires 30 pellets. A maximum of ten pellets were available for destructive quality testing, therefore constituting the use of the diametral compression test. The results from this test were used to calculate the tensile strength of tablet cut from the pellets, which is indicative of the extent or degree of bonding. Higher quality pellets will have higher tensile strengths and will be more suitable for transport and storage. Table 4.11 shows the results from the diametral compression of poplar and wheat straw (untreated and pretreated) pellets. The ANOVA on the effect of experimental variables on the tensile strength of the poplar and wheat straw (untreated and pretreated) pellets is shown in Table B.11. The pretreated feedstock pellets had a significantly higher tensile strength than pellets composed of untreated feedstock. Again, the binding capacity of the available lignin was held responsible for the increase in tensile strength. The mean tensile strength of pretreated poplar pellets (6.32-10.11 MPa) was lower than that of pretreated wheat straw pellets (9.94-13.19 MPa). Poplar pellets (0.45-1.28 MPa) had a very similar mean tensile strength to the wheat straw pellets (0.47-1.33 MPa).

Increasing the process temperature provided for significant increases in tensile strength of the pellets, presumably due to increased packing and bonding of the particles. Although temperature did not have a statistically significant effect on the tensile strength of the wheat straw pellets, the aforementioned trend still exists. While moisture content only significantly affected the tensile strength of the pretreated feedstock pellets, it affected the two pretreated feedstocks in different ways. Increasing the moisture content

Table 4.11 Dimensions, tensile fracture load, and tensile strength of poplar (untreated and pretreated) and wheat straw (untreated and pretreated) pellets compressed to a pre-set load of 4000 N.

Feedstock	Temperature (°C)	Screen size (mm)	Moisture (% wb)	Tablet thickness (mm)*	Tablet diameter (mm)*	Fracture load (N)*	Tensile strength (MPa)*
Poplar	70	0.8	9	2.00 (0.02)	6.46 (0.02)	14.53 (6.37)	0.82 (0.13)
			15	1.96 (0.04)	6.43 (0.02)	17.14 (3.36)	0.87 (0.18)
		3.2	9	1.96 (0.05)	6.51 (0.03)	9.06 (3.76)	0.45 (0.19)
			15	1.97 (0.05)	6.48 (0.04)	9.46 (1.22)	0.47 (0.06)
	100	0.8	9	1.99 (0.04)	6.47 (0.02)	25.36 (4.77)	1.25 (0.23)
			15	1.98 (0.02)	6.42 (0.01)	25.63 (4.63)	1.28 (0.23)
		3.2	9	1.96 (0.05)	6.50 (0.04)	13.93 (5.18)	0.69 (0.25)
			15	1.97 (0.07)	6.46 (0.03)	11.09 (3.09)	0.55 (0.15)
Pretreated poplar	70	-	9	1.96 (0.04)	6.42 (0.01)	125.00 (6.85)	6.32 (0.34)
			15	1.99 (0.04)	6.40 (0.01)	134.69 (27.97)	6.71 (1.33)
	100	-	9	2.00 (0.02)	6.42 (0.02)	159.29 (23.64)	7.91 (1.15)
			15	1.97 (0.08)	6.37 (0.01)	199.06 (20.13)	10.11 (1.01)
Wheat straw	70	0.8	9	1.98 (0.03)	6.48 (0.03)	10.94 (2.73)	0.54 (0.14)
			15	1.97 (0.02)	6.44 (0.01)	14.53 (3.59)	0.73 (0.18)
		3.2	9	2.00 (0.01)	6.53 (0.03)	9.69 (2.19)	0.47 (0.11)
			15	2.00 (0.04)	6.49 (0.03)	13.13 (4.58)	0.64 (0.22)
	100	0.8	9	2.00 (0.02)	6.45 (0.01)	27.03 (5.04)	1.33 (0.24)
			15	1.97 (0.07)	6.45 (0.01)	23.13 (3.34)	1.16 (0.19)
		3.2	9	1.98 (0.06)	6.49 (0.03)	20.00 (6.09)	0.99 (0.29)
			15	2.00 (0.02)	6.49 (0.05)	15.63 (4.68)	0.77 (0.23)
Pretreated wheat straw	70	-	9	2.00 (0.01)	6.39 (0.01)	233.75 (23.05)	11.65 (1.10)
			15	1.99 (0.02)	6.37 (0.02)	198.39 (37.73)	9.94 (1.90)
	100	-	9	2.00 (0.04)	6.38 (0.02)	264.72 (32.53)	13.19 (1.76)
			15	2.00 (0.02)	6.37 (0.02)	206.72 (25.69)	10.34 (1.30)

* Numbers in parentheses are standard deviations (n = 8)

served to increase the tensile strength of the pretreated poplar pellets, but decrease the tensile strength of the pretreated wheat straw pellets. Decreasing the particle (screen) size significantly increased the tensile strength of the untreated feedstock pellets.

Tabil and Sokhansaj (1996b) reported that the tensile strength of alfalfa tablets (prepared from pellets) compressed to 126 MPa ranged from 1.28 to 1.93 MPa. The pretreated feedstocks had significantly higher tensile strengths than the alfalfa tablets; however, the highest quality pellets produced from the untreated feedstocks had tensile strengths comparable to the lowest quality alfalfa tablets.

4.7 Fourier transform infrared photoacoustic spectroscopy (FT-IR PAS)

Figures 4.3 and 4.4 present the FT-IR spectra of the poplar (untreated and pretreated) and wheat straw (untreated and pretreated) feedstocks, respectively. Quantitative FT-IR results, including relative intensities of pertinent peaks, are located in Tables C.7, C.8, C.9, and C.10 for poplar, pretreated poplar, wheat straw, and pretreated wheat straw, respectively. A broad single peak around 3300 cm^{-1} is indicative of an O-H stretch band (Sun et al. 2005). In all four spectra, the peak located at approximately 2900 cm^{-1} was an aliphatic C-H stretching band of lignin and polysaccharides. A particular area of interest falls roughly between 1715 and 1734 cm^{-1}. Liu and co-workers (2005) reported that the band at 1734 cm^{-1} is characteristic of hemicellulose, while shoulders at approximately 1720 cm^{-1} are indicative of ester linkages of carboxylic groups from lignin and/or hemicellulose (Sun et al. 2005). The alteration of the lignocellulosic structure by pretreatment was evident in this region of the IR spectra. The magnitude of the 1734 cm^{-1} peak relative to the band at 1718 cm^{-1} was altered by pretreatment. The peak at 1734 cm^{-1} was pronounced in the untreated

samples, but appeared to diminish in the pretreated samples as it was not picked up by the peak identification tool in the OPUS software. A peak at 1718 cm^{-1} was identified in the pretreated samples, but not the untreated feedstocks; which is presumably due to the diminished presence of the 1734 cm^{-1} band. Collectively, the evidence was supportive of the fact that the lignocellulosic structure was disrupted, and a portion of the hemicellulose was removed/hydrolyzed. The relative peak intensity at 1718 cm^{-1} was higher for the pretreated poplar than the pretreated wheat straw, supporting the fact that a higher percentage of hemicellulose and/or lignin was present in the pretreated poplar.

Liu and co-workers (2005) reported that lignin absorbs at 1595 cm^{-1}. All four feedstocks demonstrated peaks at this wavenumber; however, the pretreated feedstocks had higher relative peak intensities than the untreated feedstocks, indicating a higher quantity of lignin was present in the pretreated feedstocks. Also the poplar had a higher relative peak intensity than the wheat straw, and a similar result was found for the pretreated feedstocks, sustaining the fact that the poplar feedstocks had a higher lignin content than their wheat straw counterparts. The results from infrared analysis of the four feedstocks support the chemical composition found in Table 4.2. A large portion of the hemicellulose was either removed or hydrolyzed during the steam explosion (pretreatment) process. As previously mentioned, the steam explosion process has been reported to melt and depolymerize the lignin (Toussaint et al. 1991). Not only was there a larger relative percentage of lignin in the pretreated samples (due to the removal of other chemical constituents), but the lignin appeared to be more available for binding. This was apparent due to the fact that the pretreated materials had higher tensile strengths than the untreated pellets, and also performed significantly better in the dimensional expansion tests. The steam explosion appeared to have an increased

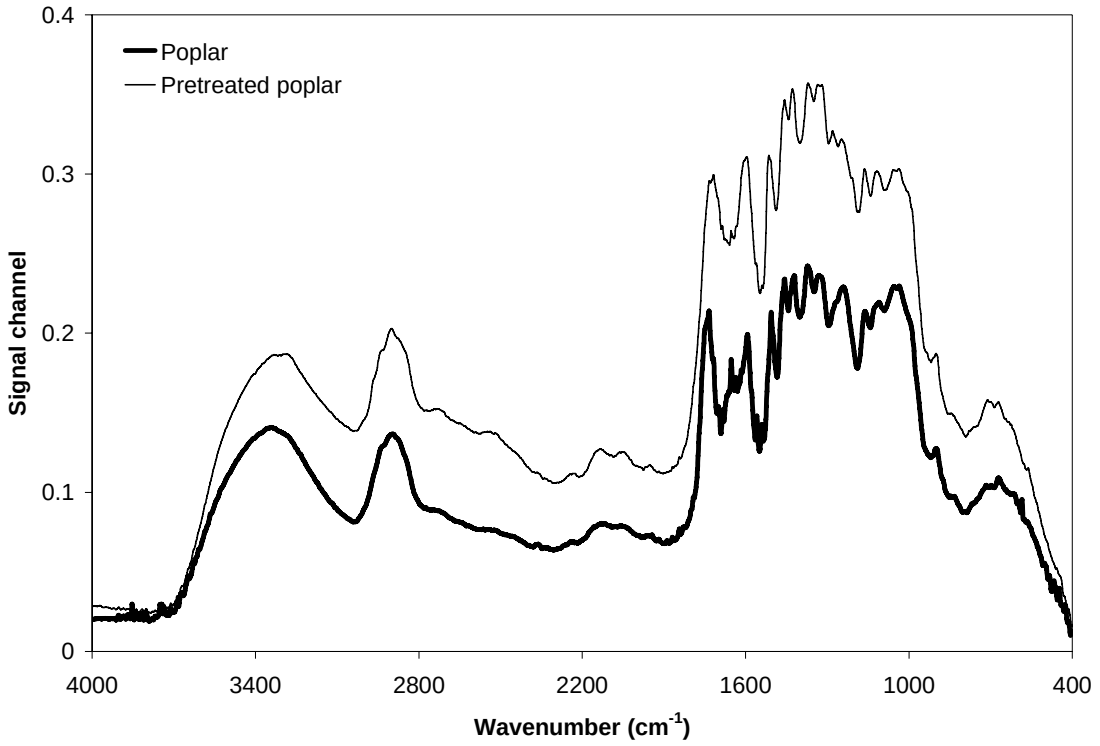

Figure 4.3 Infrared spectra of the poplar feedstocks (untreated and pretreated).

