PELLETING CHARACTERISTICS OF TORREFIED FOREST BIOMASS

by

MANUNYA PHANPHANICH

(Under the Direction of Sudhagar Mani)

ABSTRACT

Forest biomass (pine wood chips) was torrefied at different temperature (225 to 300°C) to generate energy dense and hydrophobic biomass suitable for producing pellets. It was found that torrefaction of forest biomass improved the energy density of biomass close to bituminous coal. Energy required for grinding of torrefied biomass was significantly reduced to 23 kWh/t compared to 238 kWh/t for raw pine chips. Feed and flow properties of torrefied wood powders also improved, as roundness (0.48 to 0.62), specific surface area (14 mm^{-1} to 64 mm^{-1}), and flowability increased, while, cohesiveness decreased. Pelleting of torrefied biomass required significantly more applied pressure to achieve high pellet density compared to that of untreated biomass resulted in increased compressive energy consumption. Pellets made from torrefied biomass were found in dimensionally stability, high strength and durability, and absorbed less water compared to that of untreated biomass pellets.

INDEX WORDS: forest biomass, pine chip, pretreatment, densification, torrefaction, solid fuel

PELLETING CHARACTERISTICS OF TORREFIED FOREST BIOMASS

by

MANUNYA PHANPHANICH

B.S., Kasetsart University, Thailand, 2003

A Thesis Submitted to the Graduate Faculty of The University of Georgia in Partial Fulfillment
of the Requirements for the Degree

MASTER OF SCIENCE

ATHENS, GEORGIA

2010

PELLETING CHARACTERISTICS OF TORREFIED FOREST BIOMASS

by

MANUNYA PHANPHANICH

Major Professor:	Sudhagar Mani
Committee:	Dale Greene KC Das

Electronic Version Approved:

Maureen Grasso
Dean of the Graduate School
The University of Georgia
August 2010

DEDICATION

To Phanphanich family and our community.

ACKNOWLEDGEMENTS

I would like to express my sincere appreciation to my advisor, Prof. Sudhagar Mani, for his support, guidance, and encouragement during the course of this research. His insight and passion have inspired and taught me beyond research. I also thank Dr. Dale Greene and Dr. KC Das, for serving on my thesis reading committee and providing helpful suggestions and support on this research.

Special thank to my family (Phanphanich), Micah Lewis, Siravara Krachang and her family for the encouragement to finish strong. Thank you all for making this thesis possible.

TABLE OF CONTENTS

Page

CHAPTER

APPENDICES

LIST OF TABLES

Page

LIST OF FIGURES

LIST OF SYMBOLS

ADF = Acid detergent fiber

NDF = Neutral detergent fiber

ADL = Acid detergent lignin

M = Instantaneous moisture content after a time t (% db)

C = Carbon

H = Hydrogen

O = Oxygen

N = Nitrogen

V_p = The volume of solid biomass

V_c = The volume of sample cell (m^3)

V_R = The reference volume (m^3)

P_1 = The pressure reading after pressurizing the reference volume (Pa)

P_2 = The pressure after including V_c (Pa)

VM = Volatile matter

HHV = Higher heating value (MJ/kg)

$X_{c\ min}$ = The shortest chord or width (mm)

d_{gw} = d_{50} and = The geometric mean diameter (mm)

d_{16} = The particle diameters obtained from the cumulative distribution data at 16%

d_{84} = The particle diameters obtained from the cumulative distribution data at 84%

S_{GW} = The geometric mean diameter standard deviation (mm)

$SPHT$ = Sphericity (dimensionless)

a = Measured area covered by a particle projection

P = Measured circumference of a particle projection

S_{υ} = The specific surface area (mm^{-1})

A = Surface of all particles (mm^2)

V = Volume of all particle (mm^3)

CHAPTER 1

INTRODUCTION

Forest-based biomass has become a significant alternative source to the conventional energy sources (coal, natural gas & petroleum products) due to the carbon neutral, renewable and sustainable fuel source, as well as its abundance and local availability. Potentially, 30% of today's total energy consumption worldwide is from biomass sources. It amounts for about 100 EJ/y, of which 41.6 EJ/y is shared by forest-based biomass (Parikka, 2004). The total biomass on timberland in US amounts 24,619 million dry tons (Smith, 2004). The amount in the South accounts for 35% of the total, and Georgia is the top three states, sharing this portion. Thermo-chemical conversion technologies (combustion, gasification & pyrolysis) are one way to utilize this biomass to energy, especially, direct combustion, which represents the most promising solution in the short term (Demirbas, 2005). Utilization of forest-based biomass in the form of wood pellets has been well known for residential heating and combined heat and power generation industries, as well as directly co-firing with coal in existing power plants. Currently, more than 80 pellet mills across North America produce over 1.1 million tons of wood pellets (PFI., 2010) and about 4.5 to 5 million ton in Europe annually (Bergman et al., 2005). Recently, the biomass fuels are not only used in the same region in which they are produced, they are traded in many countries especially in Northern Europe, and other Baltic regions (Vesterinen & Alakangas, 2001). The market for wood pellets for energy application has not been expanded due to significant pellet fuel cost compared to fluctuating price of fossil fuels (Coal and Natural gas).

At present, forest-based biomass is consumed for direct combustion applications. In comparison with conventional fuels such as coal, wood possesses very high hygroscopicity and low energy density, resulting in the need for large scale storage of biomass in closed containers and large amounts to provide a comparable energy yield to coal. Biomass also accumulates some volatile organic compounds during bulk storage and the storage headspace needs to be diluted or ventilated for safe handling (Hartley & Wood, 2008). Moreover, wood/ conventional pellets possess a drawback when co-firing with coal as it is tough to be pulverized. All of these drawbacks have become challenges for the development of novel technology to enhance the biomass fuel quality for efficient and economical conversion into fuels, power, and chemicals.

Gasification and co-firing of biomass with coal are difficult due to imbalance in the energy density between coal and biomass, low burning rate, and low flame temperature. It also creates handling problems due to poor flowability and poor blending. These undesirable characteristics of untreated biomass/coal mixtures reduce the thermal efficiency and capacity of existing boiler units (Hughes and Tillman, 1998; Tillman, 2000). Gasification of low quality biomass results in poor synthetic gas quality and high tar concentration. Tar is a highly viscous, higher molecular weight volatile organic compound generated during biomass gasification. A recent study reported that feedstock composition has some effect on the tar formation during gasification (Kiel et al., 2004). They reported that presence of high moisture and a high concentration of reactive (low molecular weight) hemi-cellulose and lignin fractions in the feedstock produce more tar in the syngas than that of cellulose. The hydrophilic nature of biomass compounds additional problems for safe handling and storage. A recent study on co-firing of biomass with coal reported that low energy density and uneven chemical and physical properties of biomass creates major problems during feeding and combustion and resulted in low thermal efficiency and plant capacity (Damstedt et al., 2007; Narayanan & Natarajan, 2007; Nevalainen et al., 2007).

Significant interest in upgrading wood pellets as solid fuel has also been growing throughout the decade in a number of studies such as wood characteristics as raw materials, pellet qualities, pelleting conditions, storage characteristics, combustion properties, and pre-treatments (Alizadeh et al., 2005; Bergman et al., 2004; Bergman et al., 2005; Felfli et al., 2005; Hartley & Wood, 2008; Lam et al., 2009; Lehtikangas, 1999; Lehtikangas, 2001; Lehtikangas, 2000; Shaw et al., 2009). Nevertheless, research on improving the quality of biomass before pelleting itself is still rare. To overcome poor raw biomass characteristics and pellet quality, thermal pretreatment of biomass through a process called torrefaction is proposed. Torrefaction is a thermal pre-treatment of biomass at low temperature ranges (200ºC -300ºC) under anoxic conditions. The process has well shown to enhance wood quality for thermo-chemical conversion, improving size reduction characteristics, increasing the energy density of biomass, yielding high process efficiency (94%) and having an ability to produce coal-like fuel (Uslu et al., 2008), which promisingly complement fuel densification (Arias et al., 2008; Bergman, 2005; Bergman et al., 2004; Bridgeman et al., 2008; Ferro et al., 2004; Li & Gifford, 2001; Lipinsky et al., 2002; Nimlos et al., 2003; Prins et al., 2006). Densification of torrefied biomass has not been studied so far and the compression characteristics of torrefied biomass are necessary to design uniform format, consistent quality solid biofuels for the modern biorefinery.

Torrefaction of forest biomass and its impact on preprocessing and densification of biomass are still immature. A fundamental understanding of densification of torrefied wood is critical to further advance this technology to commercial scale. This in turn will allow the design of producing a high pellet quality, thus improving the feasibility of exploitation of forest residues into green power, biofuels, and bio-based products.

OBJECTIVES

The overall goal of this proposed research was to investigate the impact of torrefaction on the grindability, fuel characteristics, and pelleting quality of forest-based biomass. The specific objectives of this research are:

1. Determine the physical and chemical properties of torrefied and untreated forest biomass.
2. Investigate the effect of torrefaction on the grindability of forest biomass.
3. Investigate the effect of torrefaction on flow properties of powdered biomass.
4. Evaluate the effect of torrefaction temperature, moisture content and compressive force on the pelleting characteristics of biomass.

CHAPTER 2

LITERATURE REVIEW

Introduction

The world's electricity and heat generation has been progressively relying on coal and other fossil fuels. As a result, the world-wide CO_2 emission from fossil fuel combustion has been increased around 38% between 1990 and 2007 (IEA, 2009). It has been projected that renewable energy will need to account for at least 15% of total world energy by 2030 in response to the rising energy demand as well as to mitigate greenhouse gas (GHG) emissions and other pollutants. Bio-fuels from biomass, as one of many renewable energy sources, need to be improved economically and environmentally in order to serve the global energy demand.

Biomass is currently used to generate heat and electricity by combustion technology. Currently, briquettes and pellets are the most commonly used compact forms of biomass. Briquettes are mainly used to replace firewood for manually charged domestic stoves, while pellets are largely used for automatically charged stoves and boilers, due to their good flowability, uniform water content, grain size, and chemical composition. Biomass can be used for co-firing in existing coal power plants and utilized solely in biomass-only dedicated plants. Typically, high quality fuels are necessary for small-scale and automatic heating systems, while lower-quality fuels, such as heterogeneous fuels, can be fed into a large scale system. More than 150 coal-fired power plants have experimented with co-firing biomass or waste, at least on a trial basis (Baxter & Koppejan, 2004). A wide variety of biomass such as short rotation woody crops, agricultural residues, and energy crops has been co-fired with these fuels.

Forest biomass

The use of forest biomass to reduce the dependency on coal has resulted in net reduction in overall greenhouse gas emissions, since burning of nonrenewable fuels, such as coal, is avoided. In 2006, a net 745 million metric t of CO_2 eq. were removed from the atmosphere and stored in forests in 48 conterminous states (Sonja et al., 2010).

Hakkila and Parikka (2002) define forest biomass as the accumulated mass, above and below ground, including leaves and bark. Woody biomass materials currently used as fuels are, almost exclusively, residues from other processes: forest residues, wood processing residues, and tertiary residues (Dominik et al., 2008). Forest residues are those derived from where timber industries utilize woody raw materials selectively, including silvicultural residues. These include undersized trees left intact after thinning operations, logging residues, above-ground low quality stems, and other tree components which are discarded at the site after timber harvesting operations. Wood processing residues are those obtained from forest-based industries that fail to completely use the wood at the mills. Bark, sawdust, slabs, cores, wood chips, and lignin-based black liquor are examples of these residues. For the most part, wood processing residues are preferred as they are clean, uniform, on-site, and low in moisture content, representing the largest commercially used biomass source for energy (Ashton & Cassidy, 2007; Parikka, 2004). Tertiary residues consist mainly of by-products of demolition and construction, offering a significant and inexpensive source of energy. Availability of forest biomass primarily depends on continuing forestry operations, accessibility to the resource, and regulations to maintain soil moisture and carbon storage (Perlack et al., 2005; Wood & Layzell, 2003).

The total above ground woody biomass in forest has been estimated in 166 countries, accounting 99% for the world's forest area (FAO, 2001). It amounts for 420 Gt or about 109 t/ha.

Approximately 55% of the global use of wood fuel and round wood is mostly in developing countries as fuel. The remaining 45% is used as industrial raw material; however, 40% of this amount is primary and secondary process residues used for energy production. Perlack et al. (2005) reported that in the U.S., large amounts of primary (98%) and secondary mill residues (60%) are presently utilized for energy and value added products. The availability of these residues ranges from 0.5 to 135 million dry t, depending on recoverability and prices (Perlack et al., 2005; Walsh, 2008). Logging residues left at harvest site in the US in 1997 were reported by Forest Inventory and Analysis Natural Program as 51.7 million dry t of biomass from growing stock and other sources, and 70% of this amount was recoverable (Smith et al., 2001).

Despite the availability and nature of forest based biomass, fuel characteristics derived from wood have become a major concern in recent years due to its low energy density, hygroscopicity, and inconsistence of physical and chemical characteristics.

Composition of lignocellulosic biomass

To be able to effectively take advantage of wood to produce energy, it is necessary to understand the wood cell wall, as plant cells in cellulosic biomass are enclosed by a rigid cell wall, which comprises of up to 95% of the plant material. Wood cell wall mainly consists of carbohydrates (cellulose and hemicellulose) and lignin together with a small proportion of extractives and less than 1% of protein (Kerr & Goring, 1975). These polymers make up the cell wall and are responsible for most of the physical and chemical properties, providing mechanical strength and tenacity (toughness) to plant structures (Carpita & McCann, 2000). Wood possesses hygroscopicity as cell wall polymers of lignocellulosic materials contain hydroxyl and other oxygen-containing groups that attract moisture through hydrogen bonding (Rowell & Banks, 1985; Stamm, 1964). Density of wood cell wall generally is in the range of 1400 to 1500 kg/m^3 (Dinwoodie, 2000).

Cellulose is a water insoluble substance which comprises 40-60% of the dry weight of plant material (Kerr & Goring, 1975). Long thin cellulose molecules are united into microfibrils. Bundles of microfibrils form into macrofibrils, which join together to constitute the cellulose fiber. Mutual coherence and orientation of crystalline microfibrils of cellulose, surrounded by a small portion of amorphous cellulose, is obtained through the cross-linked matrix of hemicellulose around the macrofibirl structure and also the presence of lignin that fastens adjacent cellulose. Therefore, the cell wall is a fiber-reinforced plastic with cellulose fibers (Shaw, 2008). Hon (Hon, 1989) stated that due to its semi-crystalline and highly bonded structure, cellulose is not a good adhesive.

Hemicellulose makes up 20-40% of the dry weight of wood (Kerr & Goring, 1975). It has lower molecular weight than cellulose. Hemicellulose has a lower presence in softwood (15-20%) than in hardwood (20-30%) (Cheremisinoff, 1980). The main differences with cellulose are that hemicellulose has a branch structure, resulting in the amorphous structure, and it consists of different sugars that are easily degraded (Pérez et al., 2002).

Lignin is a complex poly-phenolic compound that makes up 10-25% of total wood dry weight (Kerr & Goring, 1975). It is comprised of phenyl propane units (Zandersons et al., 2004). Structurally, lignin is an amorphous hetero-polymer (Ashton & Cassidy, 2007). Due to its high molecular weight and its insolubility, degradation of lignin is difficult (Pérez et al., 2002). Lignin has been reported to act as a rigidifying and binding agent, contributing to the strength of cellulose fibers. It was used as an intrinsic resin in binderless board production and many densified wood products such as plywood, particle board, and fiberboard manufacture (Anglès et al., 2001; Granada et al., 2002b; Hatakka, 2001). From a pelleting perspective, lignin in wood plays important roles as first it indicates pellet durability, and secondly, it relates to the heating value of the wood fuel (White, 1987).

Physical properties of lignocellulosic biomass

Whether co-firing biomass with coal, co-milling with coal, or being directly injected through separate burners or spreader grate, biomass needs to be handled as fine grinds in the process (Johnson, 2010). Particle shape, particle size, size distribution, moisture content, flowability, bulk density, calorific value, and flash point are the main characteristics of pulverized biomass powder (Demirbas, 2000)**.** Particle size, size distribution, particle shape, moisture content, heating value, and flash point are properties that influence the combustion characteristics (Demirbas, 2000; Demirbas & Meydan, 2004)**.** Flowability is indicative of how well the powder flows, when fed in the burner. Typically, flowability of powder increases with an increase of particle size; however, there is a critical value of the size where flowability no longer improves (Abdullah & Geldart, 1999). Bulk density is referred to as the mass of powder that can be packed into specific volume. This parameter is important in transporting and handling, as it is evaluated to explain its flow characteristics (Abdullah & Geldart, 1999). Aerated bulk density is defined as a density where particles are separated from each other by a film of air, and they are not in direct contact with each other (Svarovsky, 1987). It is measured by allowing loose packing of powder in a container under the influence of gravity. Structurally strong-powder has an ability to resist collapse when dispersed in a container, indicating low bulk density. On the other hand, powder with a weak structure will fall down easily, yielding high bulk density. Hausner (1967) found that changes in particle surface can affect friction condition of the powders, and powder mass with lower friction condition will yield higher aerated bulk density. Tapped bulk density is obtained by tapping the container, eliminating existing air in aerated powders. Packing condition is achieved when frictions between particles reduced; particles lose contact with each other and rearrange while tapping. During the taping, cohesive powders will considerably collapse; showing improved packing conditions, whereas, the free flowing or weak powders have little extent of further consolidation (Abdullah & Geldart, 1999). The ratio between the tapped density and aerated density of a powder mass is termed the Hausner ratio. The term was given by Grey and Beddow (1969), who employed this ratio to measure the cohesion of powder and friction between particles in a moving metal powder mass. The ratio was claimed to provide basic understanding of the initial stage of compaction of powders (Grey & Beddow, 1969). In the work of Hausner (1967), copper powders with similar particle size distribution but different shapes, i.e., spherical, irregular, and flake, were measured for the aerated and tapped density. Hausner's findings reveal that the powder shape diverged from spherical is more capable of being further consolidated; the higher of the ratio of tapped density to aerated density. However, considering the density alone, more spherical particles will collapse easily and yield higher density (Abdullah & Geldart, 1999; Guo et al., 1985; Yerazunis et al., 1962).