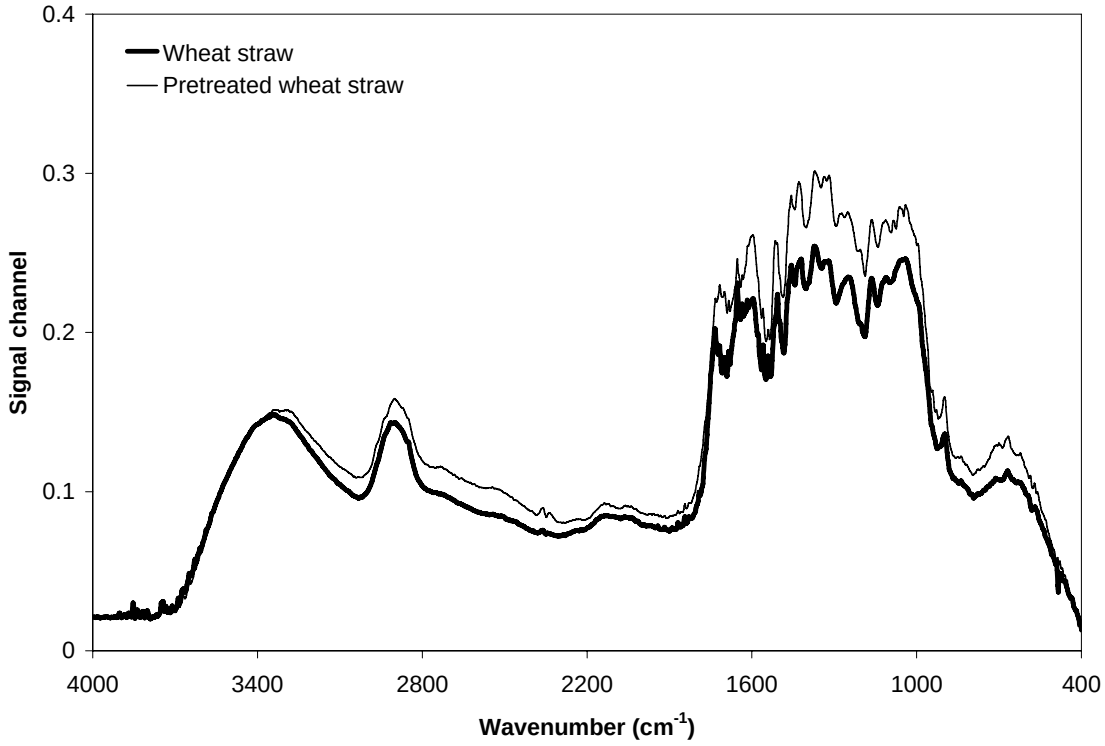

Figure 4.4 Infrared spectra of the wheat straw feedstocks (untreated and pretreated).

positive effect on the wheat straw feedstock, as the poplar pellets were higher in quality than the wheat straw pellets, whereas the pretreated wheat straw pellets were higher in quality than the pretreated poplar pellets. This would indicate that lignin alone was not responsible for the bonding of the pellets, as the poplar feedstocks had slightly higher relative percentages of lignin than the wheat straw feedstocks. Infrared analysis of the pelleted samples provided no additional information with respect to chemical composition or binding.

5 CONCLUSIONS

This chapter lists the conclusions that were draw from the experimental results of this research. The conclusions have been sub-divided and listed according to the research objectives stated in Chapter 1.1.

5.1 Dominant densification mechanisms

The following conclusion was made based on the results of fitting the Cooper-Eaton (1962) compression model to the compression data:

1. The densification of the four biomass feedstocks (poplar, pretreated poplar, wheat straw, and pretreated wheat straw) cannot be explained by particle rearrangement and deformation alone, as indicated by the Cooper-Eaton (1962) model.
2. The higher degree of stress relaxation of the pretreated feedstocks would indicate a higher degree of deformation than the untreated feedstocks, due to the fact that relaxation is indicative of internal processes within the compacted specimen.

5.2 Compression and relaxation characteristics

The following conclusions were made based on fitting compression and relaxation models to the compression and relaxation data:

1. Compressibility of the untreated biomass grinds increased with an increase in temperature, presumably due to higher moisture losses at 100°C, which reduced the packing density at lower loads.
2. Compressibility increased with a decrease in moisture content, due to the fact that higher moisture feedstock had higher packing densities at lower loads.

3. Particle size did not have a significant effect on compressibility.
4. Steam pretreatment served to decrease the compressibility of the poplar and wheat straw feedstocks, and had a greater effect at lower loads.
5. The asymptotic modulus (E_A) of the poplar feedstocks was increased by increasing the process temperature; however, temperature did not have a significant effect on the wheat straw feedstocks.
6. Decreasing the moisture content served to increase the E_A of the feedstocks; however, at higher compressive loads, the E_A of the pretreated feedstocks became higher at larger values of moisture content.
7. The E_A was also increased by decreasing the particle size of the biomass grinds; however, this effect was minimized at the lowest loads.
8. The raw poplar and wheat straw had higher E_A values than their pretreated counterparts.

5.3 Physical quality of the densified feedstocks

The following conclusions were drawn from physical quality measurements of the pellets made by compression testing:

1. Initial pellet densities were inversely proportional to the compressibility of each material.
2. Initial pellet density was increased by increasing the compressive load and temperature, along with decreasing the feedstock particle size and moisture content.
3. Pretreated feedstocks had higher initial pellet densities than the raw materials. This was attributed to the fact that the pretreated feedstocks have a higher amount of lignin available for binding.

4. Pretreated wheat straw pellets had higher initial pellet densities than pretreated poplar pellets.
5. Raw poplar pellets had higher initial pellet densities than raw wheat straw pellets.
6. The diametral expansion of the biomass pellets was decreased (or even reversed) by increasing the die temperature along with decreasing the moisture content and particle size.
7. The longitudinal expansion of the pellets was also decreased (or reversed) by increasing the die temperature and decreasing the moisture content; however, the particle size did not have a significant effect on the longitudinal expansion of the pellets.
8. Pretreated pellets generally decreased in diameter and length, increasing in density, while pellets from raw poplar and wheat straw generally expanded in diameter and length. The superior performance of the pretreated feedstocks in the dimensional expansion test is attributed to increased binding of the lignin made available during the pretreatment process.
9. Pretreated wheat straw pellets decreased dimensionally (increased in density) to a greater extent than the pretreated poplar pellets.
10. Raw poplar pellets expanded to a lesser extent than the raw wheat straw pellets.
11. The tensile strength of the pellets was increased by an increase in temperature and a decrease in particle size.
12. Moisture content only had a significant effect on the tensile strength of the pretreated feedstock pellets, and affected each in a contradictory manner.
13. The pretreated pellets had significantly higher tensile strengths than their raw counterparts, due to the increased binding capacity of the available lignin. Therefore,

the pretreated pellets had a higher physical quality and would be able to endure handling and storage better than the untreated pellets.

14. Pretreated wheat straw pellets had a higher tensile strength than the pretreated poplar pellets.
15. There was little difference in the tensile strength of the pellets produced from the raw feedstocks.

5.4 General

The following conclusions were made from general observations throughout the series of experiments reported:

1. Subtle differences in chemical composition between two different feedstocks will not significantly alter the results of compression/compaction modeling. Feedstock variables such as particle size and moisture content will have a much more profound effect than slight differences in chemical composition, especially at lower compressive loads.

6 RECOMMENDATIONS

The following list of suggestions was compiled for future research:

1. More work is required to identify the suitability of compaction models for biomass densification. Specifically, models which predict the mechanism of binding must be evaluated due to the fact that this mechanism could not be explained by particle rearrangement or deformation alone.
2. There exists a need to accurately and precisely stop the Instron cross-head at the pre-defined load. Due to momentum effects of the cross-head, this load was exceeded in certain instances, which made it difficult to compare the results.
3. It may also be advantageous to conduct a study investigating the effects of heating biomass material during the densification process. Specifically, a kinetic study which investigates the effect of temperature and time.
4. Due to the fact that the pretreated pellets were superior in quality to the untreated pellets, the next step would be an evaluation of pelleting pretreated material at the pilot or bench scale. Also, the feasibility of using steam explosion as a pretreatment step for biomass densification must be evaluated.
5. Additional densification studies are required on a number of other biomass feedstocks in order to advance the understanding of this complex process.
6. Investigations into densification equipment will be key to improving the feasibility of this process and ensure maximum efficiency. In the same way that material properties are altered and adjusted (e.g. pretreatment, grinding, conditioning), equipment must be improved in order to produce a high quality product in the most efficient manner possible.

7. Soft x-ray absorption spectroscopy would be useful in identifying the distribution of lignocellulosic components in the untreated and pretreated feedstocks, as well as in the pelleted samples. This has the potential to provide information regarding how pretreatment and pelleting affects this distribution.

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APPENDIX A – COMPRESSION MODEL PLOTS

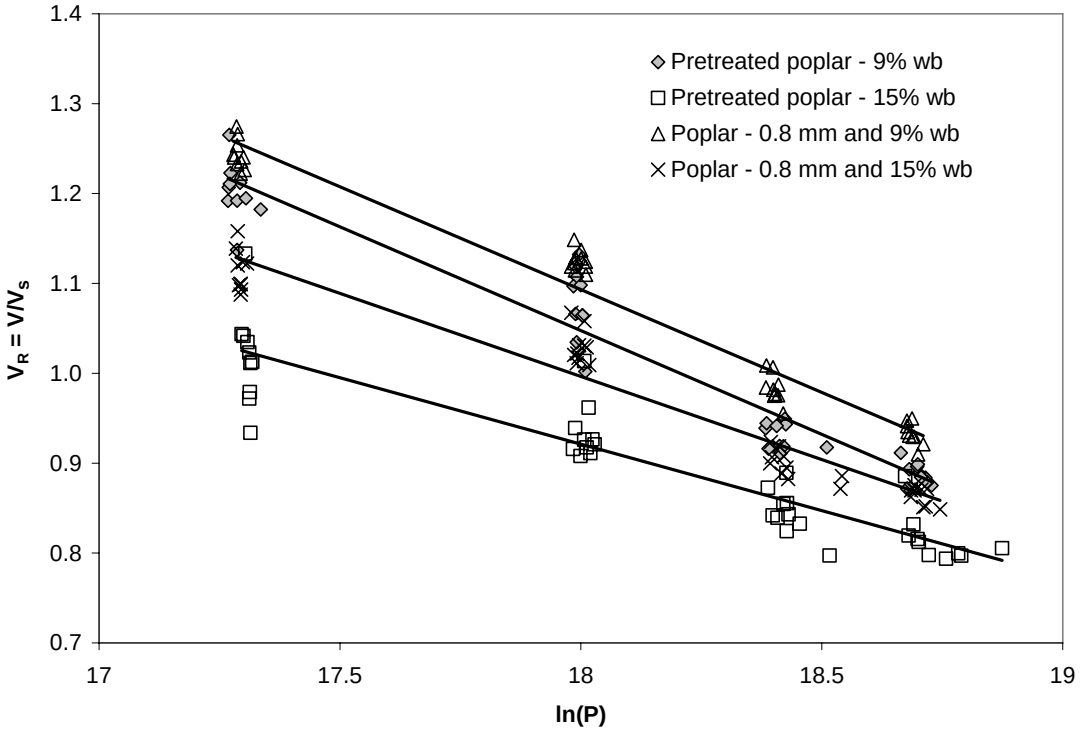

Figure A.1 Walker (1923) plot of poplar feedstocks compressed at 70°C.