The angle of repose, or angle of friction, is the internal angle formed after bulk granular materials are poured onto a horizontal surface, and a conical pile structures (Wong, 2002). The angle of repose is measured between the surface of the pile and the horizontal surface, when the granular materials come to rest. The angle is related to the density, surface area, and shapes of the particles, and the coefficient of friction of the material. Material with a low angle of repose forms flatter piles than material with a high angle of repose. Angle of repose and bulk density of powdered materials are of interest, since they are correlated, and they reflect flowability and dynamic behavior of a powder, which are responsible for fluidizing performance of the powder (Hausner, 1972; Wong, 2002; Wong, 2000; Yu et al., 1995). The higher the angle of repose and the ratio of tapped density and aerated density, the stronger the cohesive power characteristics (Dutta & Dullea, 1990). In the study of Grey and Beddow (1969), it was found that the angle of repose was increased with the increase of the ratio of the tap density to aerated density. Wong (2000) reported that the high values of angle of repose and the Hausner ratio were observed when powder particle size was less than 100 µm and the plot of the angle of repose against the ratio was fit better with powder size less than 20 µm. The findings were further explained by other researchers (Abdullah & Geldart, 1999; Seville et al., 2000) that cohesiveness from high values of those two parameters was a consequence of the increase of effects of inter-particle forces, especially van der Waals forces to the packing of powder as powders are smaller. Yu (Yu et al., 1995) studied coal agglomeration and its effect on bulk density and found that materials or agglomerates with high agglomerate density occupy high levels of inter-particle friction force, resulting in restriction in motion of the particles relative to each other in the system. Therefore, it results in high inter-porosity among particulates or agglomerates. Powders with high friction force have high angles of repose or high inter-porosity, representing powders with low bulk density (overall) (Wong, 2002).

Pretreatment of biomass for solid fuel production

Utilizing lignocellulosic materials as an alternative to conventional solid fuel such as coal raises many concerns. Woody biomass, at harvest, is wet and bulky; therefore, it needs to be transformed to a low moisture content and high density form. This will facilitate not only higher combustion efficiency but also allow cheaper logistics. Moreover, homogeneity in size and shape and ease of pulverization are desired properties of feedstock for combustion purposes.

Maximizing carbon fraction in biomass directly increases heat produced from combustion. A variety of physical, chemical, and thermal pretreatment has been developed to increase energy yield form biomass. The ideal pretreatment should not only increase the energy density of feedstock but also enhance physical properties of fuel during the handling. In addition, pretreatment needs to be effective with a wide range of biomass materials. Currently, the primary pretreatments for solid fuel production include steam explosion, pyrolysis, densification, and torrefaction. Densification and torrefaction technology will, however, be mentioned separately.

Steam explosion is a physiochemical pretreatment to enhance accessibility of cellulose and aid the conversion of biomass to fermentable sugars (ethanol). The commercial process occurs when the chipped biomass is heated and pressurized with saturated steam at high pressure up to 1,000 psig, then swiftly decompressed. The recovered solids are 70%, consisting of cellulose and lignin, while most hemicellulose is washed out during solid-liquid separation (Nunes & Pourquie, 1996). Shaw (2009) suggested that pellets produced from steam exploded wood were improved in density and tensile strength due to the relative increase of lignin.

Pyrolysis is a direct thermal decomposition of the organic matrix above 300ºC in the absence of oxygen, yielding carbonaceous charcoal, liquid (tar and other organics), and low molecular weight gases (Yaman, 2004). To maximize the char yield, process conditions such as low temperature and low heating rate are required. Charcoal yield of biomass was reported to range from 26 to 35%, and was successfully related with the lignin and extractive contents contained in the biomass (Humphreys & Ironside, 1974; Mackay & Roberts, 1982; Raveendran & Ganesh, 1998; Rhén et al., 2007). Studies of each individual component of biomass (hemicellulose, cellulose, and lignin) during pyrolysis revealed that the pyrolysis of hemicellulose and cellulose happened quickly. Mainly, weight loss of hemicellulose and cellulose occurred at 220-315ºC and 315-400ºC, respectively. Crystallinity of hemicellulose was presumed to explain its low thermal stability. Lignin, on the other hand showed the most stability to decomposition: its mass loss occurred in a broad temperature range from 160-900ºC (Alén et al., 1996; Williams & Besler, 1993; Yang et al., 2007). However, thermal decomposition of lignin was often concealed by the more prominent cellulose and hemicellulose peaks (Varhegyi & Antal, 1997). Yang also stated that thermal behavior of cellulose is endothermic, while different from the hemicellulose and lignin, which are exothermic. Reveendran and Yang (Raveendran et al., 1996; Yang et al., 2004) divided biomass pyrolysis into four stages: moisture evolution, decomposition of hemicelluloses, decomposition of celluloses, and decomposition of lignin. Heat of pyrolysis reactions of wood varied between 0 and ± 1500 kJ/kg, where the negative values mean exothermic heat and positive values mean endothermic heat (Beall, 1971; Roberts & Clough, 1963; Shafizadeh, 1978; Stamm & Harris, 1953; Thomas & Bowes, 1961). Continuous decrease of hydroxyl group with increase of temperature was reported in the study of tobacco pyrolysis (Sharma et al., 2002). Meier and Faix (1999) reported that char obtained from pyrolysis is usually porous. Some shrinkage may be observed; approximately 52 to 77% of volume reduction of charcoal was experienced (Larfeldt et al., 2000). A porosity ratio of 0.68 of birch wood was reported after the thermal treatment (Grønli, 1996). However, the author also stated that due to the slow heating inside, it is possible for charcoal to become denser towards the center. Therefore, it was concluded that the shrinking parameters varied with the radial position in the wood.

Torrefaction: thermal pretreatment

Torrefaction is considered one of dominant pre-treatment technologies to produce an alternative fuel to the solid-fuel market share with coal. The principles of biomass torrefaction were proposed since 1930's in France, where the application was conducted to produce a gasifier fuel and later used as a reducing agent in metallurgic applications. In recent years, torrefied biomass has become attractive to the energy production specifically in co-combustion and gasification to run simultaneously with coal in existing coal-fired facilities.

Torrefaction process and mechanism

The process is an interaction of a drying and an incomplete pyrolysis process, at 200ºC-300ºC in an absence of oxygen at atmospheric pressure with low heating rate (less than 50ºC/min). Nitrogen is often used as a gas media since the presence of oxygen leads to oxidation or ignition. Heating of torrefaction can be a fluidized bed heater, a rotary kiln, screw reactor, or a batch oven indirectly or directly heated with torrefaction gases recovered (Bergman et al., 2004; Bergman et al., 2005; Persson et al., 2007; Reed, 2002). The process is primarily concerned with the composition and size of biomass, heating rate, gas flow rate, and torrefaction conditions (temperature and residence time). A study on torrefaction of wood briquettes concluded that temperature had more effect on the products than the residence time (Felfli et al., 2005). Repellin (2010) reported that only duration time up to 20 min had a significant effect on the grinding energy and particle size reduction of torrefied wood, increasing to 40 and 60 min duration the improvement did not vary.

First, at low temperature, biomass is heated and drying takes place with free water removal. Until temperature reaches 160ºC, drying continues where chemically-bound water is driven off, and the formation of carbon dioxide gas begins (Gérardin et al., 2007). According to Chow and

Pickels (1971), the thermal softening of moistened wood and bark at temperature below 180ºC is more physical than chemical in nature. Once the temperature reaches 200ºC, the torrefaction begins. The stage of torrefaction contains a heating, temperature-constant periods, cooling. Beyond the temperature of 260ºC, wood starts to break down chemically and pyrolytic process take place (Bourgois et al., 1989). As the decomposition (carbonization) of hemicellulose goes on, wood begins to brown and gives off moisture, carbon dioxide and large amounts of acetic acid with some phenols from devolatisation. It was recommended that torrefaction temperature not to go beyond 280ºC. This was to avoid exothermic reaction since wood will start to be gasified instead of torrefied, therefore, once combustion and gasification start, ligneous matter is decomposed and transformed into combustible gases and tar (Couhert et al., 2009; Gevers, 2002; Lipinsky et al., 2002). Loss in volatiles accounts for up to a 30% decrease in mass, however, the initial energy content of the biomass more than 80-90% is mainly preserved in the solid product (fuel) (Persson et al., 2007). In practice, the energy loss can be recovered by combustible the torrefaction gases is used as a fuel for drying or torrefaction (Bergman et al., 2005).

Due to the different structure among the lignocellulosic components, hemicellulose, cellulose, and lignin are affected by heat in different temperature ranges, and therefore converted by specific reactions. Biodegradation may start from the lowest molecular weight polymer, hemicellulose. Hemicellulose degrades easier since it composes of various saccaride, appearing a random, amorphous, and rich of branches structure, which is very easy to remove from the main stem (Yang et al., 2007). The degradation transition of hemicellulose was rather narrow, while that of lignin was much slower and wider (Beall et al., 1970; Bergman et al., 2005). After the torrefaction, cellulose and lignin were regarded to be unaffected while hemicellulose reacted completely to volatiles and a solid product that is more condensed and stable (Yvan, 1985). As the products received after torrefaction mainly consist of cellulose and lignin, therefore hemicellulose is responsible for most of the weight loss. Deciduous wood was reported to be more reactive than coniferous under torrefaction conditions. This was explained by the fact that hemicellulose in deciduous wood (xylan) is more reactive than manan which is the hemicellulose in coniferous (Prins et al., 2006). A similar conclusion was also found in that hardwoods show a greater thermal degradation than softwoods due to the higher hemicellulose and lower lignin contents (Stamm, 1956). Grass seed hay and baggasse were also found to have lower mass yield than pine and spruce after torrefaction as they had higher hemicellulose content and lower lignin content (Kiel et al., 2008). Degradation of hemicellulose results in an increase relative lignin percentage (Bergman et al., 2004; Bergman et al., 2005; Gérardin et al., 2007). Cellulose, generally, has higher thermal stability than hemicellulose due to its crystalline. Therefore, it will start to decompose at approximately 300ºC (Alén et al., 1996; Williams & Besler, 1993; Yang et al., 2007). However, after torrefaction, it undergoes slight depolymerization and devolatisation reactions, and crystallization degree increases. Lignin also experiences depolymerization and devolatisation that softens it and releases some small phenolic fragments during the torrefaction (Lipinsky et al., 2002). Rowell (1984) reported that the hemicellulose and cellulose polymers are degraded by heat much before the lignin. This was supported by Stamm (1956) who studied the thermal degradation of Douglas-fir sawdust at 220ºC and found that weight loss percentage of hemicellulose, cellulose, sawdust and lignin were 43.1%, 37.7%, 15.9%, and 3.7% respectively. According to the same study, hemicellulose was reported to degrade thermally about four times as fast as wood during the process at 150ºC. The cellulose degrades at about the same rate as wood, while the lignin degrades at only half the rate of the wood. Thus, the thermal stability of wood components in order is lignin, cellulose, and hemicellulose (Kollmann & Fengel, 1965;

Runkel, 1951; Sanderman & Augustin, 1963; Yang et al., 2007). The conclusion of the thermal stability order of wood components, however, is different from these others (Beall et al., 1970; Bergman et al., 2005; Chow & Pickles, 1971) who regarded the cellulose as the most stable constituent among those three.

The released volatiles consist of non-condensable forms (carbon dioxide, carbon monoxide, and small amounts of methane and hydrogen) and condensable components (moisture, acetic acid and other oxygenates). This stream accounted for 30% of the dry weight and 10% of the total energy of the original biomass. However, it can be condensed for recovery of acids and combustible volatiles or for waste treatment and disposal purpose. A carboxylic acid function which was mainly present in hemicellulose decreased significantly from decomposition and devolatisation. Hydroxyl group of polysaccharides which indicates ability to form water decreases as well. Zunzi (2004) studied miscanthus, birch, willow, and wood and straw pellets and reported that higher torrefaction temperature and time resulted in lower solid yield but higher calorific value and carbon content (lower hydrogen and oxygen). A study on torrefaction of eucalyptus wood at temperature of 240ºC to 280ºC showed that the solid fuel contained less volatile matter with increase of temperature and residence time. However, the hydrogen and nitrogen of the sample remained constant during torrefaction temperature range since hydrocarbon such as CH_4 and C_2H_6 were released only at very elevated temperature (Arias et al., 2008; Couhert et al., 2009; Yang et al., 2007). Bergman (2005) selected a torrefation temperature of 280ºC and 17.5 min reaction time regarding to grindability, combustible gas, and high thermal efficiency.

Benefits of torrefaction

Torrefaction has well shown to enhance wood qualities for thermo-chemical conversion. It was also reported that wide ranges of biomass feedstock could be used since the process increased the uniformity in the product quality. In addition, difference in seasonal feedstock was also minimized (Bergman et al., 2005). The main advantages of torrefied biomass are as follows.

I. Size reduction and feeding characteristics

In general, particle size requirement for coal for a complete and intense combustion is nominally 70% wt below 74 µm sieve. Approximately 10 times finer of biomass needed to be ground to have similar combustion characteristics and equal residence time (Freeman et al., 2000; Kastberg & Nilsson, 2000). Up to 10 wt% of biomass could be co-milled with coal, however, difficulties with particle size distribution, mill power consumption, and mill wear were observed. Minimizing energy cost involved with size reduction and meeting the particle size specifications is therefore challenging. Torrefied wood has been shown to have less fibrous structure, less tenacity, and becomes friable. Bergman (2004) explained that this was due to the decomposition of hemicellulose, which resulted in destruction of wood fiber network and lose in fiber coherence. And secondly, depolymerisation of cellulose led to shorter fibers. The brittle property of torrefied biomass was observed after grinding as the milled powder had fewer sharp edges and splinters, showing good feeding and fluidization behavior for burner feeding as shorten fiber becomes more spherical. This enhanced property helps smoothing the entrained-flow gasifier feeding system of powder and can be blended, pulverized, and co-fired with coal (Bergman et al., 2005). Also, it indicated that it could be easily crushed by any known economical means. Reduction in milling power up to 70-90% and increase in the size reduction capacity with factor of 2-6.5 was reported (Bergman et al., 2005; Ouwens & Küpers, 2003;

Persson et al., 2007). Arias (2008) explained the effect of torrefaction on characteristics of wood powders that grinding of raw wood produced a mixture of particles and fibers, while only isolated particles was obtained from grinding torrefied wood. The particle size decreases with the increase of temperature and residence time. Moreover, the particles become more round, and the smaller in size of the particle was mainly due to the reduction in length rather than in diameter. Torrefaction condition of 240ºC and 30 min was found to best improve the grinding properties of eucalyptus wood and compensate with the 20% mass loss and 90% energy yield obtained (Arias et al., 2008). The brittle property of torrefied biomass facilitates use of other treatments such as hydro-liquefaction as it is easy to crush and mix.

II. Higher energy content

Carbon, hydrogen, and oxygen are major elemental constituents of wood. The first two are the major combustible elements, whereas oxygen is non-combustible but an essential structural component of cellulose, hemicellulose, lignin, and extractives. In comparison to dry wood, torrefied wood had lower H and O, which decrease with increase of torrefied temperatures. Loss of atomic H and O was due to the removal of water from dehydration during the torrefaction and possibly all hydrocarbons and oxygen-rich products are formed and released during the torrefaction, such as acetic acid, furans, methanol, and gases (mostly CO_2 and CO). In a mass energy density prospective, energy contained in C-C bonds is higher than C-O or C-H bonds. The relative increase of C indicates better combustion characteristics as it directly results in higher calorific value since lower of O/C and H/C ratios reduces thermodynamic losses (over-oxidation), smoke, and water vapor (Bergman & Kiel, 2005; Prins et al., 2006). Up to 26% reduction in oxygen of torrefied eucalyptus at 280ºC for 3 h was reported, compared to the raw wood (Arias et al., 2008). Bergman et al. (2004) reported an increase in calorific value of torrefied biomass; (LHV) 18-23 MJ/kg due to the lower O/C ratio compared to the untreated biomass 17-19 MJ/kg. Torrefied wood briquette at 270ºC for 1.5 h was found to increase the maximum HHV, up to 15% (Felfli et al., 2005). Nevertheless, volume energy density of torrefied products will be decreased since there is some energy loss after torrefaction while the particle size is fairly unchanged (Reed, 2002).

III. Low hygroscopicity

As mentioned earlier, three components of biomass have numerous hydroxyl groups attached to the main skeleton frameworks, allowing electron pairs present in oxygen atom in hydroxyl groups form hydrogen bonds with acidic hydrogen atom of water molecules, which is responsible for the water uptake phenomena in wood. However, Tjeerdsma (1998) proposed that the hydrophobic structure of wood resulted from the increase in cross-linking within the lignin-carbohydrate-complex (LCC), affecting the networks of the cellulose microfibrils to be less likely to expand and therefore have less capacity to absorb water and giving lower fiber saturation point. Kocaefe (2008) also believed that the lower ability in water uptake was from the reduction of OH bonds and the formation of O-acetyl group, which resulted in subsequent cross-link formation between the wood fibers, causing wood to become more hydrophobic. Rowell (2000) concluded that wood modified by steam at temperature of 200ºC resulted in softened lignin to block the cell pores, affecting the water uptake ability.

The unsaturated form (non-polar) resulted in lower rate of moisture uptake, and thus biological degradation. Torrefied materials become dry and more hydrophobic with maximum 3% moisture uptakes (Yvan, 1985). Bridgeman (2008) claimed that a solid product is hydrophobic because torrefaction removes moisture to final moisture content 1-2%. After water immersion for 17 days, moisture content of torrefied wood briquette in a temperature range of

250ºC -270ºC became 28% whereas torrefied wood briquette at 220ºC was 116% (Felfli et al., 2005). In this study, increases of torrefaction condition (temperature, time) also found to raise the product equilibrium moisture content. It was suggested that as the emission of volatiles was intensive at high temperature resulting in increase in porosity and hygroscopic characteristics of wood. The hydrophobic properties and low moisture content contribute to the total logistic chain more effective in transportation as storing is more secure due to lower risk of organic breakdown causing self-ignition. Fuels with low moisture content reduce the heat loss due to the moisture evaporation during the combustion and thereby increase overall efficiency. Moreover, combustion retardation and low flame temperature, which reduce steam rate capacity, can be minimized. Acceptable moisture content in finished fuel pellets is usually 6% (Ritchie, 2004). Furthermore, degradation of the fuel by a rot fungi or mold growth become less likely as water and some of the nutrients needed by wood rotting fungi were eliminated during the heat treatment (Persson et al., 2007; Vernois, 2000).