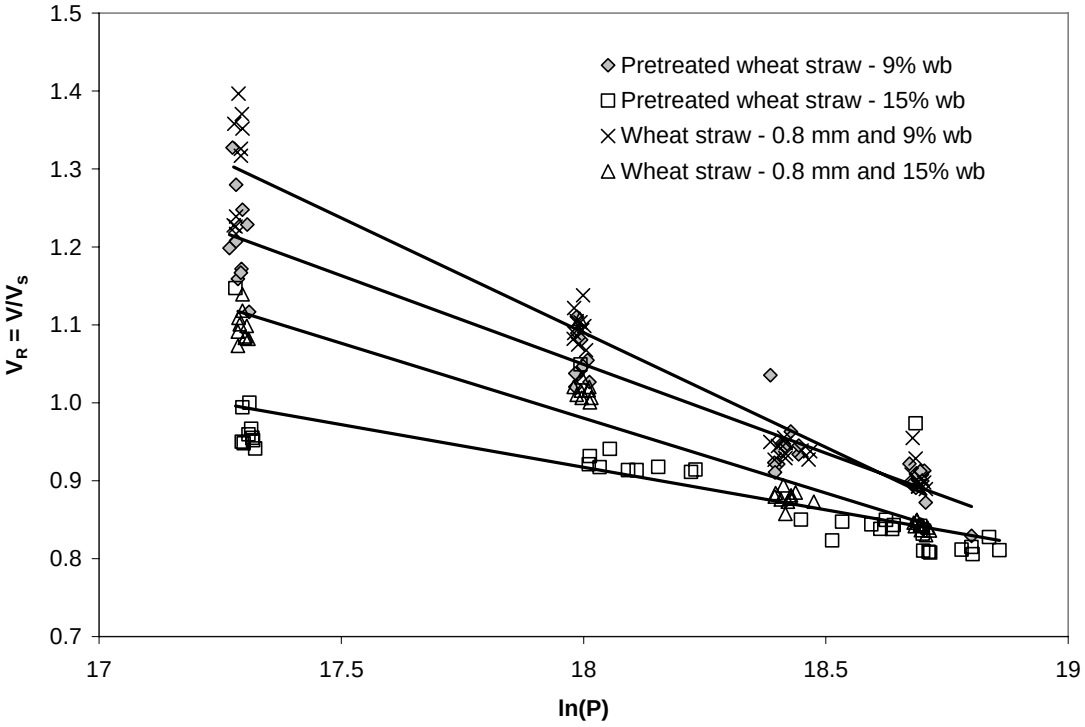

Figure A.2 Walker (1923) plot of wheat straw feedstocks compressed at 70°C.

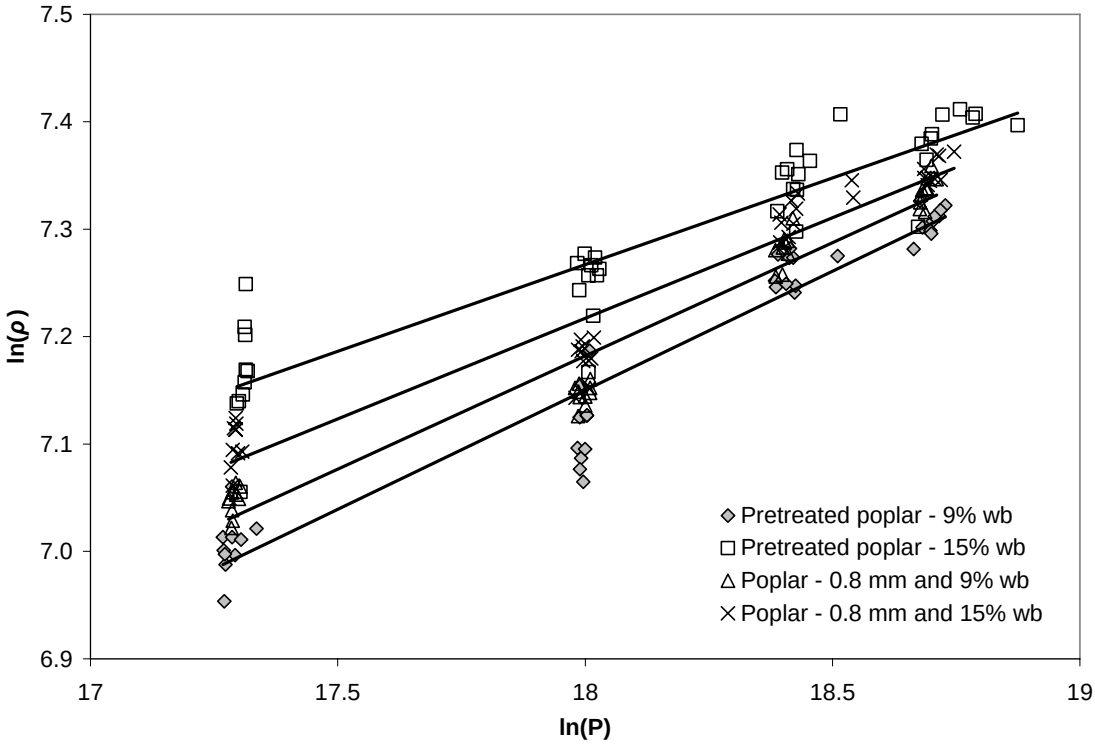

Figure A.3 Jones (1960) plot of poplar feedstocks compressed at 70°C.

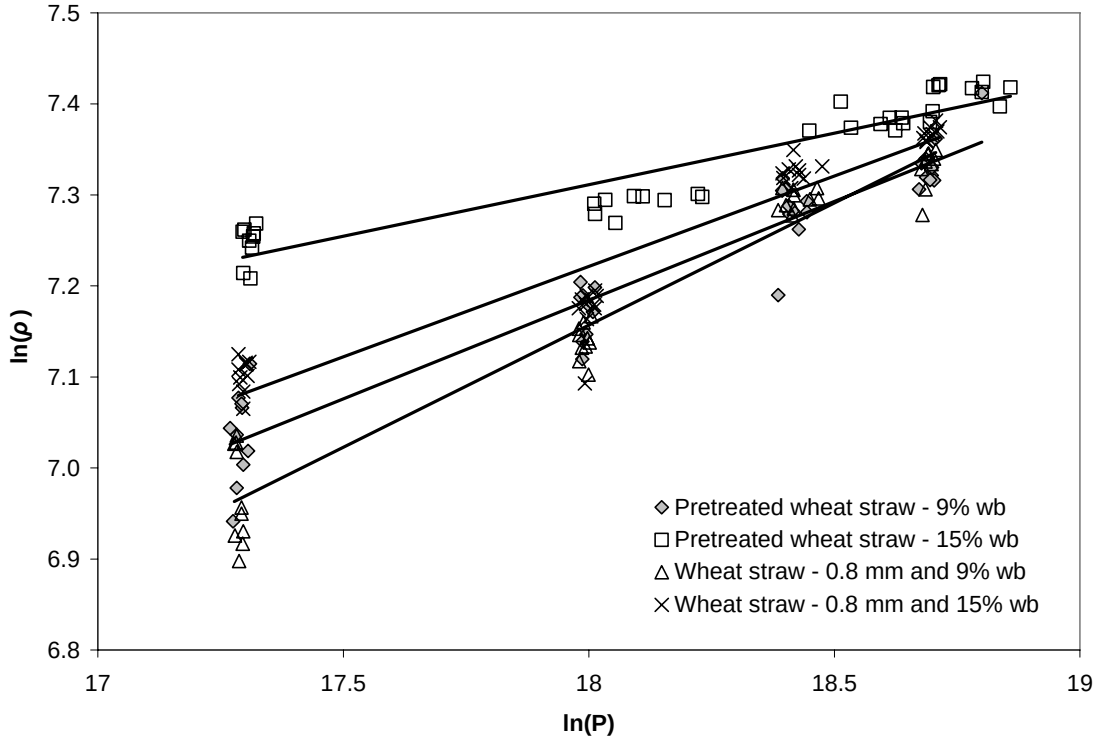

Figure A.4 Jones (1960) plot of wheat straw feedstocks compressed at 70°C.

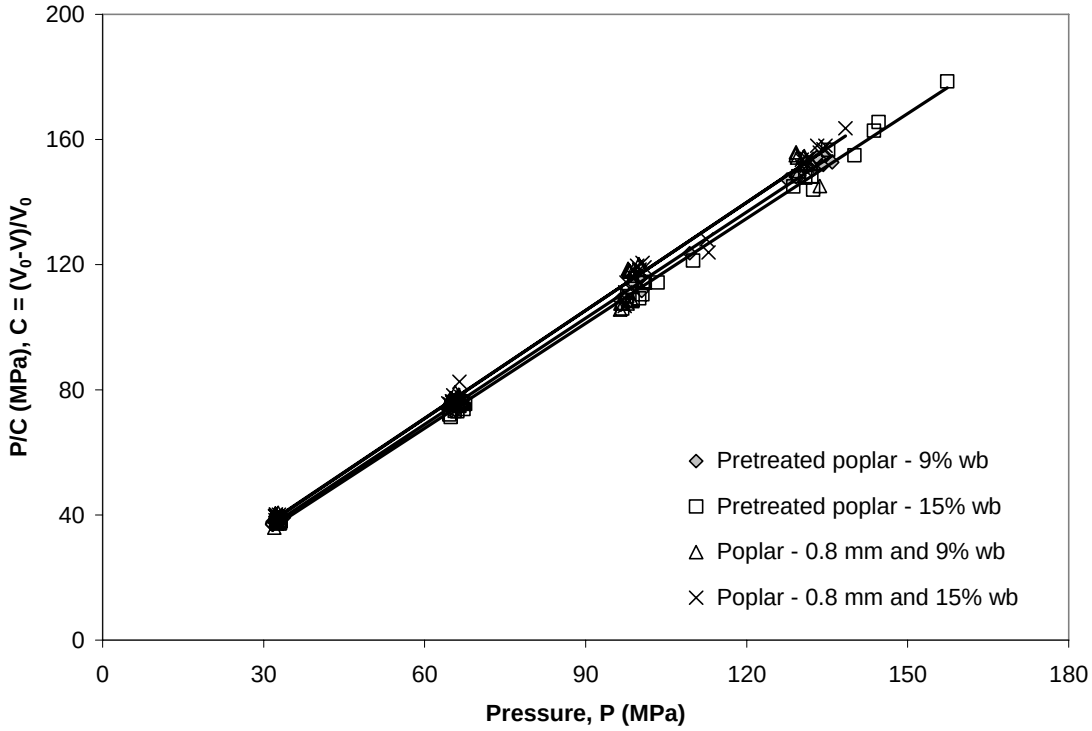

Figure A.5 Kawakita (1971) plot of poplar feedstocks compressed at 70°C.