Effect of torrefaction to water resistance of wood fuel is often investigated using FT-IR (Fourier transform infrared spectroscopy). Infrared electromagnetic radiation is in the ranges of 4000 to 400 cm^{-1} (Shaw, 2008). The data of chemical and structural information was used to examine a specific functional group, in this case namely hydroxyl as it indicates the ability of the material to bond with water. This can specifically indicate the differences in the chemical structure of untreated and pretreated feedstock as a particular molecule and bonding will absorb and display unique frequency (or wave number). The absorption of O-H bond are in the region of 3800-2700 cm^{-1} (Silverstein et al., 1991).

IV. Less emission

During the initial stage of combustion, raw wood or wood pellets suffer from their high volatile contents as it emits tremendous amount of smoke, causing losses as un-burnt fuel gas. Torrefied biomass contained substantially less moisture content and volatile compounds due to the dehydration and devolatisation during torrefaction. Therefore, torrefied wood gives less smoke than untreated wood (Arcate, 2000; Felfli et al., 2005; Pach et al., 2002; Pentananunt et al., 1990). Prins (2006) reported that both the amount of condensable and non-condensable volatiles formed increases with torrefaction temperatures. In addition to the less smoke during the combustion, the liberation of almost all acetic acid during the carbonization also reduces the risk of acid corrosion in any combustion or gasification of wood due to the acid gas produced otherwise (Yvan, 1985).

Densification of lignocellulosic biomass

Wood pelletization is the most commercially promising pre-processing providing a short-term solution to the energy crisis. The use of wood pellets has increased extensively since the 1990s, predominantly in Denmark, Sweden, and Austria, and even earlier in North America (Alakangas & Paju, 2002). The concept of the process is to physically transform bulky and wet biomass that is inconsistent in shape and size into uniform, high volumetric energy dense and dry fuel for further combustion and gasification process (Granada et al., 2002a). Wood wastes or agricultural residues, which usually contain wide variations, benefit immensely from densification as dense granulates offer more uniformity in shape, size, and component distribution in fuels. In comparison to wood chips, wood pellets offer about four times higher volumetric energy density and lower moisture content, which directly affect the lower logistic cost (Di Giacomo & Taglieri, 2009). The consistency of moisture content, size, density, and constituents in wood pellets increases fuel competiveness compared to traditional fuels: natural gas, oil, and propane as they can be fed and burnt with high combustion efficiency and low combustion residues (Li & Liu, 2000; Sokhansanj et al., 2005).

To produce pellets, bonds must be formed between powders so that they adhere together to form granules, and these bonds must be sufficiently strong to prevent fine formation in subsequent handling operations. In this matter, compact behavior is characterized by the powder mechanical properties, which bear direct relationship with the compression, decompression, and stress relaxation of particulate solids (Leuenberger, 1982; Leuenberger & Rohera, 1986; Mani et al., 2004a). Compressibility is an indirect measure of the ease of consolidation. The formula was related between tapped and aerated bulk densities. Compressibility index was defined as follow (Svarovsky, 1987).

$$Compressibility = 100\ \frac{(Tapped\ \ density - Aerated\ \ density\ )}{Tapped\ \ density} \tag{2.1}$$

Brittle materials usually consolidate or deform through fracture or fragmentation and their compressibility decreases with decreasing of particle size, while ductile materials consolidate by plastic deformation and their compressibility is independent of particle size. Compactibility is the ability of powdered materials to be compressed into a tablet of specified strength, which reflects a sufficient bond occurred during compaction. This property is often; however, of interest as obtaining the sufficient strength of a compact that the compression makes is more important than obtaining a specific volume reduction.

Various types of tests are used to evaluate mechanical properties of the densified products. In pharmaceuticals, coal, and cement concrete practice, tensile strength is commonly measured by diametral compression, due to its convenience and accuracy (Berenbaum & Brodie, 1959). The diametral compression test is the indirect tensile test or Brazilian test; it serves to determine the deformation hardness, which is the mechanical property of compact to resist against a permanent deformation (Leuenberger & Rohera, 1986). The test is performed by compressing diametrically a right circular cylindrical specimen between two opposite flat platens (Rudnick et al., 1963). Theoretically, there will be a tensile stress of constant magnitude existing across this diameter, which tends to pull the densified cylinder in half along this line. The magnitude of the tensile stress P (Pa) is given by (Timoshenko & Goodier. JN, 1951)

$$P = \frac{2F}{\pi \; l \; d} \tag{2.2}$$

Where F is the load of fracture, and l and d are the thickness and diameter of the densified cylinder, respectively. Due to the fact that for an elastic material, the loading conditions not only induce compression, but also produce a nearly uniform tensile stress over a significant portion of the diametral plane containing the applied load, the diametral compression test became widely used. Moreover, to evaluate a brittle material, applying compressive load is technically much simpler than tensile (Berenbaum & Brodie, 1959). For densified products, the test in particular, simulates the conditions that exist in pellet storage, where pellets piled at lower position in a storage container carry high load above them. Millard (1959) regarded that the strength of coal briquettes is a single valued function of the porosity of the compact.

Compression of powdered material into a cohesive mass during the formation of a pelleting is a complex and irreversible dynamic process. Newitt and Conway-Jones (Newitt & Conway-Jones, 1958) explained that agglomeration and packing behavior of coal are dependent on many factors such as moisture content and the size distribution of the feed coal. Two primary processes were proposed upon the compaction behavior of ceramic powders (Cooper & Eaton, 1962).

Mechanism of powder compaction

I. Particle rearrangement/ slippage occur at low pressure, filling the large voids with original particle size, producing closer packing. The particles retain most of their original properties, although energy is dissipated due to interparticle and particle-to-wall friction (Mani et al., 2004a).

II. At higher pressures, elastic and plastic deformations occur, resulting in particles filling the void spaces that are smaller than the original particle size. As the applied stress rises, plastic flow or fragmentation occurs. As particles are forced against each other, the inter-particular bonding increases and a coherent mass are formed. For brittle materials, mechanical interlocking will have an effect during the deformation (Gray, 1968).

As a result, both intra-and inter-particulate porosities are reduced and the overall density is increased (Broese van Groenou, 1981; Shotton & Ridgway, 1974). Stages I and II will continue until the true density is reached. If the melting point of the ingredients in the mix is reachable, particles can get melted and form strong solid bridges once it is cooled (Ghebre-Sellassie, 1989).

Mechanism of bonding

There are five classifications of bonding mechanisms responsible for the process of consolidated powders being bonded together, but usually more than one apply to any particular system (Barbosa-Cánovas, 2005). Basically, particles form bonds between particle solids under compaction condition (pressure) due to the force acting on the area of inter-particle contact.

I. Immobile liquids: In bonding bridges, adhesion and cohesion forces that are not freely moveable are the forces introduced by viscous binders or adsorption layers. Highly viscous bonding media, such as tar, harden during the agglomeration process and form solid bridge-like bonds (Pietsch, 1991). Immobile thin-adsorption layers contribute to the bonding of fine particles by smoothing out surface roughness and increasing particle contact area or by decreasing the effective inter-particle distance and allowing intermolecular forces to participate in the bonding mechanism (Ghebre-Sellassie, 1989).

II. Mobile liquids: This mechanism exhibits interfacial forces and capillary pressure at freely movable liquid surfaces. The force of particle adhesion arises from surface tension between liquid and air system, and capillary forces: attraction between water and the surface of the solid substance. However, if the liquid evaporates the bonds will withdraw (Pietsch, 1991).

III. Solid bridges: This mechanism is predominantly responsible for strength in the final product (Ghebre-Sellassie, 1989). An example of this mechanism is the melting due to the pressure, friction, or heat during the pelleting and hardening of binder during curing. The force of the cohesion depends on the diameter of the contact area and strength of the bridge material.

IV. Attraction between solid particles: Attraction of solid particles to one another through intermolecular forces: van der Waals and valence, electrostatic charges, or magnetic forces are short range forces. Therefore, the bonding is essential at the initial stage to hold and orient the particles in a contact region long enough for stronger forces to take over. It was reported that molecular forces (van der Waals forces) play an important role in compression mechanism of drug particles (Pietsch, 1991; Rumpf, 1962). Smaller particle size is ideal for these intermolecular forces to be effective.

V. Mechanical interlocking (form-closed bonds): The mechanical interlocking mechanism is prominent when fibrous or needle shaped particles are mechanically agglomerating together. Adhesive strength is primarily determined by particle shape, surface characteristics, pores, and roughness (Leuenberger & Rohera, 1986; Pizzi & Mittal, 2003). For example, materials with less spherical shape and high surface roughness are likely to form these bonds well (Shaw, 2008).

Pelletization process and equipments

The process varies depending on the moisture content, type of materials, and type of end products. However, it primarily consists of four steps.

I. Drying

Hot air or flue gases are used to reduce moisture of wet biomass after harvested. Moisture content, size, and homogeneity of feedstock affect drying time and temperature. Low moisture content of feed allows efficient size reduction and pelleting process.

II. Size reduction

This process involves major preparation, especially in pelletization. It plays an important role, as it changes the particle size, shape, and bulk density of the material, as well as eliminates heterogeneity in biomass residues. Grinding reduces air spaces between particles permitting closer surface to surface contact of particles leading to increase in bulk density in feed (Hasting et al., 1978). The result in higher total surface area of a given weight of feed also allows more space and ability of feed for steam condensation during the conditioning and increase in numbers of contact points for inter-particle bonding aiding the compaction process (Drzymala, 1993). Accordingly, mixing property and pelletibility are enhanced. Common mechanical size reduction machines are hammer mill (beating), roller mill (crushing), and knife mill (cutting).

Particle size, moisture content, and material properties are physical properties related to the energy consumption for grinding biomass. In the milling process, low moisture content and smaller top size of biomass feed are favorable in terms of power consumption, mill wear rate, and mill inlet temperature (Zulfiqar et al., 2005). The energy needed to grind the forest biomass (poplar chips, pine chips, and pine bark) to feed pulverized fuel burners with the feed rate of 10 t/h were 120, 150, and 35 kWh/t respectively (Reuther et al., 1982; Siegle, 1996). The brittle nature of bark was explained for the lower grinding energy used. Energy required in pulverizing coal is generally around 7 – 36 kWh/t, due to its brittleness. The energy was clearly lower than those of abovementioned for woody and lignocellulosic biomass.

III. Pelleting

The operation of the majority of current pellet mills is based on pressing the soft feed through open-ended holes in a metal ring-type rotating die. The compressed feed is pushed through the die continuously. Then pellets are cut into preset lengths using a knife. Sokhansanj et al. (Sokhansanj et al., 2005) reported the power required to run the mill ranging from 15 to 35 kW/ t of the feed. Energy used in pelleting is degenerated into two components. One is used to compress feed to reach its compact form. Another, however, is more than half of the whole energy, dissipated to overcome the skin friction, which is considered wasteful (Sitkel, 1986). Skin friction may cause excess heat and pellet skins harden resulting in cleavages within pellets.

IV. Cooling

The advantages of pelletizing are only guaranteed, if the product is properly cooled after leaving the mill as they are warm, soft and moist due to the heat imparted from pelleting. Generally, hard pellets are cooled to ambient temperature within 10 min. Excessive cooling may cause surface cracks resulting in decrease of hardness and dust formation. Remaining internal heat in pellets leads to condensation, resulting in risk of bacteria and mould growth (Heinemans, 1991). Dust and accumulation of heat in a worse case can cause self-ignition.

Factors affecting pelleting process on the qualities of pellets

I. Machine and process variables.

These are the equipment-set conditions imposed upon biomass feeds during densification.

Temperature: Heat may be added to the densification system by means of preheating of feed materials or the use of heated die apart from the frictional heat generated during the compression. Heated die, temperatures range from 65.5-100ºC are commercially used in pelleting to possibly soften intrinsic lignin, improving the durability and density of pellets (Groesbeck et al., 2008; Mani et al., 2006; Shaw, 2008). Smith (1977) was able to produce wheat straw briquettes with high relaxed density up to 1,300 kg/m^3 by using die with temperature in the ranges of 80-140ºC with a long heating time of 40 min. Tabil and Sokhansanj (1996a) explained that during the feed compaction, temperature of the feed system may increase as a consequence of frictions both particle-to-die wall and particle-to-particle that were dissipated as heat in the channel of grind particles in the pellet die.

Pressure: The compressive pressure applied to the raw materials directly results in higher pellet density. However, Ndiema (2002) stated that for a given die size, increase in cohesion (bonding) of agglomerates can be maximized by the certain applied die pressure, where the density cannot be higher. Holm (2006) proposed a theoretical model of the pelleting force pressing a pellet die channel and found that the roller pressure is required to be above the back pressure, which exponentially increases with increase of the channel length. Compressing hardwood grains resulted in higher back pressure than corresponding pressure of the softwood.

Typical pressures of commercial pellet mills ranging from 50- 150 Mpa, but usually higher pressure is applied during the process (Sitkel, 1986).

Die speed and residence time: For commercial pelleter, a die rotational speed generally ranges from 130-400 rpm (Hasting et al., 1978). Mani (2006) reported that a proper crosshead speed and prolonged time was necessary to capture the spring back effect. Preliminary pelleting trials of alfalfa pellets showed that rotational speed of 344 rpm was optimum to avoid longitudinal fragmentation in pellets and that low pellet durability occurred when the speeds were beyond 375 rpm. However, it was difficult to keep the feed on the inside face of the die with lower die speed (60 rpm) causing consistent plugging within the die cavity (Hill & Pulkinen, 1988). For materials with low bulk density such as alfalfa and if a large die diameter is used, low die speed was suitable to produce durable pellets. This is due to that large energy will be needed to densify the particles into their true density (MacBain, 1984). Lower velocity in both the compression chamber and the die allows lower frictional losses and compaction energy. Also, considerable less wear to the die and rollers is observed with low die speed.

Die geometry: Basically, die geometry refers to the ratio of the die thickness to a hole diameter of the die, involving production rate as it relates to amount of pelleting material and compression energy. With a constant mass of material at a particular pressure, smaller diameter die produced longer and higher density pellets, but yielding less productivity (Butler & McColly, 1959). The durability of pellets was also affected by the length-to-diameter ratio but was more noticeable in a larger die (Heffner & Pfost, 1973; Tabil & Sokhansanj, 1996b). The *l/d* ratio of 8–10 was reported to be the ideal ratio for making high quality pellets (Hill & Pulkinen, 1988; Tabil & Sokhansanj, 1996a; Winowiski, 1985). This was supported by the study of production of dehydrated alfalfa pellets and the factors affecting pellet durability that approximately 50-90% durability of pellets could be achieved by increasing die *l/d* ratio from 5 to 9 (Hill & Pulkinen, 1988). Nevertheless, the shorter and thinner pellets are favorable for high fuel feeding properties, more uniform combustion rate, particularly in small furnaces (Lehtikangas, 1999). Smaller die usually showed more resistance to the grind particle flowing through it. Particularly, an example was when alfalfa grinds moist and hot, it was gummy, which made them difficult to flow through a smaller die since a smaller die can get plugged due to the excessive moisture of the fines (Tabil & Sokhansanj, 1996a). Bigger dies, on the other hand, can tolerate wider and higher grind moisture; however, they have less resistance to the flow of grind particle through, resulting in less density of pellets.

II. Feedstock/ material variables

Pelletibility is significantly affected by unique characteristics of raw materials: moisture content, fiber content, oil content, starch content, moisture affinity (hygroscopic), bulk density, and particle size distribution.

Moisture content: Biomass feed usually contains various moisture, depending on its chemical constituents (Sokhansanj et al., 2005). Moisture content in materials plays an important role to the pelleting process as steam or water acts as film-binder exhibiting bonds via capillary sorption and promoting bonding via van der Waal's forces by increasing contact area of particles (Mani et al., 2003). Together with increasing temperature, it facilitates binding, wetting and softening between/of the particle feeds, therefore, leading to a greater compression and high durability of pellets (Hasting et al., 1978; Tabil & Sokhansanj, 1996a; Thomas & van der Poel, 1996; Thomas et al., 1997). Moreover, water in feed helps reducing friction in the piston-die system, as insufficient moisture in feed causes corking inside the holes of the dies since the friction force exceeds the compressive force (Lehtikangas, 1999). However, excessive moisture causes the feedstock to become slippery through the die, causing less pellet density. Moisture content of 11% was found to be the maximum moisture content to produce most durable hay wafers (Srivastava et al., 1981). For strong and crack-free briquettes, moisture contents in the ranges of 6-8% were reported to be suitable (Grover & Mishra, 1996). Demirbas and Sahin (2004) reported that strong briquettes made of pulping rejects and spruce wood sawdust could be achieved with materials with moisture content 7-15%. Moisture content ranges of 14-16% of grass were reported to produce maximum density of briquettes (Orth & Löwe, 1977). Similarly, Hausmann (1967) found that briquetting of wood waste can be achieved at moisture content of 15%. Hill and Pulkinen (1988) studied the effect of natural moisture and found that operating efficiency was improved, observing lower power consumption with higher moisture content. However, there was no evident relationship between pre-conditioned moisture and pellet durability.

Water content also relates with compression and relaxation behavior. Ollet (1993) studied the effect of water content on the compaction behavior of crystalline and amorphous materials. Following the study, crystalline material which exhibits both ductile and brittle deformation during the compaction process retained relatively less water content as compared to amorphous material. Increase in water content resulted in decrease in deformation stress in both materials. The author interpreted this due to plasticization phenomena for amorphous and lubrication effect for crystalline materials.

MacBain (1984) concluded the significance of steam conditioning as it increases production rate, increases the die life, reduces cost of electricity, and results in reduction of fines. Moisture content ranges from 8-12%, wb, were reported to be optimum for producing pelleting for fibrous material. When moisture content in feed stock exceeds 15%, wb, feed needs to be dried either on field or using a fuel dryer prior to the pelleting process (Sokhansanj et al., 2005).