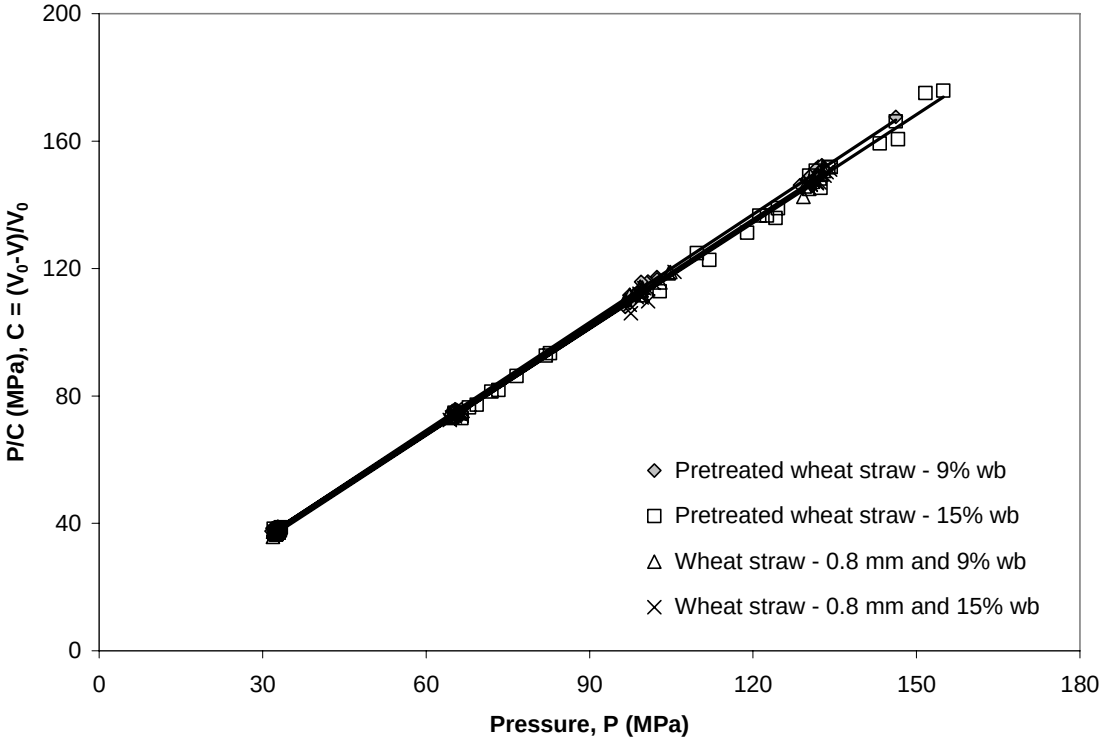

Figure A.6 Kawakita (1971) plot of wheat straw feedstocks compressed at 70°C.

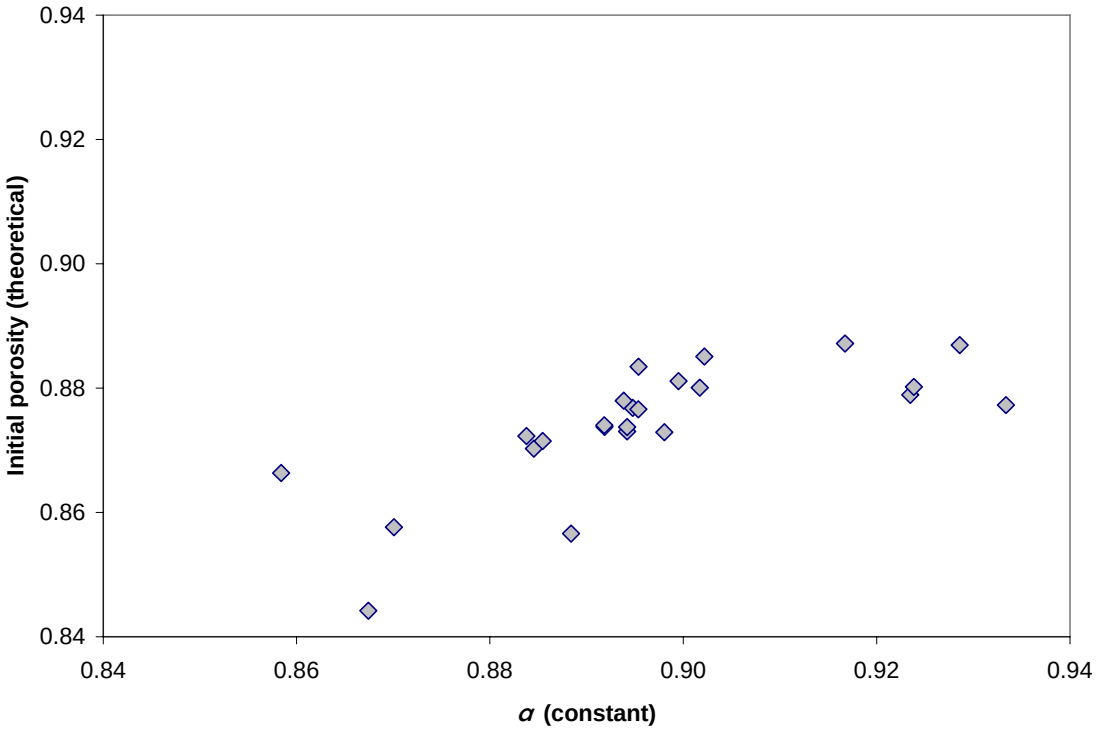

Figure A.7 Relationship between the theoretical initial porosity of the biomass feedstocks in the compression die and the constant '*a*' from the Kawakita (1971) model.

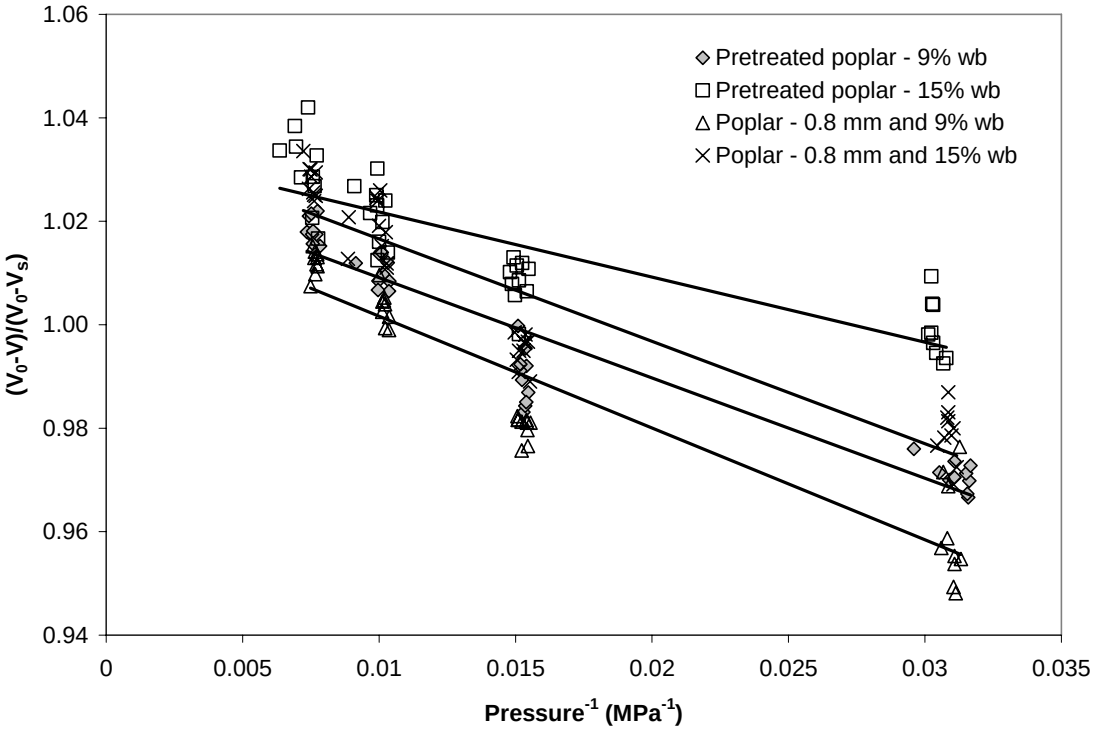

Figure A.8 Cooper-Eaton (1962) plot of poplar feedstocks compressed at 70°C.

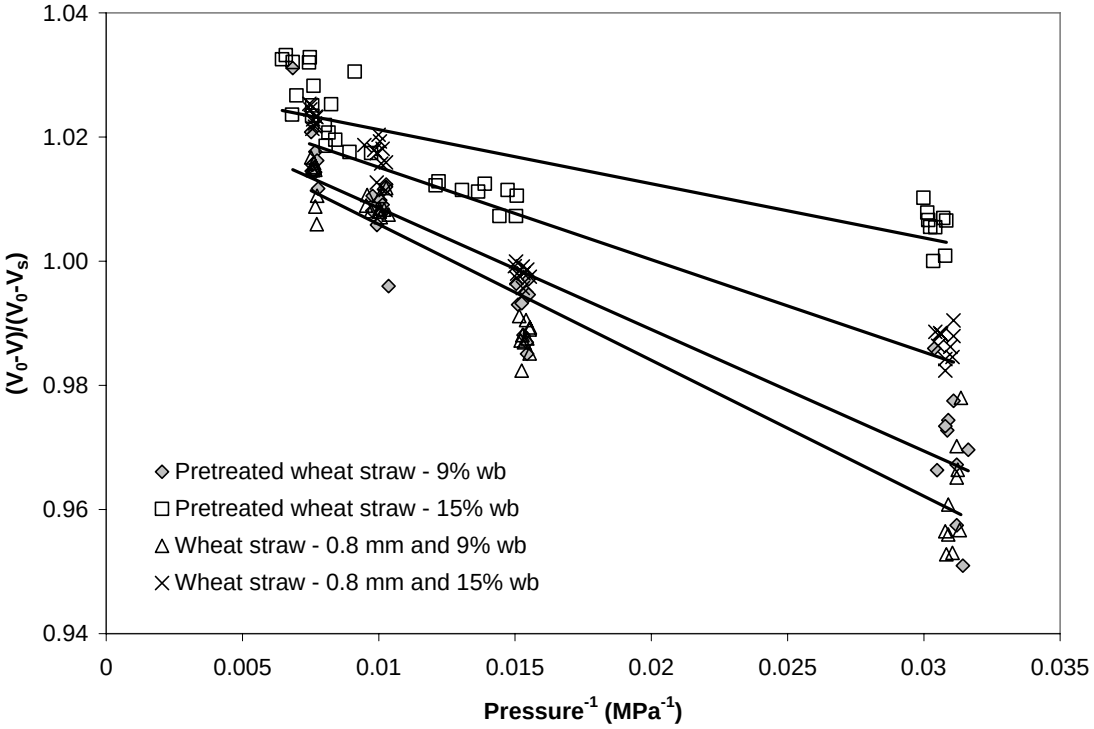

Figure A.9 Cooper-Eaton (1962) plot of wheat straw feedstocks compressed at 70°C.