Particle size, shape and distribution: Particle size is an important factor influencing pellet density and durability. The size of grinding unit screen directly affects particle size of grinds. Generally, fine grind (below 2 mm) will produce higher density pellets as it has high surface area/ volume ratio in each particle, allowing stronger bonds, better penetration of moisture (or binder) and heat, and consequently improves strength properties (Lehtikangas, 2001; Payne, 1978; Tabil & Sokhansanj, 1996a). Other researchers (Franke & Rey, 2006; Turner, 1995), however, suggested grind sizes of 0.5-0.8 mm, as they explained that particle sizes larger than 1 mm will start cracking points in pellets. Another advantage of fine grinds was to enhance pelleting capacity, as it passes through the machine easily (Dobie, 1959). Koser (1982) supported the optimization of pellet density from fine particles only at low and medium densification pressure. Standard deviation for current consumption during pelletizing of fine particle was found to have the least value (7%) compared to the coarse particles (28%) (Bergström et al., 2008). The compaction behavior due to the size and geometrical characteristics was claimed to explain the occurrence (Holm et al., 2007). However, in some other works, the difference in grinds did not significantly affect pellet density and durability (Mani et al., 2004b; Shaw, 2008; Tabil & Sokhansanj, 1996a).

Often, coarse grinds create natural fissures in the pellet, which are susceptible to breakage, resulting in less durable pellets (MacBain, 1984). When handling the pellets, they will trend to break at the surfaces of the coarse particles, creating dusts. However, a combination of fine and medium grind has been reported to be necessary to pellet qualities as the mixture will make inter-particle bonding with nearly no inter-particle spaces (Grover & Mishra, 1996;

MacBain, 1984; Mani et al., 2003; Payne, 1978). Particles having a long shape were reported to have advantages as they may stick together strongly through in interlocking mechanism (Li & Liu, 2000). The claim was, however, different from the study of the compaction of tree bark; sawmill waste, wood shavings, alfalfa hay, fresh alfalfa, and grass where materials with lower moisture content and fewer long fibers (more fines) were stated to yield more stable wafers, due to limited expansion (Mohsenin & Zaske, 1976). In the combustion point of view, effect of particle size distribution of the feed on the burning characteristics of pellets has not been known yet. However, high density pellets, a resultant of the appropriate particle size distribution, are an important influence to the combustion time. The denser the pellet; the longer the burnout time (Obernberger & Thek, 2004).

Application of binders: As the fact that biomass has tendency to resist the compressive force and spring back when it is released, binders maybe needed to reduce its springiness and maintain highest bulk density. Binding agents are additives generally added to comminuted biomass in small portions to improve pellet durability and/ or pelleting efficiency. Binding mechanism in pellets is mainly due to the solubilisation and subsequent crystallization of raw material component or due to surface tension of water and particles. Protein in grass and forages, lignin in wood residues, water, starch, and fat are some of the examples of natural binders that already contained in the biomass. Synthetic binding agents such as crude glycerol, gelatinized starch, or lignosulfonate are often added to feedstock prior the pelleting to ensure the sufficient bonds and density in pellets (Heffner & Pfost, 1973). Recommended optimum amount added of chemical binders is 0.5-5% wt/wt and 20% wt/wt or more for biological binders (Kaliyan & Vance Morey, 2009). In general, lignin was claimed to increase both pellet quality and output (Payne, 1978). The 1.5% addition of lignosulfonate was used in the study of durability of alfalfa pellets; however the improvement was negligible (Hill & Pulkinen, 1988). The limitation for the addition percentage concerns cost and emission issues. Some other binders found used in densified products are molasses and heavy pyrolysis oil, etc, (Gilbert et al., 2009; Payne, 1978).

Combination of torrefaction and pelletization

Densification of torrefied biomass further benefits utilization of biomass as energy rich fuels from torrefaction can be enhanced in terms of handlings due to the increase in density and flowability. The industry of converting wood pellets into torrefied wood pellets involves inserting torrefaction into the existing densification system that already has raw material supply, pre-drying equipment, and market channels available. The concept is to obtain maximum efficiency by torrefaction using the heat partially from recycled torrefaction gases (torgas). The recycle comprises of re-pressurization of the torgas to compensate for the pressure drop in the recycle-loop and of the heating of the recycle gas to deliver the required heat demand in the torrefaction reactor. The torgas is combusted to generate heat for both drying and torrefaction (Kiel et al., 2008).

The idea of complementing pelletization with torrefaction has been researched by many researchers. Lipinsky (2002) reviewed that densification of torrefied wood could consume less than half as much electricity required in conventional wood pelletization. Nimlos et al. (Nimlos et al., 2003) explained that hydrophobic property of torrefied biomass could greatly benefit pellet making. Kiel (2008) estimated the higher overall energetic efficiency of pelletization combined with torrefaction instead of pelletization alone to be in the range of 92-96% for densified torrefied pellets compared to 88-92% for wood pellets. The author gave an explanation of the increase of the efficiency that it was due to the superiority of the pellet qualities as it is dry and contains high calorific value. Moreover, less energy was required for grinding and pelleting. And also, about 30-80% increase of volumetric energy density or 13-17 GJ/m^3 of densified torrefied wood (mixture of soft and hardwood with high amount of bark, small branches and some needles) was stated in this report. Lipinsky (2002) predicted the enhancement in volume energy density from the densification of torrefied biomass to be about 18 GJ/m^3 or 20% higher than conventional wood pellets. Also, the author estimated that pellets can be produced cheaper as half of electricity required during the pelleting can be saved if using torrefied biomass as a raw material. In the patent of process and apparatus for making a densified torrefied fuel (Reed, 2002), pine sawdust was first torrefied (150-250^oC) and densified at 10,000 psi using 1 inch diameter die; the obtained product was called "Biomass Super-fuel." According the patent, with increase of torrefaction temperature, the density was raised and was maximized at 200ºC, then dropped; however, torrefied pine pellets, in overall, had higher density than conventional pine pellet. Bergman (Bergman, 2005) reported numerous benefits from the combination process of torrefaction and pelletization (TOP Pellets) of softwood, hardwood, demolition wood, and some herbaceous. For example, net calorific of TOP up to 19-22 MJ/kg and higher thermal efficiency (96-98.5%) were achieved. In contrast, Gilbert (2009) investigated different pre-process parameters on herbaceous crop pelletization and found that pellets made of torrefied switchgrass without binders were actually brittle and lost their strength. Although results were good for pulverization along with coal, for pelleting they were disadvantageous as it led to disintegration and dust formation. Therefore, it was suggested that further investigation should be done to examine if torrefaction should be completed above the hemicellulose degradation temperature to avoid the breakage.

End-user applications of densified torrefied products are to produce electricity and heat generation in transportation fuels production via entrained-flow gasification, small-scale combustion (pellet boilers and stoves), and large-scale co-firing power plants or even in biomass-only dedicated plants.

CHAPTER 3

MATERIALS AND METHODS

Material

Clean pine chips were received from a local pulp mill operation in Oglethorpe, Georgia. The moisture content of chips as received was 41.7% on the wet basis (wb). The pine chips dimensions were in the ranges of 20.94-70.59 mm in length, 1.88-4.94 mm in thickness and 15.08-39.70 mm in width. Chip samples were dried to 10% moisture content (wb) for safe outside storage and were used for torrefaction study.

Reactor description and operating procedure

Torrefaction of wood chips was conducted in a batch torrefaction reactor placed inside an externally heated electric furnace (Figure 3.1). A thermocouple was inserted in the sample bed for temperature control and was data logged to monitor and control the torrefaction experiment. A nitrogen flow of 2 L/min was used as a carrier gas throughout the experiment to eliminate the presence of oxygen, thereby avoiding oxidation and ignition. The exhaust from the batch reactor was passed through series of metal condensers immersed in an ice bath before exhausted to the atmosphere. The purpose of condensers was to collect all the potential condensable generated from the torrefaction reaction. A known amount of samples (1-1.5 kg) was charged into the reactor at room temperature and the reactor was heated at 10°C/min under atmospheric pressure. Clean pine chips were torrefied at four different temperatures (225°C, 250°C, 275°C, and 300°C) and at 30 min residence time. The torrefaction residence time of 30 min was chosen to be optimal for torrefaction reaction from preliminary studies. After the treatment, samples were cooled and weighed to determine the solid yields. The scope of this study was primarily focused on the torrefied solid biomass received during this experiment and was for further analysis.

Experimental design

The sample was tested for torrefaction conditions at four different temperatures (225ºC, 250ºC, 275ºC, and 300ºC). The torrefied chips will be labeled as "TPC-xxx" samples, where "xxx" indicates the torrefaction temperature in degree Celsius. The torrefied chips will be compared for further analysis with the untreated one, which is labeled as "CT-PC."

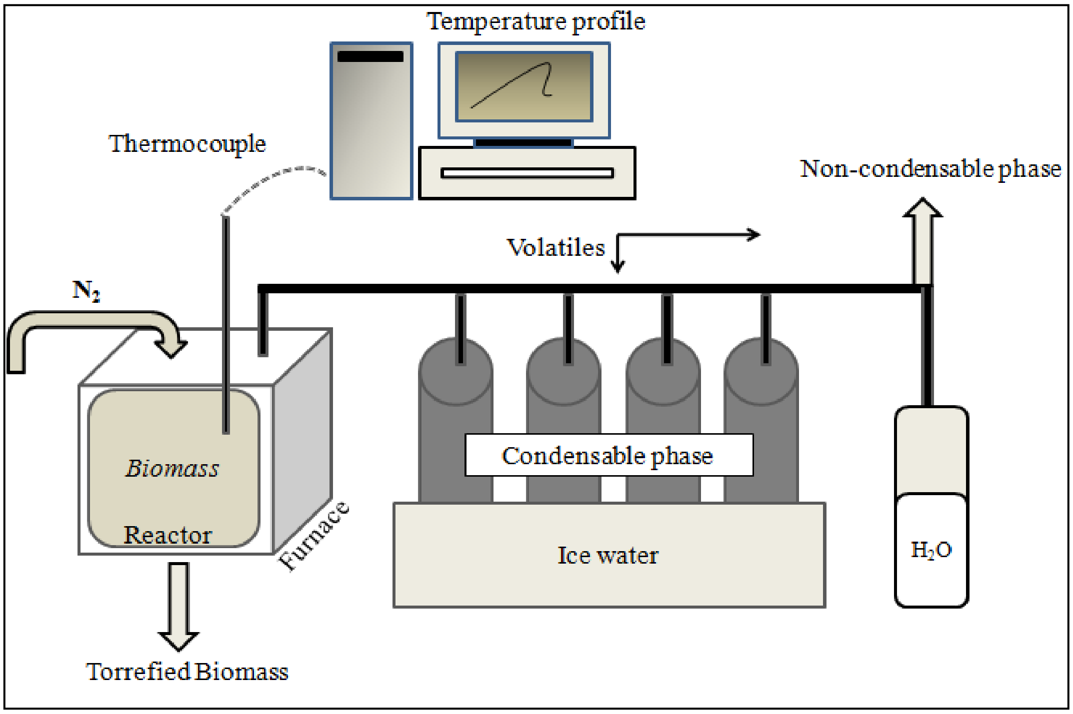

Figure 3.1: Laboratory torrefaction unit using a batch pyrolysis reactor.

Grinding experiment

Grinding unit description

A laboratory heavy-duty cutting mill (Retsch SM 2000, Germany) was used in the grinding experiments. The knife mill used in this study consisted of a cutting blade rotor (1690 rpm, 60 Hz) powered by a 1.5 kW electric motor. The bottom sieve openings of 1.5 mm were used in this study as it was recommended for producing good quality pellets and for combustion applications (Kaliyan & Vance Morey, 2009; Turner, 1995). Untreated wood was also tested for grinding experiments under the same grinding conditions for comparisons. Uniform grinding conditions were controlled by a uniform feed rate, which was determined by pretesting the optimum interval time and feed weight in order to achieve homogenous grinding of all sample batches without any sample being jammed.

Operating method

The grinding operation was divided into three time periods. The cutting mill was allowed to run freely without sample for the first minute. And then, a known amount of sample (~100 g) was fed to the cutting mill from the top. The machine was allowed to comminute the wood for five minutes before fed with the same amount of wood again. The feeding was repeated in the same manner for five times. After the feeding finished, the machine ran empty again for the last minute. The three time intervals of grinding operation were continued one after another without shutting down the machine. Pine chips were comminuted mainly by shearing action by the cutting blades. The ground wood was caught by the aluminum container attached to the bottom part of the cutting unit.

Estimation of energy consumption

A computer with a data logger assembled with a multi function transducer (CR Manetics Inc., MO) was connected to the mill to measure the power consumption during the grinding experiment. Instantaneous power consumption data were recorded for every two s by the computer for further data processing. The specific energy consumption for grinding was determined by integrating the area under the power consumption curve (P-t) for the total time required grinding sample (Balk, 1964; Mani et al., 2004). The calculation of the energy did not include the first and the last minute when the machine was running empty. Five replications of the specific energy consumption were conducted.

Physical and chemical characteristics

Moisture content

The untreated and torrefied samples were analyzed for moisture content according to ASABE S358.2 (ASABE. 2006) standard protocol. A known amount of samples were dried in the convective oven at 103±2°C for 24 h and the mass loss was recorded to calculate sample moisture content. ASTM Standard D 3173-87 (ASTM, 1998) for coal and coke was employed to determine moisture content of coal sample. The moisture content data were reported in wet basis. Each test was repeated three times.

Proximate analysis

A proximate analysis (ash, volatiles, fixed carbon, and moisture content) was performed using a Thermo Gravimetric Analyzer (Model TGA701, LECO Corporation, St. Joseph, MI) based on the procedure of ASTM D 5142-04 for coal and coke (ASTM. 2002a). Approximately one to two grams of grinds was placed in an aluminum crucible which was placed and heated in a muffle furnace. Ash content and volatile matter were expressed in dry basis. The fixed carbon, in dry basis, was calculated from subtracting a hundred percentages with ash and volatile matter.

Ultimate analysis

Elemental analysis of the samples was performed according to the ASTM D3176-89 standard test method for coal and coke (ASTM. 2002b). The C, H, N, S contents were measured using an elemental analyzer (LECO CHNS 932, LECO Corporation, MI). Oxygen was estimated by the difference. All thermal and chemical measurements were conducted in triplicates.

Heat content

The adiabatic oxygen bomb calorimeter (IKA C 2000, IKA Works, Inc., NC) was used for determination of gross calorific value of grinds based on the ASTM D 5865-03, standard test method for coal and coke (ASTM. 2003). Initially, a known amount of grinds (~ 0.5 g) was placed in a nickel crucible and burned inside the bomb calorimeter surrounded by a water jacket. The sample was ignited by a pure cotton thread in the presence of oxygen. Upon the ignition, the released heat is transferred to the water jacket causing temperature to rise. The increase in temperature was used to calculate the heating value of the sample. The calorific value was expressed in MJ/kg.

Chip size measurement

About 100 g of wood chips from each torrefaction temperature was randomly selected and measured in dimensions and weight for the particle size distribution calculation to investigate any shrinkage after the heat treatment. The measurement was performed using a digital caliper in millimeter units. The wood chips were categorized into four group size: L>50, W> 15, 5<W<15, W<5 and recorded for weight in each faction. The letter L represents its length, and W represents its width. Particle size distribution determination was repeated three times.

Particle size and particle size distribution

An image analyzer (HORIBA CAMSIZER, Instruments, Inc. CA, USA) equipped with two digital cameras was used to measure the average particle size and size distribution using a similar procedure as reported in (ASABE. 2008; Bernhart & Fasina, 2009). Since the samples were electro-statically charged, an ultrasonic probe disperser was applied during the measurement to better characterize the needle shaped particles. To conduct the test, a 20-40 g sample of the grinds was loaded onto the hopper of the instrument. The sample was conveyed and dropped via a vibratory feeder onto the measurement field of the cameras. The size and shape of powders were recorded and analyzed by the software provided by the equipment manufacturer. The series of sieves followed the Standard ANSI/ASAE S319.4 (ASABE. 2008), and were set on the software as the following: 6.7, 6.3, 5.6, 4.75, 4, 3.5, 2.8, 2.36, 2, 1.7, 1.4, 1.18, 1, 0.85, 0.71, 0.6, 0.5, 0.425, 0.355, 0.3, 0.25, 0.212, 0.18, 0.15, 0.125, 0.106, 0.09, 0.075, 0.063, 0.053, 0.045, 0.038, 0.032, 0.025 mm, and 0.02 mm (corresponding to sieve numbers 0.265", 0.25, #3.5, #4, #5, #6, #7,#8, #10, #12, #14, #16, #18, #,20, #25, #30, #35, #40, #45, #50, #60, #70, #80, #70, #80, #100, #120, #140, #170, #200, #230, #270, #325, #400, #450, #500, and # 635)

Four parameters were analyzed, including: a) *geometric mean diameter* (d_{gw}) – the size at 50% cumulative distribution; b) *the geometric mean diameter standard deviation*(S_{gw}) (Equation 3.1) – the measurement of the variation in the particle sizes of the wood powders; c) *the sphericity* ($SPHT$) (Equation 3.2) –roundness value ranges from 0 to 1 (a perfect sphere has a value of 1); and d) *the specific surface area* (S_v) (Equation 3.3) –the value directly shows the results of size reduction and indicates combustion properties of fuel.

$$S_{gw} = \frac{1}{2}\,[d_{84} - d_{16}] \tag{3.1}$$

$$SPHT = \frac{4\pi a}{P^2} \tag{3.2}$$

$$S_v = \frac{A}{m} \tag{3.3}$$

Where d_{84} and d_{16} are particle diameters obtained from the cumulative distribution data at 84% and 16%, respectively. The Particle size distribution and cumulative passing percentage were constructed against the shortest chord or width ($X_{c\ min}$), which is the dimension that fits to sieve results because with sieving, the particle passes the mesh with its smallest dimension. Each run was repeated twice.

Chemical compositions of torrefied wood

To support the conclusion of effects of torrefaction on the wood cell wall, a chemical approach was performed. Torrefied grind at 225ºC, 250ºC, 275ºC, and 300ºC and untreated samples were analyzed by the commercial Feed and Environmental Water Laboratory (FEW), Athens, GA using sequential detergent methods (Van Soest & Robertson, 1980). First, the sample was dried and treated in a neutral detergent solution (30.0 g Sodium dodecyl sulfate, USP; 18.61g Ethylenediaminetetraacetic disodium salt, 44ehydrate; 6.81 g Sodium borate; 4.56 g Sodium phosphate dibasic, anhydrous; and 10.0 ml Triethylene glycol, in 1 L distilled H_2O). The insoluble residues were neutral detergent fiber (NDF); hemicellulose, cellulose, and lignin. Then, cellulose and lignin were separated from hemicellulose; sample was digested with acid-solution (20 g of cetyl trimethylammonium bromide (CTAB) to 1 L of H_2SO_4). After digestion, the hemicelluloses dissolved and were filtered away. Secondly, acid detergent lignin (ADL) was measured by further treating ADF (the insoluble fiber residues remained after digesting which consisted mainly of cellulose and lignin) with 72% H_2SO_4, which dissolved cellulose. The cellulose content was derived by subtracting ADF values from ADL values. Calculations of cellulose and hemicellulose percentages given by

$$\%\ \text{Hemicellulose} = \%\ \text{NDF} - \%\ \text{ADF} \tag{3.5}$$

$$\%\ \text{Cellulose} = \%\ \text{ADF} - \%\ \text{ADL} \tag{3.6}$$

Flow properties of torrefied wood powders

Bulk density

To compare the bulk properties and further experiment in pelleting characteristics, particle size distribution of torrefied sample was needed to be uniform. Particle size distribution of untreated wood was selected to be followed. Due to the brittleness characteristic of torrefied wood, torrefied sample from each temperature was ground using a knife mill with a bigger bottom sieve size than 1.5 mm, but sieved by the same sieve series. Only certain weight of torrefied grinds caught at each sieve was taken to follow the particle size distribution of the untreated wood. All samples were dried in a convective oven at 103 ± 2^{o}C for 24 h.

The aerated and tapped bulk density determination of grinds was performed according to the ISO 3923-1; 2008 Metallic powders –Determination of apparent density: Funnel method. To form the aerated density, powders were poured freely to flow under gravity into a known-volume cylinder from a funnel right above it. Excess powder was scraped from the top of the cylinder by leveling the powder surface with a ruler. The aerated density is very susceptible; therefore, the removal needs to be done gently to prevent compaction of the loosely settled powders. Tapped density was measured in a similar manner with aerated density. By performing a few tapped density measurements at different number of taps, the number of taps required for tapping bulk density to reach its maximum could be determined (65 times). The tapping step was done by a manual vertical dropping the container from a height of 1 in onto a hard surface to allow consolidation until there is no significant collapse seen. Both densities were calculated by the ratio of mass of the wood powder to volume, which it occupied in the cylinder and were measured at least three times in each case.

Angle of repose

The procedure determining the angle of repose followed the one described by Svarovsky (Svarovsky, 1987). A metal funnel with a circular opening of 10 mm and a slope of 60° to the horizontal was fixed at a free standing bar. The round opening was initially blocked with a finger. Then, wood grinds (~100 g) was gently charged into it. A powder heap was formed by removing the finger permitted the powder to flow onto a horizontal surface directly beneath. Stirring by a thin rod time to time was needed in case of long grains blocked the funnel neck. Still photos were taken by a digital camera and evaluated using a scale by a protractor to determine the angle of repose. The test was conducted three times for each sample.

Particle density

A gas multi-pycnometer (MPV-D160-E, Quantachrome Corporation, FL) was used to measure the particle density of grinds by measuring the pressure difference when a known quantity of helium (He) under pressure is allowed to flow from a precisely known reference volume (V_R) into a sample cell (V_c) containing the solid material. The true volume of the sample (V_p) was calculated from Equation 3.4. The particle density of the sample is its mass divided by V_p and was expressed in Mg/m^3. Particle density measurement was repeated three times on the same sample.

$$V_P = V_C - V_R \left[\frac{P_1}{P_2} - 1\right] \tag{3.4}$$

where V_p is the volume of solid biomass (m^3), V_c is the volume of sample cell (m^3), V_R is the reference volume (m^3), P_1 is the pressure reading after pressurizing the reference volume (Pa), and P_2 is the pressure after including V_c (Pa).

Pelleting experiment

Pelleting apparatus

A study on compressibility of torrefied ground wood was carried out in a basic single pelleter assembly (plunger and cylindrical die). An 8 mm plunger cut from drill rod was attached to the Insight 30 (MTS Systems Corporation, Eden Prairie, MN) universal testing machine equipped with a 3000 N load cell providing the means to compress the biomassshown in the Figure 3.2.

The internal chamber height of the cylindrical die was 5 inches. The cylindrical die chamber was wrapped with a band heater and covered with aluminum tapes and insulation material. 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 (die). Another type-T thermocouple, also connected to the outer cylinder wall, allowed verification of the die temperature via a digital thermocouple reader.

Operating procedures

The die was previously heated to 90ºC to imitate the heating condition during commercial pelleting process. Approximately 0.5 ± 0.03 g of sample was inserted in the die chamber. To produce the uniform l/d ratio of a pellet, required mass from each sample batch was varied, depending on its particle density and feed moisture content. Compression of material is obtained by the Insight 30 was set to lower the plunger with the crosshead speed of 50 mm/min pressing the wood powders in the die chamber until it is against a fixed back stop, which was set on the steel base to achieve a uniform compaction. Once the specified preset load was reached. The plunger then was stopped and remained in the position with constant strain for 60 s, to allow stress to relax. The data on a force deformation and force relaxation test were recorded to study the compression and stress relaxation behavior of the biomass materials. After withdrawing the plunger, a single pellet was collected by replacing the back stop with the hollow stainless steel base, and applying a gentle force using the plunger to push the pellet through. Twenty five pellets were made at each batch.

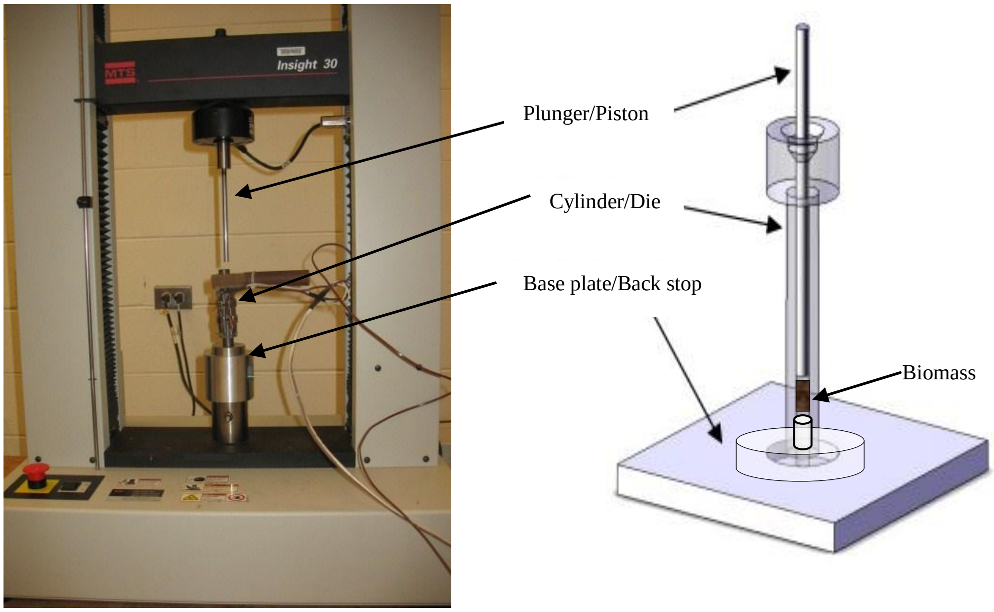

Figure 3.2: Single pelleting experimental test apparatus

Moisture conditioning

Prior to the pelleting experiment, wood grind samples were all dried to bone dry. A calculated quantity of water was sprayed on the wood grinds and mixed thoroughly to reach moisture content of 3.5, 7, and 10.5 % (wb). The conditioned wood grinds were stored in a moisture tight freezer bag and kept in the refrigerator at a temperature (4ºC) for at least 72 h prior to confirming the actual moisture content of the sample before pelleting.

Experimental design

Table 3.1 outlines the levels of the experimental factors selected for pelleting experiment. A complete factorial design was employed with three independent variables (torrefaction temperature, moisture content of feedstock, and compression force). The torrefaction temperature of 300ºC was not included in the compressive test. This is because in the preliminary study, grinds received from this temperature were not pelletible. Namely, when tested at low compressive pressure, a pellet could not be formed. And when tested at high compressive pressure, the production struggled as the pellet was plugged in the chamber. In the present study, three levels of moisture content in feedstocks were tested, starting from 3.5% with the increment of 3.5%. The first level was 3.5 % wb, as it was the upper range of the moisture content of torrefied wood of all torrefaction temperature at as received. The next moisture content level was 7% wb, as it was received of regular dried wood. And the last was 10.5% wb, as it was approximately the level suggested optimum moisture level in pelleting for cellulosic materials. Pressure ranges of 8000 N, 13000 N, and 18000 N were chosen to ensure that stable pellets especially those made of torrefied ground wood at high temperature can be formed at the present conditions. The die diameter of 8 mm was selected since preliminary work showed there was tremendous friction and biomass plugged in the pellet chamber when compressing torrefied wood even at low pressure, affecting the difficulty in the production.

Table 3.1: Experimental variables, and their respective levels, for densification of pine chips.

Experimental variables		Levels			
Feedstock	Torrefaction temperature (^{o}C)	control	225	250	275
	Geometric mean diameter (mm)	0.71 (± 0.41)			
	Moisture content (% wb)	3.5	7	10.5	
Machine	Compressive force (N)	8000	13000	18000	
	Die temperature	90 ± 3			
	Die diameter (mm)	8			

Pellet density and dimension expansion measurement

After cooling, each pellet was weighed and measured in length and diameter using a digital scale and a digital caliper, respectively to calculate pellet density. The aforementioned measurements of the pellet were measured again after storing at ambient conditions for two weeks to determine pellet stability. This was to investigate the diametric and longitudinal expansion, as well as the relaxed density which reveals the stress relaxation occurred under constant strain.

Abrasive resistant test (durability)

Durability of pellets were tested by regarding to ASABE Standard S269.4 (ASABE. 1991), using a DURAL tester developed at University of Saskatchewan for testing alfalfa cubes (Sokhonsanj & Crerar, 1999), which suggested a more sensitive method to compare pellet’s hardness. Three pellets were weighed and put it in the DURAL tester and tumbled at 1600 rpm for 30 seconds. The samples were removed from the DURAL tester and passed through a sieve with an aperture size of 5.95 mm screen. The ratio of the mass of the pellet retained on the sieve after testing to the mass of pellets before tumbling is called Durability. Durability is regarded to be high when the measured value is above 80%, medium when between 70% and 80%, and low when below 70% (Tabil & Sokhansanj, 1996a). The test was repeated at least three times.

Compressive resistant test (diametral compression test)

Tensile strength of pellets was measured using diametral compressive test on two opposite metal platens 30 kN load cell. The upper one was attached to the Insight 30, while the bottom one was fixed at the base. The speed of the upper mobile platen was set at 30 mm/min to compress the pellet. The tensile strength of a pellet from each batch was determined from carefully observing the crushing load needed to break the pellets in radial direction. When the rupture point was identified, the pressing then was stopped and the first rupture peak is taken as a breaking load. Identification of the correct point of breakage was crucial to the determination of tensile strength (Shaw et al., 2009). The test was repeated at least five times.

Water resistance test (hygroscopicity)

The test protocol was modified from the apparatus used to test water absorption of fish feeds, where the diets were placed on a sieve and immersed in a 40-l fish tank containing water at 15°C for periods of 10, 60, or 180 s (Hilton et al., 1981). However, in this study, testing temperature was adjusted to a room temperature and the test duration was only for 10 s and 30 s as to avoid loss of pellets due to the excessive disintegration, not being able to be measured for the weight change. After the test duration, a high water absorbent cloth was used to eliminate excess water on the sieve and pellets. The weight of the pellets and the sieve was measured altogether before and after the water submersion to avoid loss if disintegration. Disintegration of pellets was also observed. The percentage of water uptake was computed by dividing the mass of excess water absorbed by a pellet to the original mass of the pellet. Six replications of water uptake tested were conducted.

Energy consumption

Energy consumption during pelleting is a good indicator of production efficiency for different biomass materials. In this study, work done during the compression by the plunger was calculated by integrating the area under the compressive force (N) and extension (mm) data collected during single pelleting experiment. By dividing the work with the pellet weight, specific energy required for pelleting was determined and reported in MJ/t.

Statistical analysis

Statistical analysis

The effect of torrefaction temperature, moisture content of the feeds, and compressive force on energy consumption, pellet density, relaxed density, dimensional expansion, hardness, durability, and water uptake was analyzed using SAS by analysis of variance (ANOVA) and Duncan multiple range tests at the level of statistical significance, alpha < 0.05. An example of SAS code used for three-way ANOVA analysis was given in the APPENDIX C.

CHAPTER 4

RESULTS AND DISCUSSIONS

Characteristics of torrefied wood chips

Mass and energy yield

Mass and energy yields of pine chips at various torrefaction temperature conditions are shown in the Table 4.1. Energy yield data represents the ratio of actual energy retained after the torrefaction process to initial energy content of biomass. According to the Table 4.1, the mass yield of torrefied pine chips decreased with increase in torrefaction temperature. The mass yield started to decline dramatically from temperature of 275°C and became only about one-half of the original weight when torrefied temperature reaching 300°C. The mass loss was likely primary due to thermal decomposition of hemicellulose and some short chain lignin compounds (Bergman & Kiel, 2005). Comparative mass and energy yields were found in similar studies for wood fuels (Lipinsky et al., 2002) and wood briquettes (Felfli et al., 2005). The decomposed volatiles can be captured and used for various applications. Detailed compositions of condensable volatile products and non-condensable gases can be obtained from Mani (2009). Figure 4.1 shows the physical changes occurred during torrefaction of wood chips at various temperatures.

Table 4.1: Effect of torrefaction temperature on weight and energy yield of torrefied wood.

Wood chips	Yield of torrefied wood chips (%)	Energy yield (%)
TPC-225	89	94
TPC-250	82	90
TPC-275	73	87
TPC-300	52	71

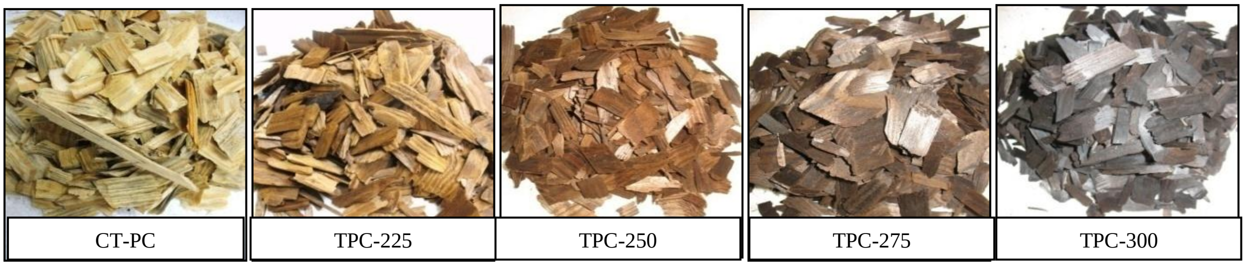

Figure 4.1. Physical changes during torrefaction of pine wood chips

Chemical and thermal characteristics

Data from proximate, ultimate and heating value analyses of torrefied pine chips were given in Table 4.2. Moisture content of torrefied biomass decreased as the torrefaction temperature increased when stored at room temperature. It indicates that torrefied biomass cannot absorb moisture significantly compared to untreated wood. This behavior may be due to loss of hydroxyl (-OH) groups from biomass during torrefaction reaction. The volatile matter in the sample was decreased slightly at temperature of 225°C and 250°C, while noticeable reduction was observed at torrefied temperatures of 275°C and 300°C. Similar observations were also reported in the study of torrefied wood briquette and other biomass species (Felfli et al., 2005; Pimchuai et al., 2010). The overall result is in agreement with these researchers on the trend that is towards a reduction in volatile matter and increase of fixed carbon ash content

(Bridgeman et al., 2008; Couhert et al., 2009). An observed increase in ash content of torrefied biomass was mainly due to the loss of volatiles, and concentration effect during torrefaction reaction. Lehtikangas (2001) also regarded the increase of ash content of pellet products after pelletization as it was due to the loss of volatiles of raw materials during drying.

As the torrefaction temperature increased, the elemental carbon content of torrefied biomass was increased. At the same time, hydrogen and oxygen contents of torrefied biomass decreased, resulting in decreased H/C and O/C ratios (Figure 4.2), which shows that torrefied woods have fuel properties improved close to other solid fuels. The observations are sharp at torrefaction temperature of 275^{o}C. Lower hydrogen and oxygen contents of torrefied biomass also support the fact of reduction in hydroxyl (-OH) groups during torrefaction. Arias (Arias et al., 2008) studied on torrefied eucalyptus reported that after torrefaction of biomass, hydrogen and nitrogen content remained unchanged (240-280^{o}C) only when the temperature beyond 280^{o}C, hydrogen content decreased slightly. Yang's findings (2007) supported that as he identified that hydrocarbon such as H2, CH_4, C_2H_6 were released largely beyond torrefaction temperatures, while some of CO_2 and CO (mainly from hemicellulose) could be formed starting at 280°C. The current study proved that torrefaction removed oxygen, therefore increased energy density. This was confirmed by the higher heating value (HHV) of torrefied biomass was significantly increased with increase in torrefaction temperature. According to the Figure 4.2, the chemical compositions of torrefied biomass were very similar to that of lignite coal or peat for potential co-firing application. Increase in energy density of biomass during torrefaction was comparable with other similar studies for agricultural residues (Pimchuai et al., 2010), wood chips (Prins et al., 2006) and sawdust (Nimlos et al., 2003).

Table 4.2: Properties of torrefied pine chips (%, db).