APPENDIX B – ANOVA TABLES

Table B.1 Analysis of variance (ANOVA) table for experimental variables affecting the asymptotic modulus of the poplar feedstocks.

Source	SS	df	MS	F	Sig.
Poplar					
Force (*f*)	442335.18	3	147445.06	17112.36	0.000
Temperature (*t*)	49.41	1	49.41	5.73	0.017
Screen size (*s*)	516.95	1	516.95	60.00	0.000
Moisture content (*m*)	650.85	1	650.85	75.54	0.000
f x *t*	36.57	3	12.19	1.41	0.239
f x *s*	229.10	3	76.37	8.86	0.000
t x *s*	10.45	1	10.45	1.21	0.272
f x *t* x *s*	12.46	3	4.15	0.48	0.695
f x *m*	155.89	3	51.96	6.03	0.001
t x *m*	9.99	1	9.99	1.16	0.283
f x *t* x *m*	34.39	3	11.46	1.33	0.265
s x *m*	40.18	1	40.18	4.66	0.032
f x *s* x *m*	12.58	3	4.19	0.49	0.692
t x *s* x *m*	5.30	1	5.30	0.62	0.433
f x *t* x *s* x *m*	8.43	3	2.81	0.33	0.806
Error	2438.41	283	8.62		
Total	446992.92	314			
Pretreated Poplar					
Force (*f*)	252459.41	3	84153.14	687.37	0.000
Temperature (*t*)	1143.03	1	1143.03	9.34	0.003
Moisture content (*m*)	1342.60	1	1342.60	10.97	0.001
f x *t*	1283.13	3	427.71	3.49	0.017
f x *m*	4309.27	3	1436.42	11.73	0.000
t x *m*	1233.87	1	1233.87	10.08	0.002
f x *t* x *m*	1369.55	3	456.52	3.73	0.013
Error	17262.32	141	122.43		
Total	281074.61	156			

Table B.2 Analysis of variance (ANOVA) table for experimental variables affecting the asymptotic modulus of the wheat straw feedstocks.

Source	SS	df	MS	F	Sig.
Wheat straw					
Force (*f*)	403818.99	3	134606.33	19745.94	0.000
Temperature (*t*)	1.96	1	1.96	0.29	0.592
Screen size (*s*)	143.04	1	143.04	20.98	0.000
Moisture content (*m*)	1718.74	1	1718.74	252.13	0.000
f x *t*	17.13	3	5.71	0.84	0.474
f x *s*	208.98	3	69.66	10.22	0.000
t x *s*	17.80	1	17.80	2.61	0.107
f x *t* x *s*	23.03	3	7.68	1.13	0.339
f x *m*	301.01	3	100.34	14.72	0.000
t x *m*	77.88	1	77.88	11.42	0.001
f x *t* x *m*	43.92	3	14.64	2.15	0.094
s x *m*	47.52	1	47.52	6.97	0.009
f x *s* x *m*	21.72	3	7.24	1.06	0.366
t x *s* x *m*	26.95	1	26.95	3.95	0.048
f x *t* x *s* x *m*	95.90	3	31.97	4.69	0.003
Error	1949.64	286	6.82		
Total	409143.76	317			
Pretreated wheat straw					
Force (*f*)	226797.85	3	75599.28	397.28	0.000
Temperature (*t*)	348.47	1	348.47	1.83	0.178
Moisture content (*m*)	27788.37	1	27788.37	146.03	0.000
f x *t*	262.53	3	87.51	0.46	0.711
f x *m*	18347.65	3	6115.88	32.14	0.000
t x *m*	61.70	1	61.70	0.32	0.570
f x *t* x *m*	1695.61	3	565.20	2.97	0.034
Error	26450.79	139	190.29		
Total	298898.29	154			

Table B.3 Analysis of variance (ANOVA) table for factors affecting specific energy required for compression of the poplar feedstocks.

Source	SS	df	MS	F	Sig.
Poplar					
Force (*f*)	9179.30	3	3059.77	1877.05	0.000
Temperature (*t*)	7.66	1	7.66	4.70	0.031
Screen size (*s*)	1134.20	1	1134.20	695.79	0.000
Moisture content (*m*)	115.70	1	115.70	70.97	0.000
f x *t*	61.56	3	20.52	12.59	0.000
f x *s*	30.58	3	10.19	6.25	0.000
t x *s*	1.37	1	1.37	0.84	0.361
f x *t* x *s*	7.79	3	2.60	1.59	0.191
f x *m*	25.38	3	8.46	5.19	0.002
t x *m*	0.20	1	0.20	0.13	0.724
f x *t* x *m*	22.95	3	7.65	4.69	0.003
s x *m*	3.53	1	3.53	2.17	0.142
f x *s* x *m*	21.88	3	7.29	4.47	0.004
t x *s* x *m*	2.98	1	2.98	1.83	0.177
f x *t* x *s* x *m*	8.65	3	2.88	1.77	0.153
Error	456.43	280	1.63		
Total	11031.08	311			
Pretreated Poplar					
Force (*f*)	3611.44	3	1203.81	352.61	0.000
Temperature (*t*)	157.72	1	157.72	46.20	0.000
Moisture content (*m*)	1285.31	1	1285.31	376.48	0.000
f x *t*	123.41	3	41.14	12.05	0.000
f x *m*	171.49	3	57.16	16.74	0.000
t x *m*	4.60	1	4.60	1.35	0.248
f x *t* x *m*	67.30	3	22.43	6.57	0.000
Error	481.38	141	3.41		
Total	5889.29	156			

Table B.4 Analysis of variance (ANOVA) table for factors affecting specific energy required for compression of the wheat straw feedstocks.

Source	SS	df	MS	F	Sig.
Wheat straw					
Force (*f*)	10529.40	3	3509.80	739.15	0.000
Temperature (*t*)	13.45	1	13.45	2.83	0.094
Screen size (*s*)	2252.45	1	2252.45	474.36	0.000
Moisture content (*m*)	543.18	1	543.18	114.39	0.000
f x *t*	607.33	3	202.44	42.63	0.000
f x *s*	44.22	3	14.74	3.10	0.027
t x *s*	2.50	1	2.50	0.53	0.469
f x *t* x *s*	126.83	3	42.28	8.90	0.000
f x *m*	54.05	3	18.02	3.79	0.011
t x *m*	111.24	1	111.24	23.43	0.000
f x *t* x *m*	23.21	3	7.74	1.63	0.183
s x *m*	17.64	1	17.64	3.71	0.055
f x *s* x *m*	9.02	3	3.01	0.63	0.594
t x *s* x *m*	21.06	1	21.06	4.43	0.036
f x *t* x *s* x *m*	17.23	3	5.74	1.21	0.306
Error	1343.81	283	4.75		
Total	15748.18	314			
Pretreated wheat straw					
Force (*f*)	3362.23	3	1120.74	147.92	0.000
Temperature (*t*)	214.09	1	214.09	28.26	0.000
Moisture content (*m*)	1069.13	1	1069.13	141.10	0.000
f x *t*	3.14	3	1.05	0.14	0.937
f x *m*	245.59	3	81.86	10.80	0.000
t x *m*	0.38	1	0.38	0.05	0.823
f x *t* x *m*	15.92	3	5.31	0.70	0.553
Error	1053.19	139	7.58		
Total	6156.61	154			

Table B.5 Analysis of variance (ANOVA) table for factors affecting specific energy required for extrusion of the poplar feedstocks.

Source	SS	df	MS	F	Sig.
Poplar					
Force (*f*)	0.22	3	0.07	6.00	0.001
Temperature (*t*)	0.00	1	0.00	0.00	0.946
Screen size (*s*)	0.73	1	0.73	60.83	0.000
Moisture content (*m*)	0.01	1	0.01	0.54	0.464
f x *t*	0.09	3	0.03	2.61	0.054
f x *s*	0.09	3	0.03	2.50	0.062
t x *s*	0.01	1	0.01	1.01	0.317
f x *t* x *s*	0.10	3	0.03	2.72	0.048
f x *m*	0.01	3	0.00	0.22	0.885
t x *m*	0.00	1	0.00	0.37	0.543
f x *t* x *m*	0.04	3	0.01	1.04	0.376
s x *m*	0.00	1	0.00	0.03	0.860
f x *s* x *m*	0.09	3	0.03	2.56	0.058
t x *s* x *m*	0.01	1	0.01	1.23	0.269
f x *t* x *s* x *m*	0.03	3	0.01	0.70	0.552
Error	1.44	120	0.01		
Total	2.96	151			
Pretreated Poplar					
Force (*f*)	0.53	3	0.18	18.23	0.000
Temperature (*t*)	0.09	1	0.09	9.43	0.003
Moisture content (*m*)	0.20	1	0.20	21.19	0.000
f x *t*	0.46	3	0.15	15.84	0.000
f x *m*	0.00	3	0.00	0.17	0.918
t x *m*	0.00	1	0.00	0.04	0.846
f x *t* x *m*	0.07	3	0.02	2.44	0.073
Error	0.58	60	0.01		
Total	1.97	75			

Table B.6 Analysis of variance (ANOVA) table for factors affecting specific energy required for extrusion of the wheat straw feedstocks.

Source	SS	df	MS	F	Sig.
Wheat straw					
Force (*f*)	0.24	3	0.08	3.55	0.016
Temperature (*t*)	0.05	1	0.05	2.38	0.126
Screen size (*s*)	1.36	1	1.36	59.92	0.000
Moisture content (*m*)	0.02	1	0.02	0.85	0.359
f x *t*	0.66	3	0.22	9.74	0.000
f x *s*	0.03	3	0.01	0.40	0.751
t x *s*	0.00	1	0.00	0.12	0.734
f x *t* x *s*	0.09	3	0.03	1.32	0.272
f x *m*	0.07	3	0.02	1.08	0.359
t x *m*	0.07	1	0.07	3.01	0.085
f x *t* x *m*	0.04	3	0.01	0.66	0.581
s x *m*	0.00	1	0.00	0.01	0.911
f x *s* x *m*	0.03	3	0.01	0.42	0.741
t x *s* x *m*	0.00	1	0.00	0.03	0.857
f x *t* x *s* x *m*	0.06	3	0.02	0.85	0.467
Error	2.84	125	0.02		
Total	5.61	156			
Pretreated wheat straw					
Force (*f*)	0.36	3	0.12	11.68	0.000
Temperature (*t*)	0.01	1	0.01	0.52	0.475
Moisture content (*m*)	0.24	1	0.24	23.28	0.000
f x *t*	0.02	3	0.01	0.54	0.658
f x *m*	0.14	3	0.05	4.68	0.005
t x *m*	0.05	1	0.05	4.97	0.029
f x *t* x *m*	0.03	3	0.01	0.82	0.488
Error	0.65	63	0.01		
Total	1.50	78			

Table B.7 Analysis of variance (ANOVA) table for factors affecting the initial pellet density of the poplar feedstocks.