Wood grinds	MC (%, wb)	VM	Ash	FC	C	H	N	O	HHV (MJ/kg)
CT-PC	6.69	85.98	0.27	13.76	47.21	6.64	0.17	45.76	18.46 (0.13)
TPC-225	3.30	84.78	0.27	14.95	49.47	6.07	0.15	44.03	19.48 (0.02)
TPC-250	2.88	82.52	0.25	17.24	51.46	5.86	0.14	42.02	20.08 (0.01)
TPC-275	2.46	76.40	0.35	23.26	54.91	6.20	0.20	38.17	21.82 (0.08)
TPC-300	2.57	58.72	0.43	40.85	63.67	5.58	0.20	29.99	25.38 (0.07)

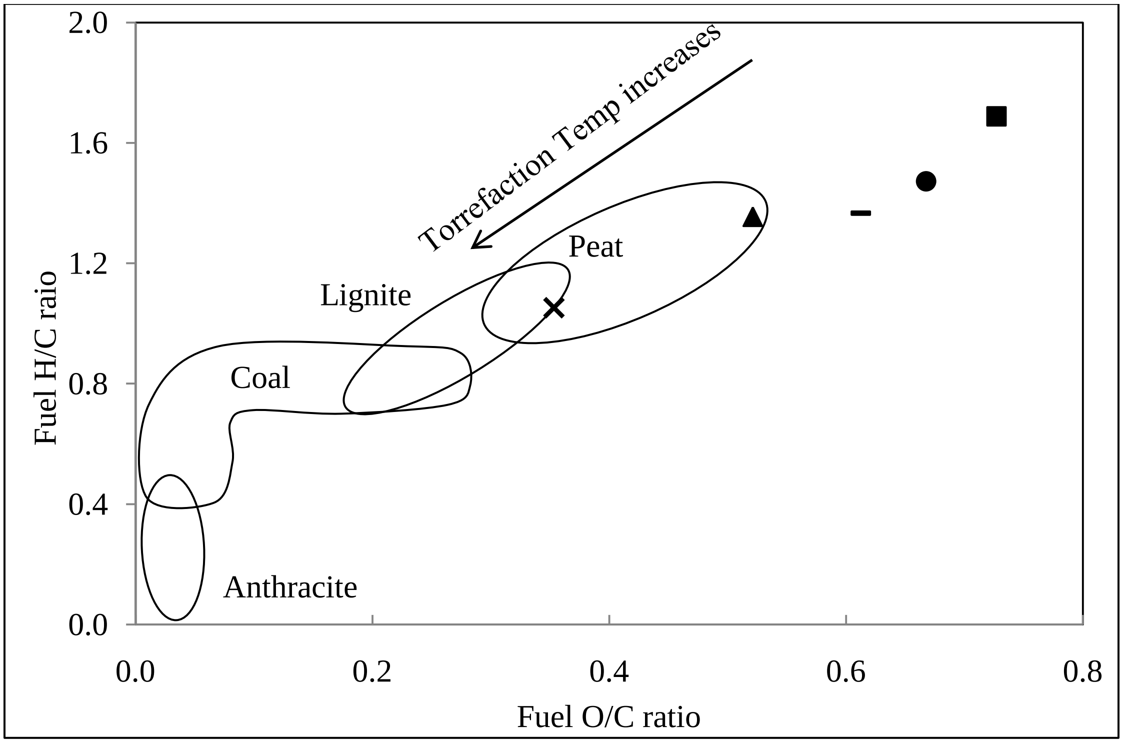

Figure 4.2: Fuel H/C and O/C ratios of torrefied pine chips at various torrefaction temperatures. The comparison data of various solid fuels was obtained from (Van Loo & Koppejan, 2008)

■ : CT-PC, ● =TPC-225, ▬ = TPC-250, ▲= TPC-275, **X** = TPC-300.

Table 4.3 shows the change in chemical composition of torrefied biomass at various temperatures. Hemicellulose and cellulose decreased, while lignin increased with increase of torrefaction temperature. As it was well known that cellulose did not decompose below 300°C (Bourgois et al., 1989; Yang et al., 2007), the reduction in cellulose content of torrefied biomass in this study, therefore, was only that indicative of acid soluble cellulose portion of the sample. The acid insoluble portion of cellulose was accounted with lignin fibers present in torrefied biomass. As a result, the acid insoluble fiber content of torrefied biomass increased with increase of torrefaction temperature. Therefore, it may be concluded that torrefied biomass is not be suitable for extracting simple sugars and further converted into ethanol. The relative increase of lignin content also contributed to the higher heating values of torrefied wood. Lignin was regarded rich in carbon and hydrogen, and that the structures of lignin were linked by a multitude of inter-unit bonds, including ether and carbon-carbon linkages (Mansouri & Salvadó, 2006; Van Loo & Koppejan, 2008), therefore it had a higher heating value compared to carbohydrates (hemicellulose and cellulose).

Table 4.3: Chemical compositions[a] of torrefied pine chips.

Biomass	Hemicellulose (wt. %)	Acid soluble Cellulose (wt. %)	Acid insoluble fibers (mostly Lignin) (wt. %)
CT-PC	15.19	48.57	26.16
TPC-225	12.87	41.23	38.42
TPC-250	6.93	41.90	45.70
TPC-275	0.99	39.54	53.30
TPC-300	0.56	12.84	79.99

[a] The reported values are presented in dry ash free percentage.

Grindability of torrefied wood chips

Specific energy consumption for grinding

Figure 4.4 shows the effect of torrefaction temperature on the specific energy required to grind torrefied pine chips. Specific grinding energy consumption of untreated wood chips was very high (238 kWh/t) and was comparable to other similar studies (Esteban & Carrasco, 2006). Specific energy consumption for grinding was significantly reduced with increase in torrefaction temperature. Specific grinding energy consumption of torrefied biomass was strongly linearly correlated well with the torrefaction temperature (R^2 >0.9). However, Bergman (2004) discovered a non-linear relation between torrefaction temperature and power consumption of grinding over 200-280°C. Grindability of torrefied wood was improved dramatically at 275°C and 300°C as the specific energy required for grinding (23-52 kW h/t) were as low as that needed to grind grasses: wheat straw, barley straw, corn, and switchgrass (43.6, 27.1, 19.8, and 58.5 kWh/t respectively) using a similar sieve size of 1.6 mm (Mani et al., 2004; Schell & Harwood, 1994) and similar to energy needed to grind coal (7-36 kWh/t). Compared to untreated counterparts, grinding energy consumption was decreased by 9 times at 300^{o}C torrefaction temperature for torrefied pine chips. Improved grindability of torrefied biomass may primarily be due to relative increase in biomass brittleness and breakdown of fibrous compounds during torrefaction (Arias et al., 2008; Mani, 2009).

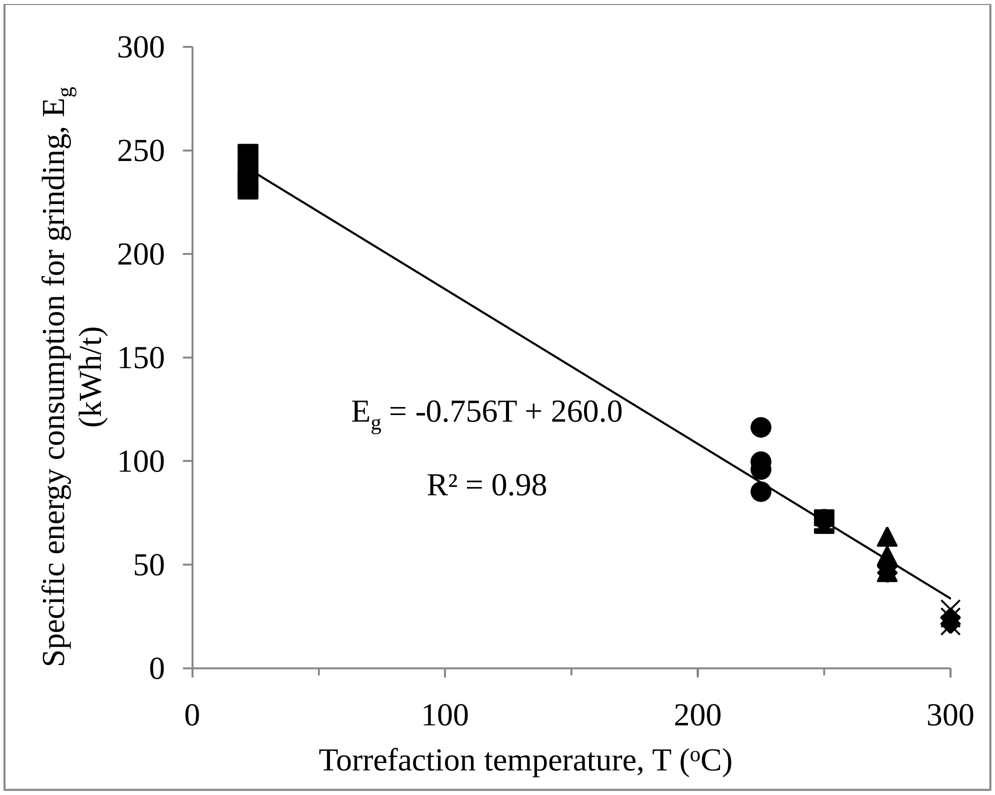

Figure 4.3: Effect of torrefaction temperature on specific energy consumption for grinding of pine chips: ■ = CT-PC, ● = TPC-225, ▬ = TPC-250, ▲ = TPC-275, **X** = TPC-300.

Particle size and particle size distribution (PSD)

Figure 4.4 shows the effect of torrefaction temperature on geometric mean particle size of ground torrefied biomass using the same screen size (1.5 mm). Mean particle size of ground torrefied biomass was affected significantly by torrefaction temperature. Overall, torrefaction of biomass not only decreased the energy required for grinding but also decreased the average particle size of ground biomass. A second order polynomial model was developed to correlate mean particle diameter of torrefied biomass and the torrefaction temperature. The model fitted very well with the experimental data having an R^2 value of 0.99.

Figure 4.5 shows the percent particle size distribution and cumulative percent passing of ground torrefied pine chips. The particle size distribution curves for pine chips showed that torrefied biomass produced significantly smaller particles than that of untreated biomass. The particle size distribution curve was skewed towards smaller particle sizes as the torrefaction temperature increased. The similar skewed distribution of ground biomass was also observed from other studies (Himmel et al., 1985; Mani et al., 2004). Cumulative percent passing curve also showed the similar behavior for torrefied biomass. For example, in the torrefied ground wood, only 40% of the particles were smaller than 0.5 mm. The increase in cumulative passing percentage with torrefaction temperatures (57.4%, 65.8%, 73.0%, and 77.4% in temperatures of 225°C, 250°C, 275°C, and 300°C, respectively) indicated the increase of the brittleness structure of torrefied wood with increase of torrefaction temperature, and therefore the higher grindability. Overall, torrefied biomass produced relatively narrower or uniform particle size ranges compared to untreated biomass due to intense brittleness of torrefied biomass similar to coal. This behavior was directly supported by the lower grinding energy consumption of torrefied biomass.

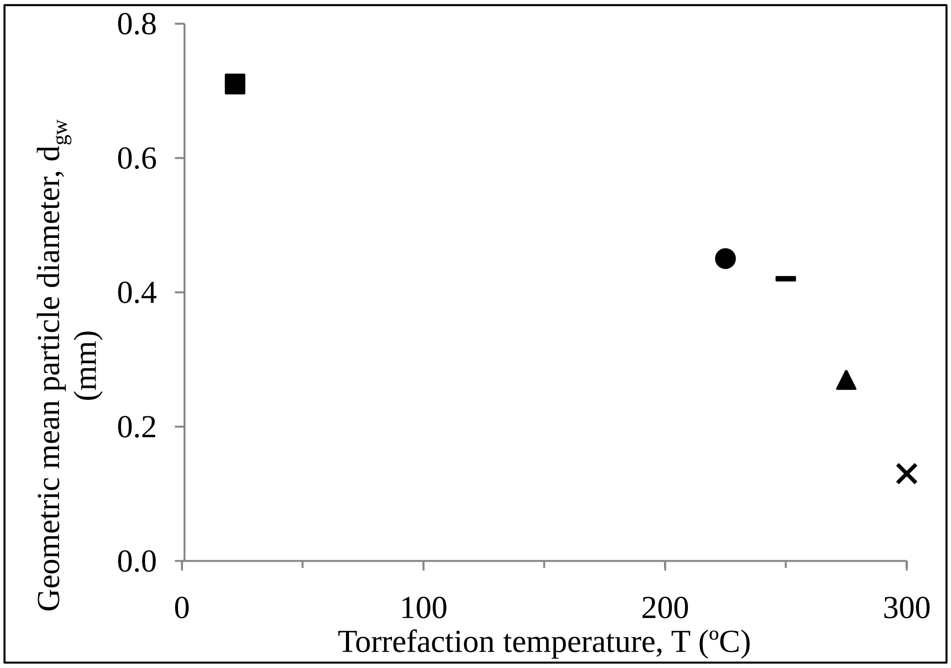

Figure 4.4: Effect of torrefaction temperature on the geometric mean particle diameter of torrefied wood grinds: ■= CT-PC, ●= TPC-225, ▬= TPC-250, ▲= TPC-275, **X** = TPC-300.

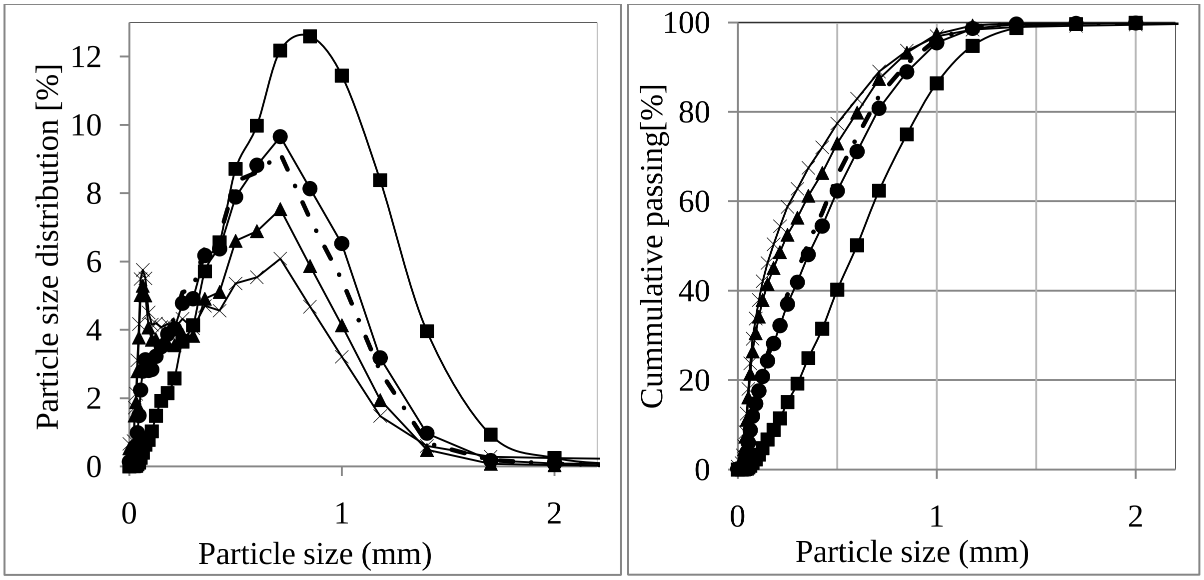

Figure 4.5: Particle size distributions of wood grinds at various torrefaction temperatures (left) and the cumulative passing graphs (right): ■ = CT-PC, ● = TPC-225, ▬ = TPC-250, ▲ = TPC-275, **X** = TPC-300.

Sphericity and particle surface area

Table 4.4 summarizes the physical properties of ground torrefied pine chips at various torrefaction temperatures. Sphericity of pine chips was significantly improved from 0.48-0.62 as the torrefaction temperature was increased. Higher sphericity value of torrefied pine chips indicated that the shape of ground torrefied pine chip was significantly changed. Particle surface area of torrefied biomass was significantly increased compared to that of untreated biomass indicating again the brittleness of torrefied biomass. Overall, an increase in particle surface area or a decrease in particle size of torrefied biomass can be the desired properties of torrefied biomass for efficient combustion and co-firing applications (Xiumin et al., 2002). Additionally, particle size, shape, and surface area had significant impact on combustion characteristics of biomass and coal (Lu et al., 2008; Saastamoinen et al., 2010)

Table 4.4: Physical properties of wood grinds and specific energy consumption for grinding using knife mill.

Biomass grinds[a]	d_{gw} (mm)	S_{gw} (mm)	*SPHT* (Dimensionless)	S_v (mm^{-1})	E_g (kWh/t) Specific energy consumption for grinding
CT-PC	0.71	0.41	0.48 (99.2)[b]	13.5	237.7 (6.6)[c]
TPC-225	0.45	0.40	0.52 (98.2)	30.4	102.6 (13.4)
TPC-250	0.42	0.38	0.51 (98.3)	32.6	71.4 (3.6)
TPC-275	0.27	0.36	0.60 (95.3)	48.6	52.0 (7.3)
TPC-300	0.13	0.31	0.62 (92.4)	64.2	23.9 (3.0)

[a] All grinds are received from using knife mill screen size of 1.5 mm.

[b] Number enclosed in parenthesis represents fraction of samples that is less than 0.9 sphericity.

[c] Number enclosed in parenthesis represents standard deviation of five replications.

Figure 4.6: Pictures of torrefied wood grinds at various torrefaction temperatures.

Flow properties of torrefied wood powders

Table 4.5 shows the flow properties of torrefied wood grinds. The results showed that particle density of torrefied grinds was decreased with increase of torrefaction temperature. Torrefied wood from the temperature of 300°C showed a dramatic reduction in particle density relative to the untreated wood. Koufopanos (2009) explained the occurrence as severe volatile and gaseous products migrating through the solid pores during the heat treatment. Therefore, it indicated that torrefaction temperature affected wood to become less dense, occupying more porous structure.