Source	SS	df	MS	F	Sig.
Poplar					
Force (*f*)	2243134.76	3	747711.59	1795.60	0.000
Temperature (*t*)	38423.76	1	38423.76	92.27	0.000
Screen size (*s*)	307841.72	1	307841.72	739.27	0.000
Moisture content (*m*)	19672.74	1	19672.74	47.24	0.000
f x *t*	23045.26	3	7681.75	18.45	0.000
f x *s*	15444.81	3	5148.27	12.36	0.000
t x *s*	1824.79	1	1824.79	4.38	0.037
f x *t* x *s*	2051.31	3	683.77	1.64	0.180
f x *m*	9946.71	3	3315.57	7.96	0.000
t x *m*	1489.79	1	1489.79	3.58	0.060
f x *t* x *m*	782.38	3	260.79	0.63	0.599
s x *m*	2290.13	1	2290.13	5.50	0.020
f x *s* x *m*	1767.50	3	589.17	1.41	0.239
t x *s* x *m*	1.35	1	1.35	0.00	0.955
f x *t* x *s* x *m*	269.54	3	89.85	0.22	0.885
Error	116595.90	280	416.41		
Total	2788321.07	311			
Pretreated Poplar					
Force (*f*)	822036.12	3	274012.04	391.50	0.000
Temperature (*t*)	77426.80	1	77426.80	110.63	0.000
Moisture content (*m*)	344295.27	1	344295.27	491.92	0.000
f x *t*	45035.42	3	15011.81	21.45	0.000
f x *m*	50067.60	3	16689.20	23.85	0.000
t x *m*	1187.34	1	1187.34	1.70	0.195
f x *t* x *m*	7742.83	3	2580.94	3.69	0.014
Error	99385.56	142	699.90		
Total	1449812.65	157			

Table B.8 Analysis of variance (ANOVA) table for factors affecting the initial pellet density of the wheat straw feedstocks.

Source	SS	df	MS	F	Sig.
Wheat straw					
Force (*f*)	2434480.77	3	811493.59	1627.15	0.000
Temperature (*t*)	86352.68	1	86352.68	173.15	0.000
Screen size (*s*)	378359.52	1	378359.52	758.66	0.000
Moisture content (*m*)	92.38	1	92.38	0.19	0.667
f x *t*	18435.44	3	6145.15	12.32	0.000
f x *s*	1370.84	3	456.95	0.92	0.433
t x *s*	8354.44	1	8354.44	16.75	0.000
f x *t* x *s*	1992.70	3	664.23	1.33	0.264
f x *m*	15355.52	3	5118.51	10.26	0.000
t x *m*	10514.24	1	10514.24	21.08	0.000
f x *t* x *m*	6534.11	3	2178.04	4.37	0.005
s x *m*	74.16	1	74.16	0.15	0.700
f x *s* x *m*	57.36	3	19.12	0.04	0.990
t x *s* x *m*	0.08	1	0.08	0.00	0.990
f x *t* x *s* x *m*	307.55	3	102.52	0.21	0.893
Error	140639.02	282	498.72		
Total	3135045.21	313			
Pretreated wheat straw					
Force (*f*)	452881.25	3	150960.42	112.80	0.000
Temperature (*t*)	87052.38	1	87052.38	65.05	0.000
Moisture content (*m*)	19439.57	1	19439.57	14.53	0.000
f x *t*	23515.46	3	7838.49	5.86	0.001
f x *m*	113954.67	3	37984.89	28.38	0.000
t x *m*	13313.40	1	13313.40	9.95	0.002
f x *t* x *m*	10032.58	3	3344.19	2.50	0.062
Error	186016.35	139	1338.25		
Total	917039.91	154			

Table B.9 Analysis of variance (ANOVA) table for factors affecting the diametral expansion of the biomass feedstocks.

Source	SS	df	MS	F	Sig.
Poplar					
Temperature (*t*)	0.93	1	0.93	6.22	0.015
Screen size (*s*)	1.75	1	1.75	11.65	0.001
Moisture content (*m*)	2.82	1	2.82	18.79	0.000
t x *s*	0.33	1	0.33	2.18	0.144
t x m	0.05	1	0.05	0.33	0.569
s x *m*	0.20	1	0.20	1.30	0.258
t x *s* x *m*	0.06	1	0.06	0.37	0.543
Error	10.37	69	0.15		
Total	16.74	76			
Pretreated Poplar					
Temperature (*t*)	0.12	1	0.12	1.53	0.225
Moisture content (*m*)	1.55	1	1.55	20.29	0.000
t x *m*	0.04	1	0.04	0.49	0.487
Error	2.60	34	0.08		
Total	4.29	37			
Wheat straw					
Temperature (*t*)	1.11	1	1.11	8.17	0.006
Screen size (*s*)	1.81	1	1.81	13.34	0.000
Moisture content (*m*)	3.29	1	3.29	24.28	0.000
t x *s*	0.10	1	0.10	0.74	0.391
t x m	1.42	1	1.42	10.48	0.002
s x *m*	0.10	1	0.10	0.75	0.388
t x *s* x *m*	0.012677	1	0.012677	0.093531	0.76063
Error	9.623299	71	0.135539		
Total	17.53	78			
Pretreated wheat straw					
Temperature (*t*)	0.20	1	0.20	1.44	0.239
Moisture content (*m*)	0.01	1	0.01	0.08	0.773
t x *m*	0.13	1	0.13	0.96	0.335
Error	4.37	31	0.14		
Total	4.78	34			

Table B.10 Analysis of variance (ANOVA) table for factors affecting the longitudinal expansion of the biomass feedstocks.

Source	SS	df	MS	F	Sig.
Poplar					
Temperature (*t*)	209.61	1	209.61	60.66	0.000
Screen size (*s*)	4.74	1	4.74	1.37	0.246
Moisture content (*m*)	441.64	1	441.64	127.82	0.000
t x *s*	7.70	1	7.70	2.23	0.140
t x m	7.73	1	7.73	2.24	0.139
s x *m*	28.34	1	28.34	8.20	0.006
t x *s* x *m*	7.65	1	7.65	2.21	0.141
Error	234.96	68	3.46		
Total	970.80	75			
Pretreated Poplar					
Temperature (*t*)	8.39	1	8.39	9.19	0.005
Moisture content (*m*)	38.18	1	38.18	41.83	0.000
t x *m*	1.36	1	1.36	1.49	0.231
Error	30.12	33	0.91		
Total	78.43	36			
Wheat straw					
Temperature (*t*)	200.87	1	200.87	17.29	0.000
Screen size (*s*)	3.56	1	3.56	0.31	0.582
Moisture content (*m*)	349.25	1	349.25	30.05	0.000
t x *s*	26.70	1	26.70	2.30	0.134
t x m	183.37	1	183.37	15.78	0.000
s x *m*	0.16	1	0.16	0.01	0.906
t x *s* x *m*	16.28392	1	16.28392	1.401316	0.240686
Error	778.5703	67	11.62045		
Total	1571.95	74			
Pretreated wheat straw					
Temperature (*t*)	4.72	1	4.72	2.04	0.164
Moisture content (*m*)	4.63	1	4.63	2.00	0.168
t x *m*	1.62	1	1.62	0.70	0.409
Error	71.82	31	2.32		
Total	83.62	34			

Table B.11 Analysis of variance (ANOVA) table for factors affecting the tensile strength of the biomass feedstocks.

Source	SS	df	MS	F	Sig.
Poplar					
Temperature (*t*)	1.27	1	1.27	36.57	0.000
Screen size (*s*)	3.84	1	3.84	111.06	0.000
Moisture content (*m*)	0.00	1	0.00	0.06	0.803
t x *s*	0.26	1	0.26	7.40	0.009
t x m	0.03	1	0.03	0.90	0.348
s x *m*	0.04	1	0.04	1.09	0.302
t x *s* x *m*	0.02	1	0.02	0.50	0.481
Error	1.77	51	0.03		
Total	7.38	58			
Pretreated Poplar					
Temperature (*t*)	48.17	1	48.17	46.29	0.000
Moisture content (*m*)	12.91	1	12.91	12.41	0.002
t x *m*	6.24	1	6.24	6.00	0.021
Error	28.10	27	1.04		
Total	97.80	30			
Wheat straw					
Temperature (*t*)	3.47	1	3.47	79.91	0.000
Screen size (*s*)	0.80	1	0.80	18.45	0.000
Moisture content (*m*)	0.00	1	0.00	0.03	0.858
t x *s*	0.34	1	0.34	7.75	0.007
t x m	0.57	1	0.57	13.04	0.001
s x *m*	0.00	1	0.00	0.11	0.738
t x *s* x *m*	0.00	1	0.00	0.05	0.829791
Error	2.43	56	0.04		
Total	7.61	63			
Pretreated wheat straw					
Temperature (*t*)	7.33	1	7.33	3.11	0.089
Moisture content (*m*)	40.29	1	40.29	17.10	0.000
t x *m*	2.54	1	2.54	1.08	0.308
Error	63.62	27	2.36		
Total	113.71	30			

APPENDIX C – DATA TABLES

Table C.1 Asymptotic moduli of poplar feedstocks.