Aerated bulk density of torrefied wood powder increased to maximum at a torrefaction of 225°C and then decreased at a torrefaction of 275°C. The aerated density of torrefied wood of 300°C went up. As the porous structure of torrefied wood progresses with torrefaction temperature, the mass per a fixed volume decreased, yielding lower bulk density. Abdullah & Geldart (1999) also found that porous powders had lower aerated bulk densities compared to non porous particles in all particle size mixture. The bulk density of wood grinds from 300C was however higher than that of 250°C and 275°C bulk density may be understood that torrefied wood at 300°C severely destructed by the high heat, occupied an extreme weak structure; as it could be crushed by hand. This fragile powder structure was characterized similarly to coal agglomeration (Yu et al., 1995). When agglomeration system had low inter-friction or free flowing, they will fall down easily, resulting in low inter-voidage, and therefore high overall density.

Tapped density was observed to have a similar trend with the aerated density as mentioned above. The highest tapped density of torrefied wood from 225°C was due to the optimum of mixture of powder and shape of the powder system that allow proper portion of large particles to yield unoccupied voids and enough small particles to fill those voids and give the densest packing. The density of untreated wood was also lower as it occupies insufficient fine particle percentage to fill voids therefore, resulting in less pack condition. Abdullah & Geldart (1999) proposed a diagram explaining packing density variation with composition for bimodal mixture, where density increased as the percentage of large particles increased to one point then the increase of large particle portion resulted in lower density. However, the result of the tapped density of torrefied wood from 300°C yields higher tapped density even when its fine particle percentage was regarded the greatest among the samples. This may be due to the weak structure of the powder, which resulted in possibly in further consolidation. Rastogi (1993) studied ultrafine coal (mean diameter from 7 to 25 μm) and also found the same conclusion even with tapping over 1000 times, the packing condition was inconsistent and HR was still increased.

Table 4.5: Flow properties of torrefied wood grinds.

Biomass grinds[a]	Particle density (kg m^{-3})	Bulk density (kg m^{-3}) (Aerated)	Bulk density (kg m^{-3}) (Tapped)	Angle of repose (degree)	Hausner ratio (kg m^{-3}/ kg m^{-3})
CT-PC	1463.4 (35)	333.5 (2.5)[b]	418.4 (0.2)[b]	44.5 (0.7)[b]	1.26
TPC-225	1402.3 (8)	347.0 (1.0)	424.2 (1.8)	42.3 (0.6)	1.22
TPC-250	1354.1 (10)	222.8 (0.5)	268.0 (1.5)	41.7 (1.0)	1.20
TPC-275	1285.2 (38)	211.0 (3.6)	250.7 (1.3)	41.8 (1.3)	1.19
TPC-300	869.7 (62)	307.0 (0.5)	352.6 (2.5)	39.0 (0.0)	1.15

[a] All grind sample is uniform in particle size distribution.

[b] Number enclosed in parenthesis represents standard deviation from three replications.

Even though the powders from each batch were uniform in size, and size distribution, the particle density, shape, and intra-porosity varied due to intermolecular forces and may be a dominant factor leading in particular fluidization behavior (Geldart et al., 1984). AOR and HR have been claimed as reasonable indicators of powder flowability in many studies (Alavi & Caussat, 2005; Harnby et al., 1987; Li et al., 2004; Wong, 2000; Wouters & Geldart, 2004). Figure 4.7 shows a linear relationship between HR and AOR with correlation coefficient of 0.97. It was seen that the higher the torrefaction temperature; the lower HR and AOR. In general, the larger the AOR and HR; the more cohesive the powders are. In this study, all of the wood samples that were torrefied fell in the range of AOR (38-45 degree) and HR (<1.25). Therefore, they were classified in the Geldart A type material: non-cohesive, free-flowing, easy to fluidize group. The untreated wood fell in the range of AOR (45 degree) and HR (>1.25) and was classified in the Geldart A+C type material: semi-cohesive, and had very poor flowability. Bergman (Bergman et al., 2004) was also able to produce Geldart A powder from torrefied willow at 270°C, 30 min reaction time. Moreover, at this condition the powder showed to be fluidized smoothly, but only in a narrow range of fluidization velocities. Further increase of torrefaction temperature was suggested to further shorten the cellulose fibers, widening this range.

The reduction of HR with increase of torrefaction temperature of wood grinds was due to the fact that wood powders became more porous (less dense) and more spherical shape-like, which resulted in less cohesiveness and less ability to be consolidated, therefore smaller HR. This observation was found in agreement with other studies (Abdullah & Geldart, 1999; Furnas, 1931; Geldart, 1973; Hausner, 1967). Torrefied wood grinds was less cohesive resulted in less friction and adhesion forces between particles, limiting the movement of the wood powders while poured onto the pile of particles, therefore yielding low angle of repose. The torrefied wood grinds were considered to have better flowability relative to untreated wood.

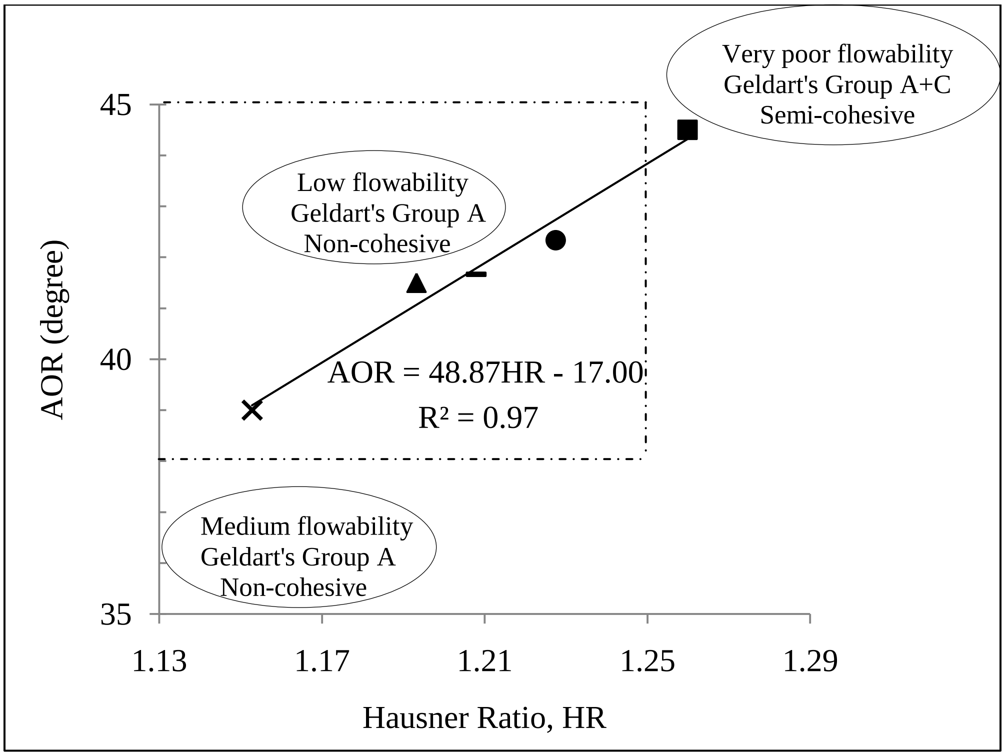

Figure 4.7: Linear relationship of angle of repose and Hausner ratio: ■= CT-PC, ●= TPC-225, ▬ = TPC-250, ▲= TPC-275, **X** = TPC-300. Flow characteristics of torrefied wood grinds are regarded to angle of repose and Hausner ratio (Alavi & Caussat, 2005; Geldart et al., 1984).

Pelleting characteristics of torrefied wood powders

Effects of torrefaction temperature, moisture content, and compressive force on the compression and relaxation characteristics of torrefied wood grinds and the qualities of the pellets (density, tensile strength, durability, water resistance) were evaluated.

Specific energy required for compression of pellets

Results from ANOVA and multiple comparisons of experimental factors affecting the specific energy required for compression of the torrefied wood are shown in Table B1.1 and B1.2, respectively. The specific energy required to compress the torrefied wood is shown in Table C1. ANOVA tests showed that compressive force had the significant effect on the specific energy used in compressing torrefied wood, followed by torrefaction temperature and moisture content, respectively. Increasing of the pre-set load significantly increased the specific energy required for compression. The highest compressive force used at 18,000 N consumed the maximum energy and then 13,000 N, and 8,000 N respectively. Specific energy required to compress increased with increase of torrefaction temperature. The untreated wood needed the least specific energy. Increasing the moisture content of the torrefied wood grinds resulted in less energy required in compression.

The effect of the level of compressive force used on the specific energy was obvious and direct. Difference in specific energy consumption of various temperature torrefied woods was explained, regarding to powder cohesiveness property. As reported in the powder mechanical property earlier, untreated wood had the most cohesiveness property and was easier to deform (Peleg & Mannheim, 1973). Therefore, the compressibility of untreated wood was higher and so less energy of compression is needed. Table 4.6 represents compressibility, an ability of a powder to decrease in volume under pressure. Compressibility decreased with increase of torrefaction temperature: 20.3, 18.2, 16.9, 15.8, and 12.9%. Torrefaction was found to decrease wood compressibility. The finding was identical with Shaw's, where compressibility performance of wood and straw treated from the steam explosion was lower than the raw counterparts (Shaw, 2008).

Moist powder deform easily compared to dry powder (Peleg & Moreyra, 1979). Specific energy required for compression could be reduced, as water in moist feedstock facilitated in lubricating between the wood-wood and wood-die which eased frictional forces (Shaw, 2008).

Specific energy in densification using piston press was 134.6 MJ/t of sawdust (Reed et al., 1980) and 277.2 MJ/t for grass (Shepperson & Marchant, 1978), respectively. While, lower energy consumption for wood residues using pellet mill was observed 108-162 MJ/t (Miles & Miles Jr, 1980; Reed & Byrant, 1978). By using a circular die, Faborode (Faborode & O'Callaghan, 1987) found that energy required in compression for fibrous agricultural materials were in range of 18-31 MJ/t depending on size of raw material. The mean specific energy for compression of pellets in this study was in range of 23.0-86.16 MJ/t.

Table 4.6: Compressibility of torrefied wood grinds.

Biomass grinds	Compressibility (%)
CT-PC	20.29
TPC-225	18.20
TPC-250	16.87
TPC-275	15.84
TPC-300	12.93

Effect on pellet density

Initial pellet density data are shown in Table B2.1, B2.2, and C2 for ANOVA, multiple comparisons, and data table, respectively. According to the ANOVA, moisture content had the most effect on the initial density. Initial density decreased when moisture content was increased. Torrefaction temperature negatively affected pellet density as untreated wood yielded the maximum density, while pellet density decreased with increase of torrefaction temperature. Compressive force influenced on pellet density was comparatively small. Pellet initial density was improved at low range of the preset load, while increase of the compressive force of 13,000 N and 18,000 N did not significantly increase the initial pellet density.

In general, water in the feed system helped promoting liquid bridges and plasticizing particles through water sorption during compaction. However, in this study, adding moisture content to the torrefied powders seemed to negatively affect the compact system. During the compression test, the author observed that the bottom of a pellet made from 10.5% batch was darker due to the trapped excessive water that did not distribute through a pellet. The maximum density of pellet (1127 kg/m^3) was obtained when using feed at moisture content of 3.5%, which was the lowest range. Shaw & Tabil (2007) agreed that lower moisture content produce denser pellets.

Difficulty in producing high pellet qualities from torrefied material has also been experienced by Nimlos (2003) who produced pellets from torrefied hardwood sawdust in a hydraulic press using pressure close to the upper level pressure used in the present study (159-358 MPa). The work resulted in flaky pellets, which did not show a significant improvement in pellet density compared to that from untreated wood, except only when pressed with heated die. Pyle (1976) expressed difficulty in compacting pyrochar (without heat or binder applied) that densified mass was fragile. However, it was suggested that by adjusting condition operation temperature to about 93ºC at high compressive pressure (7-34 MPa), durable pellet could be possibly made at about 800 kg/m^3. According to the current study findings, torrefied wood showed a low performance in producing high pellet density due to the lack of cohesiveness and compressibility. As mention earlier, cohesive material was easier to deform and is likely to retain stress within its solid mass. Torrefied wood was free flowing/ cohesiveless and hard to consolidate, therefore, hindered the compression behavior, yielding low pellet density.

The interaction term between torrefaction temperature and moisture content revealed that increase of torrefaction temperature resulted in decreasing in initial density but the effect was stronger at a moisture content of 10.5%.

Effect on relaxed density and dimensional expansions

Relaxation characteristics are analyzed based on ANOVA table, multiple comparisons and data table. ANOVA tables are shown in Table B3.1, B4.1, B5.1, multiple comparisons are shown in Table B3.2, B4.2, B5.2, and data tables are found in C3, C4, and C5 for relaxed density, longitudinal expansion and diametral expansion, respectively. According to the results, at all levels of all variables, pellet density decreased after relaxation under constant strain for two weeks. Expansions in length and diameter were mainly responsible for the decrease in pellet density since record showed that pellet mass did not significantly change after relaxation. Significant effect on the relaxation characteristics (relaxed density, longitudinal expansion and diametral expansion) were in order as moisture content and torrefaction temperature. Effect of compressive force was not significant. The order was also equivalent to the one affecting initial density. The effect of moisture content on relaxation behavior was that pellet relaxes less with increase of moisture content. Higher torrefaction temperature results in less relaxation intensity. Pellets produced from untreated wood showed the most pellet density reduction (-4.5%), while pellets from torrefaction temperature of 250ºC and 275ºC relax were the least (-1.2 to -1.8%). Interaction term between moisture content and compressive force in diametral expansions reveals compressive force, affecting percent relaxation depended on the moisture content. At moisture content of 3.5, increase of compressive force resulted in higher extent of pellet expansions, while pellets produced from moisture content of 10.5% relaxed less when compressive force increased. At moisture content of 7%, compressive force did not show significant influence.

Higher expansions of pellets produced from low moisture contents may be due to the fact that the water was not sufficient to promote binding, wetting between the particles feeds. Effect of moisture in relaxation behavior was important in terms of liquid bridges and plasticity of the bed solid matrix (Moreyra & Peleg, 1980). Li and Liu (2000) found that moisture content equal or less than 4% wb resulted in pellets to absorb water in the air, therefore expand greatly. Also, lignin in wood may not become active as a binder to hold the compact since softening point was hard to reach. Goring & Lehtikangas (Goring, 1963; Lehtikangas, 2001) reported lignin may melt at temperature (100-135ºC). But in pelleting, it can soften at lower temperatures due to the presence of moisture and pressure. Soft feed at room temperature can be brought to near pelleting temperature (85ºC) by adding 4-6% moisture steam. The reduction in dimensional expansions when moisture content increased was also found in the findings of Shaw's study (Shaw, 2008). Available lignin for binding mechanism in torrefied wood was held to response to the least dimensional stability (Lehtikangas, 2001). Lignin content was greater in high torrefaction-temperature wood, therefore pellets expand less. Moshenim & Zaske (1976) found that grass wafer showed a less expansion when feedstock was drier. However, both levels of moisture content tested in that study (8 and 25%) were higher than that of the current study. Among torrefied wood itself, pellets of torrefaction temperature 250ºC showed the smallest expansion. The mean values were 10.55-11.37% and 1.07-2.18%, for longitudinal and diametral expansion, respectively. Shaw (2008) produced steam exploded treated poplar wood pellets with particle sizes 0.29-0.84 mm using die diameter of 6.35 mm. Temperature, moisture content and screen size were found to contribute to the treated poplar pellets to have the dimensions decreased: 0.49-0.03% diametrally and -2.41 to 0.58% longitudinally. Heat treated pellets in this study experience more dimensional expansion than that of the steam treated pellets may be due to the insufficient bonds.

Table 4.7: Pellet density, longitudinal and diametral expansion torrefied wood pellets.

Torrefaction temperature (ºC)	MC (% wb)	Force (kN)	Initial pellet density (kg/m^3)	Relaxed pellet density (kg/m^3)	Longitudinal expansion (%)	Diametral expansion (%)
CT	3.5	8	1148 (5)	1032 (2)	11.37 (0.58)	1.07 (0.09)
		13	1177 (5)	1071 (2)	10.55 (0.55)	1.83 (0.06)
		18	1181 (5)	1050 (2)	11.24 (0.45)	2.18 (0.07)
	7	8	1170 (5)	1139 (2)	2.27 (0.08)	0.81 (0.10)
		13	1180 (5)	1145 (2)	2.87 (0.18)	0.76 (0.05)
		18	1175 (6)	1146 (2)	2.01 (0.20)	0.87 (0.00)
	10.5	8	1090 (5)	1074 (3)	-1.03 (0.18)	0.54 (0.10)
		13	1079 (5)	1071 (2)	-0.61 (0.20)	0.48 (0.12)
		18	1093 (4)	1089 (1)	-0.22 (0.17)	0.21 (0.06)
225	3.5	8	1123 (5)	1076 (2)	5.56 (0.36)	1.17 (0.07)
		13	1177 (5)	1105 (4)	5.92 (0.42)	1.14 (0.10)
		18	1191 (5)	1131 (2)	5.77 (0.50)	1.34 (0.06)
	7	8	1126 (5)	1106 (0)	1.03 (0.09)	0.64 (0.05)
		13	1157 (5)	1148 (1)	0.89 (0.06)	0.41 (0.06)
		18	1150 (5)	1141 (2)	1.21 (0.06)	0.60 (0.18)
	10.5	8	963 (5)	969 (6)	-1.66 (0.31)	0.10 (0.14)
		13	933 (4)	957 (3)	-1.74 (0.28)	-0.14 (0.28)
		18	910 (8)	949 (13)	-3.59 (2.87)	-0.03 (0.47)
250	3.5	8	1091 (5)	1049 (1)	3.57 (0.49)	0.69 (0.11)
		13	1151 (5)	1117 (1)	3.94 (0.35)	0.79 (0.07)
		18	1170 (5)	1136 (1)	3.11 (0.44)	1.09 (0.06)
	7	8	1063 (5)	1062 (2)	0.49 (0.11)	0.35 (0.05)
		13	1083 (4)	1084 (2)	0.47 (0.13)	0.39 (0.05)
		18	1089 (5)	1074 (2)	0.33 (0.05)	0.49 (0.11)
	10.5	8	986 (5)	977 (1)	-0.86 (0.26)	0.53 (0.06)
		13	981 (5)	976 (3)	-0.81 (0.11)	0.16 (0.06)
		18	952 (3)	967 (4)	-1.12 (0.13)	-0.53 (0.10)
275	3.5	8	995 (5)	955 (3)	3.55 (0.49)	0.59 (0.05)
		13	1073 (5)	1043 (1)	3.31 (0.43)	0.57 (0.07)
		18	1092 (5)	1019 (2)	4.24 (0.39)	1.48 (0.00)
	7	8	985 (5)	976 (2)	0.88 (0.06)	0.43 (0.07)
		13	1026 (5)	1025 (3)	0.69 (0.05)	0.49 (0.14)
		18	1032 (5)	1022 (2)	0.81 (0.12)	0.33 (0.10)
	10.5	8	935 (5)	918 (3)	0.08 (0.17)	0.20 (0.06)
		13	938 (5)	938 (1)	-0.66 (0.12)	0.41 (0.10)
		18	925 (4)	935 (5)	-0.56 (0.10)	0.06 (0.07)

Effect on tensile strength

Tensile strength is used to further evaluate pellet quality, defined as a mechanical property of compact to resist against permanent deformation. It is also used as a measure of the plasticity of the material, characterizing compactibility. ANOVA table, multiple comparisons, and data table on the effect of torrefaction temperature, moisture content and compressive force on tensile strength of pellets are shown in Table B6.1, B6.2, and C6, respectively. According to the results, respectively, torrefaction temperature and moisture content were found to affect the hardness of pellets the most (F-value = 410 and 333 respectively, while F-value of compressive force is 23). Increase of torrefaction temperature resulted in increase in pellet tensile strength. Except pellet from torrefaction temperature of 250ºC showed the superior tensile strength over that of 275ºC. Moisture content also reflected tensile strength of torrefied pellets. Moisture content of 7% was found to best producing hardest pellets, while pellets made from 10.5% moisture content yielded the weakest. At low moisture contents (3.5 and 7%), increase of torrefaction temperature increased pellet hardness. The effect was found stronger at moisture content of 3.5% and at torrefaction temperature of 250ºC. On the other hand, at high moisture content (10.5%), increase of torrefaction temperature reduced pellet strength in overall, but tensile strength rose up at torrefaction temperature of 250ºC again.