Feedstock	Pre-set load (N)	Temperature (°C)	Screen size (mm)	Moisture (% wb)	Mean peak load (N)	Asymptotic modulus, E_A (MPa)*
Poplar	1000	70	0.8	9	1022 (8)	26.5 (1.4)
				15	1026 (7)	25.9 (0.7)
			3.2	9	1021 (6)	26.1 (0.4)
				15	1025 (8)	25.3 (0.5)
		100	0.8	9	1032 (8)	26.7 (0.7)
				15	1036 (10)	25.8 (0.6)
			3.2	9	1023 (5)	26.5 (0.4)
				15	1030 (8)	25.6 (0.4)
	2000	70	0.8	9	2071 (24)	57.4 (0.9)
				15	2076 (25)	55.0 (2.4)
			3.2	9	2062 (21)	56.2 (0.9)
				15	2071 (18)	52.5 (1.8)
		100	0.8	9	2076 (9)	56.9 (2.6)
				15	2097 (27)	55.9 (1.3)
			3.2	9	2071 (20)	56.4 (1.4)
				15	2089 (19)	53.5 (2.0)
	3000	70	0.8	9	3108 (34)	90.6 (4.6)
				15	3223 (187)	88.5 (6.1)
			3.2	9	3116 (32)	88.5 (2.1)
				15	3135 (41)	83.9 (3.5)
		100	0.8	9	3114 (33)	94.0 (1.7)
				15	3140 (41)	88.8 (4.2)
			3.2	9	3115 (38)	91.4 (2.5)
				15	3118 (39)	85.0 (2.6)
	4000	70	0.8	9	4133 (46)	130.3 (1.7)
				15	4208 (79)	129.2 (4.8)
			3.2	9	4151 (46)	126.2 (1.9)
				15	4168 (60)	121.4 (3.8)
		100	0.8	9	4148 (42)	131.3 (5.3)
				15	4253 (81)	127.4 (6.1)
			3.2	9	4146 (63)	127.7 (3.8)
				15	4173 (48)	123.2 (4.1)
Pretreated poplar	1000	70	-	9	1018 (22)	22.5 (1.0)
				15	1042 (7)	19.4 (1.8)
		100	-	9	1025 (8)	20.6 (0.6)
				15	1042 (9)	17.2 (0.5)
	2000	70	-	9	2071 (16)	44.7 (3.3)
				15	2098 (31)	40.4 (3.3)
		100	-	9	2083 (23)	46.9 (2.4)
				15	2106 (24)	41.7 (2.9)
	3000	70	-	9	3157 (118)	80.9 (6.6)
				15	3198 (116)	80.2 (15.0)
		100	-	9	3133 (75)	80.9 (2.2)
				15	3556 (379)	101.8 (24.3)
	4000	70	-	9	4184 (83)	115.9 (4.0)
				15	4353 (286)	124.8 (25.1)
		100	-	9	4158 (45)	114.7 (6.7)
				15	4695 (269)	148.3 (19.4)

* Numbers in parentheses are standard deviations (n = 10)

Table C.2 Asymptotic moduli of wheat straw feedstocks.

Feedstock	Pre-set load (N)	Temperature (°C)	Screen size (mm)	Moisture (% wb)	Mean peak load (N)*	Asymptotic modulus, E_A (MPa)*
Wheat straw	1000	70	0.8	9	1019 (7)	26.1 (0.7)
				15	1029 (8)	24.9 (0.5)
			3.2	9	1017 (8)	26.6 (0.3)
				15	1024 (8)	25.2 (0.7)
		100	0.8	9	1019 (5)	26.9 (0.4)
				15	1024 (6)	25.1 (0.9)
			3.2	9	1023 (7)	27.6 (0.5)
				15	1025 (7)	24.9 (0.7)
	2000	70	0.8	9	2061 (20)	56.7 (1.1)
				15	2078 (26)	53.2 (1.6)
			3.2	9	2055 (14)	57.6 (1.0)
				15	2070 (26)	52.4 (1.8)
		100	0.8	9	2063 (20)	56.6 (1.7)
				15	2082 (28)	52.9 (2.5)
			3.2	9	2059 (20)	57.4 (1.5)
				15	2069 (26)	52.3 (2.7)
	3000	70	0.8	9	3175 (91)	89.8 (1.2)
				15	3171 (75)	86.0 (2.9)
			3.2	9	3144 (97)	88.4 (1.7)
				15	3150 (89)	81.5 (4.3)
		100	0.8	9	3102 (38)	91.5 (1.7)
				15	3136 (43)	84.2 (3.0)
			3.2	9	3091 (31)	91.9 (2.1)
				15	3120 (28)	81.2 (4.1)
	4000	70	0.8	9	4148 (42)	124.8 (2.6)
				15	4172 (48)	124.0 (3.3)
			3.2	9	4145 (41)	122.8 (2.6)
				15	4159 (41)	116.3 (4.6)
		100	0.8	9	4173 (42)	127.3 (1.5)
				15	4211 (50)	118.3 (5.2)
			3.2	9	4154 (44)	122.7 (3.5)
				15	4171 (48)	118.0 (6.2)
Pretreated wheat straw	1000	70	-	9	1022 (13)	19.9 (1.1)
				15	1039 (13)	16.9 (1.0)
		100	-	9	1027 (8)	18.0 (0.3)
				15	1069 (45)	16.7 (1.5)
	2000	70	-	9	2066 (21)	38.2 (0.9)
				15	2286 (203)	62.9 (13.9)
		100	-	9	2072 (25)	40.3 (3.5)
				15	2484 (286)	70.9 (18.4)
	3000	70	-	9	3141 (65)	65.7 (6.0)
				15	3802 (301)	119.8 (12.5)
		100	-	9	3123 (40)	64.1 (4.4)
				15	3971 (114)	126.5 (5.1)
	4000	70	-	9	4200 (158)	98.3 (19.3)
				15	4470 (309)	135.2 (22.9)
		100	-	9	4358 (333)	116.8 (27.2)
				15	4474 (391)	127.6 (30.8)

* Numbers in parentheses are standard deviations (n = 10)

Table C.3 Specific compression and extrusion energy of poplar feedstocks.

Feedstock	Pre-set load (N)	Temperature (°C)	Screen size (mm)	Moisture (% wb)	Specific compression energy (MJ/t)*	Specific extrusion energy (MJ/t)**
Poplar	1000	70	0.8	9	10.74 (0.36)	0.44 (0.06)
				15	10.63 (0.55)	0.46 (0.09)
			3.2	9	13.31 (0.94)	0.56 (0.16)
				15	13.30 (1.37)	0.47 (0.05)
		100	0.8	9	11.30 (0.41)	0.47 (0.17)
				15	10.81 (0.39)	0.42 (0.03)
			3.2	9	14.31 (0.71)	0.60 (0.06)
				15	13.63 (1.08)	0.63 (0.11)
	2000	70	0.8	9	16.93 (0.68)	0.42 (0.04)
				15	16.08 (1.29)	0.47 (0.06)
			3.2	9	22.12 (1.57)	0.84 (0.17)
				15	20.41 (2.03)	0.68 (0.18)
		100	0.8	9	16.15 (0.64)	0.45 (0.05)
				15	14.62 (0.68)	0.50 (0.08)
			3.2	9	19.38 (0.90)	0.63 (0.10)
				15	18.51 (1.21)	0.59 (0.07)
	3000	70	0.8	9	21.49 (1.18)	0.48 (0.08)
				15	20.15 (1.31)	0.35 (0.06)
			3.2	9	26.17 (2.29)	0.54 (0.10)
				15	23.13 (1.69)	0.53 (0.27)
		100	0.8	9	21.58 (1.01)	0.49 (0.06)
				15	20.47 (0.87)	0.50 (0.09)
			3.2	9	25.29 (1.72)	0.54 (0.13)
				15	25.06 (1.13)	0.58 (0.08)
	4000	70	0.8	9	25.85 (0.71)	0.41 (0.04)
				15	23.40 (1.61)	0.43 (0.10)
			3.2	9	29.14 (0.75)	0.51 (0.05)
				15	29.30 (1.37)	0.59 (0.21)
		100	0.8	9	26.24 (0.82)	0.43 (0.13)
				15	22.65 (1.16)	0.33 (0.07)
			3.2	9	29.40 (2.09)	0.48 (0.07)
				15	27.73 (2.41)	0.53 (0.12)
Pretreated poplar	1000	70	-	9	13.26 (0.91)	0.55 (0.11)
				15	10.06 (0.81)	0.37 (0.02)
		100	-	9	12.69 (0.90)	0.44 (0.05)
				15	9.04 (0.87)	0.37 (0.09)
	2000	70	-	9	22.09 (2.69)	0.69 (0.10)
				15	16.51 (1.67)	0.57 (0.09)
		100	-	9	15.85 (1.28)	0.45 (0.09)
				15	13.70 (1.94)	0.38 (0.09)
	3000	70	-	9	24.38 (1.74)	0.50 (0.14)
				15	18.48 (1.33)	0.49 (0.12)
		100	-	9	26.11 (1.80)	0.78 (0.06)
				15	16.76 (2.68)	0.57 (0.06)
	4000	70	-	9	28.76 (1.45)	0.52 (0.06)
				15	21.88 (3.43)	0.39 (0.15)
		100	-	9	27.17 (1.67)	0.29 (0.12)
				15	18.02 (2.06)	0.31 (0.14)

* Numbers in parentheses are standard deviations (n = 10); ** (n = 5)

Table C.4 Specific compression and extrusion energy of wheat straw feedstocks.

Feedstock	Pre-set load (N)	Temperature (°C)	Screen size (mm)	Moisture (% wb)	Specific compression energy (MJ/t)*	Specific extrusion energy (MJ/t)**
Wheat straw	1000	70	0.8	9	15.03 (1.12)	0.25 (0.14)
				15	12.69 (0.68)	0.39 (0.04)
			3.2	9	19.31 (1.47)	0.31 (0.07)
				15	16.45 (1.86)	0.53 (0.15)
		100	0.8	9	14.91 (0.52)	0.51 (0.10)
				15	14.68 (0.98)	0.40 (0.10)
			3.2	9	19.42 (2.15)	0.46 (0.09)
				15	19.71 (3.22)	0.79 (0.61)
	2000	70	0.8	9	21.86 (1.04)	0.64 (0.21)
				15	19.74 (1.14)	0.44 (0.06)
			3.2	9	29.71 (2.09)	0.41 (0.06)
				15	25.91 (3.80)	0.71 (0.16)
		100	0.8	9	19.44 (1.92)	0.62 (0.14)
				15	18.08 (1.48)	0.32 (0.03)
			3.2	9	23.19 (3.60)	0.36 (0.06)
				15	19.71 (1.38)	0.41 (0.03)
	3000	70	0.8	9	25.50 (0.97)	0.57 (0.15)
				15	22.40 (1.84)	0.34 (0.06)
			3.2	9	31.91 (5.05)	0.33 (0.05)
				15	25.84 (1.79)	0.45 (0.08)
		100	0.8	9	26.67 (0.61)	0.43 (0.12)
				15	24.63 (1.44)	0.41 (0.05)
			3.2	9	33.49 (2.48)	0.53 (0.09)
				15	32.75 (2.79)	0.62 (0.03)
	4000	70	0.8	9	31.58 (1.61)	0.76 (0.19)
				15	27.85 (1.33)	0.31 (0.09)
			3.2	9	39.13 (2.97)	0.33 (0.06)
				15	32.63 (1.99)	0.49 (0.08)
		100	0.8	9	29.33 (1.26)	0.56 (0.12)
				15	27.03 (2.20)	0.29 (0.05)
			3.2	9	34.76 (2.64)	0.33 (0.03)
				15	33.12 (2.58)	0.39 (0.07)
Pretreated wheat straw	1000	70	-	9	13.00 (0.96)	0.49 (0.22)
				15	9.50 (1.06)	0.39 (0.11)
		100	-	9	11.01 (0.78)	0.48 (0.06)
				15	7.21 (0.55)	0.40 (0.12)
	2000	70	-	9	19.50 (1.05)	0.41 (0.05)
				15	13.56 (1.85)	0.38 (0.11)
		100	-	9	16.10 (1.56)	0.50 (0.09)
				15	11.45 (2.87)	0.39 (0.04)
	3000	70	-	9	23.28 (2.64)	0.51 (0.13)
				15	15.00 (1.38)	0.38 (0.06)
		100	-	9	22.31 (1.64)	0.71 (0.13)
				15	11.86 (1.67)	0.48 (0.09)
	4000	70	-	9	26.06 (2.21)	0.64 (0.08)
				15	23.07 (6.81)	0.34 (0.12)
		100	-	9	23.37 (4.70)	0.45 (0.12)
				15	20.76 (5.67)	0.37 (0.08)

* Numbers in parentheses are standard deviations (n = 10); ** (n = 5)

Table C.5 Packing and initial pellet densities of poplar feedstocks.

Feedstock	Pre-set load (N)	Temperature (°C)	Screen size (mm)	Moisture (% wb)	Packing density (kg/m^3)*	Initial pellet density (kg/m^3)*
Poplar	1000	70	0.8	9	1149 (15)	859 (11)
				15	1213 (24)	880 (21)
			3.2	9	1123 (22)	794 (27)
				15	1178 (21)	796 (14)
		100	0.8	9	1090 (14)	874 (8)
				15	1149 (10)	881 (9)
			3.2	9	1059 (21)	807 (22)
				15	1107 (18)	788 (23)
	2000	70	0.8	9	1270 (13)	975 (14)
				15	1312 (24)	962 (17)
			3.2	9	1238 (27)	900 (32)
				15	1260 (21)	872 (18)
		100	0.8	9	1427 (22)	1018 (10)
				15	1475 (49)	994 (14)
			3.2	9	1420 (21)	966 (21)
				15	1376 (76)	926 (35)
	3000	70	0.8	9	1453 (24)	1044 (7)
				15	1504 (28)	1027 (19)
			3.2	9	1423 (19)	979 (20)
				15	1464 (35)	954 (32)
		100	0.8	9	1356 (14)	1063 (13)
				15	1385 (14)	1047 (14)
			3.2	9	1339 (21)	1012 (30)
				15	1360 (17)	984 (25)
	4000	70	0.8	9	1391 (448)	1086 (24)
				15	1563 (18)	1071 (18)
			3.2	9	1518 (9)	1043 (13)
				15	1531 (19)	1025 (18)
		100	0.8	9	1570 (40)	1096 (9)
				15	1645 (59)	1071 (29)
			3.2	9	1527 (23)	1055 (27)
				15	1568 (65)	1040 (13)
Pretreated poplar	1000	70	-	9	1103 (30)	966 (27)
				15	1293 (66)	1095 (37)
		100	-	9	1110 (19)	1024 (31)
				15	1308 (29)	1182 (19)
	2000	70	-	9	1230 (47)	1082 (34)
				15	1408 (46)	1200 (25)
		100	-	9	1422 (43)	1178 (29)
				15	1501 (115)	1265 (38)
	3000	70	-	9	1425 (22)	1191 (13)
				15	1556 (47)	1251 (18)
		100	-	9	1300 (24)	1169 (20)
				15	1489 (38)	1271 (26)
	4000	70	-	9	1492 (20)	1226 (12)
				15	1612 (51)	1269 (32)
		100	-	9	1380 (480)	1249 (28)
				15	1681 (51)	1296 (12)

* Numbers in parentheses are standard deviations (n = 10)

Table C.6 Packing and initial pellet densities of wheat straw feedstocks.

Feedstock	Pre-set load (N)	Temperature (°C)	Screen size (mm)	Moisture (% wb)	Packing density (kg/m^3)*	Initial pellet density (kg/m^3)*
Wheat straw	1000	70	0.8	9	1064 (57)	745 (16)
				15	1215 (22)	795 (13)
			3.2	9	1061 (38)	654 (27)
				15	1162 (36)	703 (24)
		100	0.8	9	1062 (13)	774 (13)
				15	1091 (59)	776 (9)
			3.2	9	1008 (40)	719 (29)
				15	1047 (45)	721 (19)
	2000	70	0.8	9	1261 (24)	864 (31)
				15	1304 (37)	873 (10)
			3.2	9	1221 (28)	785 (20)
				15	1249 (40)	794 (25)
		100	0.8	9	1380 (96)	932 (27)
				15	1420 (108)	912 (20)
			3.2	9	1341 (128)	865 (24)
				15	1435 (35)	846 (19)
	3000	70	0.8	9	1473 (16)	951 (10)
				15	1519 (17)	937 (19)
			3.2	9	1453 (19)	871 (21)
				15	1489 (36)	866 (42)
		100	0.8	9	1354 (10)	964 (18)
				15	1383 (18)	959 (10)
			3.2	9	1270 (189)	901 (18)
				15	1352 (37)	894 (29)
	4000	70	0.8	9	1525 (35)	999 (25)
				15	1584 (11)	1001 (11)
			3.2	9	1518 (16)	925 (27)
				15	1415 (460)	927 (18)
		100	0.8	9	1594 (56)	1026 (18)
				15	1648 (54)	1004 (18)
			3.2	9	1544 (46)	970 (33)
				15	1618 (66)	957 (27)
Pretreated wheat straw	1000	70	-	9	1137 (58)	997 (44)
				15	1381 (77)	1147 (38)
		100	-	9	1216 (26)	1127 (21)
				15	1381 (18)	1194 (23)
	2000	70	-	9	1303 (36)	1164 (29)
				15	1450 (59)	1196 (22)
		100	-	9	1497 (98)	1215 (78)
				15	1531 (99)	1230 (24)
	3000	70	-	9	1453 (50)	1210 (34)
				15	1613 (25)	1203 (25)
		100	-	9	1422 (48)	1265 (34)
				15	1502 (23)	1205 (36)
	4000	70	-	9	1535 (49)	1257 (11)
				15	1620 (97)	1247 (52)
		100	-	9	1627 (70)	1286 (36)
				15	1724 (83)	1279 (29)

* Numbers in parentheses are standard deviations (n = 10)

Table C.7 Quantitative results from the analysis of poplar (9% wb moisture) using FT-IR PAS (only prominent peaks of interest listed).

Wavenumber (cm^{-1})	Relative peak intensity	Peak integration result	Chemical significance
*	*	0.227	β-Glycosidic linkages between sugar units (Sun et al. 2005)
1036	0.085	0.642	Polysaccharide vibrations (Lawther et al. 1996)
1457	0.022	0.747	CH deformations and aromatic ring vibrations (Xiao et al. 2001)
1506	0.057	1.209	Associated with lignin; aromatic C=C stretch (Sun et al. 2005) or aryl H vibrations (Lawther et al. 1996)
1593	0.070	1.567	Lignin (Liu et al. 2005)
1636	0.009	0.043	Carbonyl stretching conjugated with aromatic rings (Xiao et al. 2001)
1734	0.097	1.083	Hemicellulose band (Liu et al. 2005), or Ester linkage between hemicellulose and lignin (Liu et al. 2005; Sun et al. 2005)
2895	0.059	6.119	Aliphatic CH stretching of lignin and polysaccharides (Sun et al. 2004; Sun et al. 2005)
3343	0.108	-	OH stretch band (Sun et al. 2005)

Table C.8 Quantitative results from the analysis of pretreated poplar (9% wb moisture) using FT-IR PAS (only prominent peaks of interest listed).

Wavenumber (cm^{-1})	Relative peak intensity	Peak integration result	Chemical significance
*	*	0.296	β-Glycosidic linkages between sugar units (Sun et al. 2005)
1037	0.076	0.511	Polysaccharide vibrations (Lawther et al. 1996)
1457	0.014	0.696	CH deformations and aromatic ring vibrations (Xiao et al. 2001)
1515	0.037	1.416	Associated with lignin; aromatic C=C stretch (Sun et al. 2005) or aryl H vibrations (Lawther et al. 1996)
1596	0.090	2.037	Lignin (Liu et al. 2005)
*	*	0.008	Carbonyl stretching conjugated with aromatic rings (Xiao et al. 2001)
1718	0.051	0.909	Hemicellulose band (Liu et al. 2005), or Ester linkage between hemicellulose and lignin (Liu et al. 2005; Sun et al. 2005)
2899	0.129	6.771	Aliphatic CH stretching of lignin and polysaccharides (Sun et al. 2004; Sun et al. 2005)
3292	0.085	-	OH stretch band (Sun et al. 2005)

* Peak not detected at the 3% thresholding value

Table C.9 Quantitative results from the analysis of wheat straw (9% wb moisture) using FT-IR PAS (only prominent peaks of interest listed).

Wavenumber (cm^{-1})	Relative peak intensity	Peak integration result	Chemical significance
897	0.015	0.286	β-Glycosidic linkages between sugar units (Sun et al. 2005)
1040	0.083	0.609	Polysaccharide vibrations (Lawther et al. 1996)
1457	0.014	0.297	CH deformations and aromatic ring vibrations (Xiao et al. 2001)
1507	0.043	0.947	Associated with lignin; aromatic C=C stretch (Sun et al. 2005) or aryl H vibrations (Lawther et al. 1996)
1596	0.032	0.526	Lignin (Liu et al. 2005)
1635	0.009	0.044	Carbonyl stretching conjugated with aromatic rings (Xiao et al. 2001)
1734	0.034	0.954	Hemicellulose band (Liu et al. 2005), or Ester linkage between hemicellulose and lignin (Liu et al. 2005; Sun et al. 2005)
2915	0.051	5.260	Aliphatic CH stretching of lignin and polysaccharides (Sun et al. 2004; Sun et al. 2005)
3344	0.113	-	OH stretch band (Sun et al. 2005)

Table C.10 Quantitative results from the analysis of pretreated wheat straw (9% wb moisture) using FT-IR PAS (only prominent peaks of interest listed).

Wavenumber (cm^{-1})	Relative peak intensity	Peak integration result	Chemical significance
898	0.020	0.397	β-Glycosidic linkages between sugar units (Sun et al. 2005)
1040	0.087	0.723	Polysaccharide vibrations (Lawther et al. 1996)
1457	0.010	0.361	CH deformations and aromatic ring vibrations (Xiao et al. 2001)
1514	0.048	1.167	Associated with lignin; aromatic C=C stretch (Sun et al. 2005) or aryl H vibrations (Lawther et al. 1996)
1596	0.071	0.614	Lignin (Liu et al. 2005)
*	*	0.017	Carbonyl stretching conjugated with aromatic rings (Xiao et al. 2001)
1717	0.020	0.795	Hemicellulose band (Liu et al. 2005), or Ester linkage between hemicellulose and lignin (Liu et al. 2005; Sun et al. 2005)
2901	0.103	5.155	Aliphatic CH stretching of lignin and polysaccharides (Sun et al. 2004; Sun et al. 2005)
3335	0.078	-	OH stretch band (Sun et al. 2005)

* Peak not detected at the 3% thresholding value