Higher binding capacity of available of lignin in high temperature torrefied-materials may be responsible for higher pellet strength. Superior in steam-pretreated wood pellets in over untreated feedstock was also claimed that it was due to the contribution the lignin (Shaw, 2008). Lehtikangas (Lehtikangas, 2001) regarded that lignin helped adhere particles in pellets, promoting strength and dimensional stability. Pellets made of torrefaction temperature of 250ºC had a superior strength over that of 275ºC may be due to advantage of particle size and shape. As grinds from torrefaction of 275ºC may contains too many of shorter ones and too little of the coarse ones. This resulted the mixture to have less void spaces for smaller ones to fill in, therefore less strength pellets (Abdullah & Geldart, 1999). Compaction of mix that contained stick shape particles benefited from those stick together strongly and form interlocking mechanism (Li & Liu, 2000). Though, effect of compressive pressure on tensile strength was small, the trend still existed Higher pressure created stronger bonds in compacted materials, hence higher tensile strength. The mean tensile strength of sample from torrefaction temperature of 250ºC, moisture content of 7% and compressive force of 18000N was compared with those from Shaw (Shaw, 2008), who produced steam treated pellets from particle screen size ranged from 0.8-3.2 mm, preset load was 4000N. The best tensile of the current study was higher than that of poplar pellets (0.45-1.28 MPa) and wheat straw pellets (0.47-1.33 MPa) but lower than that of steam-pretreated poplar pellets (6.32-10.11 MPa) and steam-pretreated wheat straw pellets (9.94-13.19 MPa). Wood residues torrefied at 240-280ºC for 15-30 min was reported to produce high mechanical strength pellets due to the lignin containing (Bergman & Kiel, 2005).

Effect on durability

Durability of pellets is considered an important factor regarding to storage, transport, handling and combustion (Lehtikangas, 1999; Tabil & Sokhansanj, 1996). ANOVA table, multiple comparisons, and data table on the effect of torrefaction temperature, moisture content and compressive force on durability of pellets are shown in Table B7.1, B7.2, and C7, respectively. The statistical result regarding to the significant factors of durability was analogous to the result and trend of tensile strength, except that torrefaction temperature is the only outstanding significant factor affecting pellet durability. Durability of pellet increased with increase of torrefaction temperature. Except pellet of torrefaction temperature 250ºC was more durable than that of 275ºC. Untreated wood and wood from low torrefaction temperature showed the bad performance on durability test.

According to data table (Table C8), high durability index (70-80%) was in the most part found in torrefied wood pellets of 250ºC and 13,000N and 18,000N at moisture content of 3.5% and 7%. The values were in a range of 77.81-83.97% and could be defined as intermediate to high quality. Lehtikangas (2001) reported that durability of pellets was largely influenced by the lignin content and the positive moisture content, promoting stronger bonds and more dimensional stability of pellets. According to the findings, the percentage of fines after tumbling of pellets produced from wood residues decreased with increasing lignin content. Effect of torrefaction temperature was again claimed as explained in tensile strength effect on the contribution of lignin. The percentage of fines after tumbling decreased with increasing of lignin content was explained by the fact that strength properties of wood were dependent on the amorphous components present such as lignin and hemicellulose (Back & Salmen, 1982).

Table 4.8: Mechanical properties of torrefied wood pellets.

Torrefaction temperature (ºC)	MC (% wb)	Force (kN)	Tensile strength of pellets (MPa)	Durability of pellets (%)
CT	3.5	8	0.71 (0.10)	2.98 (0.36)
		13	0.79 (0.07)	2.21 (0.14)
		18	0.69 (0.08)	1.27 (0.40)
	7	8	2.08 (0.17)	3.59 (1.10)
		13	2.06 (0.22)	8.03 (2.60)
		18	2.05 (0.16)	5.96 (1.19)
	10.5	8	1.48 (0.17)	6.26 (0.95)
		13	1.74 (0.08)	11.82 (6.76)
		18	1.91 (0.19)	9.12 (1.10)
225	3.5	8	1.89 (0.12)	1.96 (0.67)
		13	2.13 (0.23)	3.68 (0.66)
		18	2.34 (0.31)	5.34 (1.37)
	7	8	2.37 (0.26)	4.32 (0.99)
		13	2.46 (0.35)	3.74 (0.53)
		18	2.40 (0.17)	5.26 (1.08)
	10.5	8	0.93 (0.13)	8.11 (0.04)
		13	0.70 (0.36)	8.01 (0.01)
		18	0.84 (0.21)	7.98 (0.00)
250	3.5	8	3.16 (0.39)	49.30 (7.47)
		13	3.91 (0.18)	78.79 (3.80)
		18	4.30 (0.21)	83.97 (2.89)
	7	8	2.89 (0.41)	63.74 (3.40)
		13	3.31 (0.24)	78.86 (1.77)
		18	3.36 (0.12)	77.81 (0.45)
	10.5	8	2.22 (0.30)	36.37 (4.69)
		13	1.97 (0.21)	46.95 (0.60)
		18	1.75 (0.11)	37.79 (0.48)
275	3.5	8	2.39 (0.27)	26.26 (2.54)
		13	3.36 (0.20)	69.73 (0.68)
		18	2.98 (0.32)	78.73 (3.84)
	7	8	2.52 (0.17)	39.38 (1.31)
		13	3.05 (0.17)	66.17 (0.46)
		18	3.08 (0.14)	69.23 (1.60)
	10.5	8	1.84 (0.15)	16.44 (0.15)
		13	1.83 (0.13)	24.12 (8.09)
		18	1.78 (0.23)	21.26 (4.53)

Effect on water uptake

Analysis of effect of torrefaction temperature, moisture content and compressive force on water uptake percentage was performed at two stages; 10 s and 30 s after water submersion. The increase rate from 10 s to 30 s was also evaluated. For water uptake after 10 s, the data are shown in Table B8.1, B8.2 and C8 for ANOVA, multiple comparison, and data table, respectively. For water uptake after 30 s, the data are shown in Table B9.1, B9.2 and C9 for ANOVA, multiple comparison, and data table, respectively. Table B10.1, B10.2, and C10 show ANOVA, multiple comparison, and data table for increase rate of water uptake after 10 s to after 30 s.

According to the statistical analysis, torrefaction temperature and moisture content were significant factors affecting water uptake percentage in the order of appearance. Theoretically, the hygroscopicity of torrefied material was decreased with increase of torrefaction (Yvan, 1985). Untreated wood absorbed water in the maximum level in both time durations. However, the proposed claim was not applicable for water uptake after 10 s. It was observed that in the most case, effect of torrefaction temperature on water uptake was sharper when immersing pellets for longer time (30 s). As observed that water uptake after 30s and also the rate of increase of water uptake from 10 s to 30 s were in agreement of the claim.

Water uptake of pellets decreased with increase of moisture content. Again, the trend was not obvious for water uptake after 10 s. Although, to a lesser extent; effect of compressive force on water uptake existed. Pellets compressed at higher load absorbed more water.

Reduction in water uptake of wood from torrefaction temperature was mainly due to the destruction of hydroxyl groups attached to wood cell wall components, especially hemicellulose (Gérardin et al., 2007). Gerardin explained that the electron-donating component, affected by heat as the degradation of hemicellulose after torrefaction, resulted in less or no ability of its hydroxyl group to form hydrogen bonds with acidic hydrogen atoms of water molecules through the electron pairs present on the oxygen atom. The effect of torrefaction temperature on the water uptake after 10 s was not clear as pellets may not be exposed to the water long enough. The unclear pattern of the effect of moisture content was also explained in the same manner. Moisture content of 3.5% of feedstock allowed more water absorption maybe due to the higher hydroxyl group available to form hydrogen bonds with water than that of feedstock that already had water in it. Li & Liu (2000) found that moisture content equal or less than 4% wb resulted in pellets to absorb water in the air, therefore expanded greatly. Rhen (2005) evidenced hygroscopicity of pellets when they were dried out. He gave an example when increase of pelleting temperature from 90-120ºC affected in increase moisture uptake by 0.3-0.5% as pellets were drier.

CHAPTER 5

CONCLUSIONS

The present research investigated the grinding and pelleting characteristics of torrefied biomass generated at various temperatures. Experimental evaluation of this research produced the following conclusions.

- Gas (3.7% to 28.3%) and liquid (7.4% to 29.9%) products from torrefaction increased with increase of temperature, while torrefied wood decreased (88.9% to 51.9%).
- Mass energy density increased (18.5 MJ/kg to 25.4 MJ/kg) with increase of torrefaction temperature, while volumetric energy density was regarded not significantly improved as the volume of torrefied wood chips remained constant.
- Torrefaction restricted moisture content of torrefied wood to a maximum of 3.5%. The reduction in water absorption may be attributed to the reduction of -OH groups in wood.
- Reduction in volatiles was marked (76.4% to 58.7%) at higher torrefaction temperature range (275°C and 300°C, respectively). This resulted in particularly rising of fixed carbon (23.3% to 40.9%).
- Hydrogen and nitrogen remained constant, while oxygen was removed after torrefaction (45.8% to 30.0%), yielding higher relative carbon content (47.2% to 63.7%). Lower O/C and H/C ratios and the higher HHV together proved torrefied wood as an upgraded fuel.
- Hemicellulose decreased dramatically after torrefaction (15.2% to 0.6%), while relative lignin content increased (26.2% to 80.0%) due to the concentration effect and as accounted from acid insoluble portion of cellulose.

- Torrefaction increased wood brittleness, resulting in marked reduction in grinding energy consumption (-56.8% to -89.9%). Compared to the raw wood, grinding energy could be saved 57%, 70%, 78%, and 90%, when wood was torrefied at temperature of 225°C, 250°C, 275°C, and 300°C, respectively.
- Decrease in particle mean size (-36.6% to -81.7%) after grinding was evident in improvement in grindability of torrefied wood.
- Torrefied powder was suitable for combustion purposes as the enhancement in sphericity (8.3% to 29.2%) and surface area (125.2% to 375.6%).
- In addition, fluidization of torrefied wood was improved. As criteria indicating flowability of wood fuels, Geldart classification together with angle of repose expressed that, torrefied wood were grouped in the Geldart A type material: non-cohesive, free-flowing, easy to fluidize group, while, the raw wood fell in the range of Geldart A+C type material: semi-cohesive, poor flowability.
- All tested pelleting characteristics were affected by torrefaction temperature. Cohesiveness property played an important role in compressibility, specific energy required in compression, and initial density of pellets. Torrefied wood, with less cohesiveness characteristics, had a poor compressibility compared to the parent wood, and therefore resulted in higher energy needed to compression and results in lower pellet initial density.
- Regardless of the low compressibility of torrefied wood, its bonding ability was strong and believed to be attributed to the higher lignin percentage of lignin in torrefied products. This resulted in high performance in relaxation behaviors, tensile strength, durability, and water resistance of torrefied wood pellets.

- Torrefied wood appeared a superior in fluidization behaviors by its cohesiveless and flowability, however, in term of compaction characteristic, torrefied wood was found not ideal feedstocks for densification. Adjusting pelleting methods and application of foreign binders may improve the pelleting performance and make combinations of densification and torrefaction more feasible.

CHAPTER 6

RECCOMMENDATIONS AND FUTURE WORKS

The following list of suggestions are complied for future work

- Size distribution of torrefied wood at various torrefaction temperatures was studied and able to be controlled, but particle shape was visually observed to be different. Analysis of particle shapes of torrefied biomass at various temperatures and how this factor affects combustion and pelleting characteristics is needed.
- If adding a foreigner binder to torrefied wood and is studied in future work, the mixing characteristics of water resistant-torrefied wood and water-based binder should be taken into consideration.
- Validity of lignin contribution in torrefaction combined with densification is complex and can be another separate research to experimentally prove the assumption from this study.
- Economical analysis of combining densification and torrefaction is needed to evaluate if the combined processes are efficient and can be scale up to commercial level.

REFERENCES

Abdullah, E.C., Geldart, D. 1999. The use of bulk density measurements as flowability indicators. Powder Technology, 102(2), 151-165.

Alakangas, E., Paju, P. 2002. Wood pellets in Finland–technology, economy, and market. OPET Report, Finland. <www.tekes.fi/opet/pdf/OPET_report5_june2002.pdf> (accessed 08. 28. 06).

Alavi, S., Caussat, B. 2005. Experimental study on fluidization of micronic powders. Powder Technology, 157(1-3), 114-120.

Alén, R., Kuoppala, E., Oesch, P. 1996. Formation of the main degradation compound groups from wood and its components during pyrolysis. Journal of Analytical and Applied Pyrolysis, 36(2), 137-148.

Alizadeh, H., Teymouri, F., Gilbert, T.I., Dale, B.E. 2005. Pretreatment of switchgrass by ammonia fiber explosion (AFEX). Applied Biochemistry and Biotechnology, 124(1), 1133-1141.

Anglès, M.N., Ferrando, F., Farriol, X., Salvadó, J. 2001. Suitability of steam exploded residual softwood for the production of binderless panels. Effect of the pre-treatment severity and lignin addition. Biomass and Bioenergy, 21(3), 211-224.

Arcate, J. 2000. New process for torrefied wood manufacturing. Bioenergy Update, 2(4).

Arias, B., Pevida, C., Fermoso, J., Plaza, M.G., Rubiera, F., Pis, J.J. 2008. Influence of torrefaction on the grindability and reactivity of woody biomass. Fuel Processing Technology, 89(2), 169-175.

ASABE. 1991. ASAE S269.4 Cubes, pellets, and crumbles - definitions and methods for determining density, durability, and moisture content. In: ASABE Standards, 608. St. Joseph, MI.: American Society of Agricultural and Biological Engineers.

ASABE. 2006. ASAE S358.2 Moisture measurement - forages. In: ASABE Standards, 608. St. Joseph, MI.: American Society of Agricultural and Biological Engineers.

ASABE. 2008. ANSI/ASAE S319.4 Method of determining and expressing fineness of feed materials by sieving. In: ASABE Standards, 608. St. Joseph, MI.: American Society of Agricultural and Biological Engineers.

Ashton, S., Cassidy, P. 2007. Wood processing residues. Module 5 Utilization of biomass. Fact sheet 5.1 Sustainable forestry for bioenergy and bio-based products, Athens, GA. Southern forestry research partnership, Inc. pp. 163-165.

ASTM. 2002a. ASTM D5142-04 - Standard test methods for proximate analysis of the analysis sample of coal and coke by instrumental procedures. In: Annual book of ASTM standards, Section 5, Vol. 05.06. West Conshohocken, PA: American Society for Testing and Materials.

ASTM. 2002b. ASTM D3176-89 - Standard practice for ultimate analysis of coal and coke. In: Annual book of ASTM standards, Section 5, Vol. 05.06. West Conshohocken, PA: American Society for Testing and Materials.

ASTM. 2003. ASTM D5865-03 - Standards test methods for gross calorific value of coal and coke. In: Annual Book of ASTM Standards, Vol. 05.06. West Conshohocken, PA.: American Society for Testing and Materials.

Back, E., Salmen, N. 1982. Glass transitions of wood components hold implications for molding and pulping processes. Tappi, 65, 107-110.

Baileys, R.T., Blankenhorn, P.R. 1982. Calorific and porosity development in carbonized wood. Name: Wood Sci.

Balk, W.A. 1964. Energy requirements for dehydrating and pelleting coastal Bermuda grass. Transactions of the ASAE, 4, 349-351.

Barbosa-Cánovas, G.V. 2005. Food powders: physical properties, processing, and functionality. Kluwer Academic/Plenum publishers, New York.

Baxter, L., Koppejan, J. 2004. Co-combustion of biomass and coal. Euroheat and Power, 34, 34-39.

Beall, F.C. 1971. Differential calometric analysis of wood and wood components. Wood Science and Technology, 5(3), 159-175.

Beall, F.C., Eickner, H.W., Forest Products Lab Madison, W.I.S. 1970. Thermal degradation of wood components: a review of the literature, Forest Products Laboratory, Madison, WI.

Berenbaum, R., Brodie, I. 1959. Measurement of the tensile strength of brittle materials. British Journal of Applied Physics, 10, 281-287.

Bergman, P.C.A. 2005. Combined torrefaction and pelletisation. The TOP process. Project no. 2020-02-12-14-001, Energy research Centre of the Netherlands (ECN), ECN Biomass, Utrecht, NL.

Bergman, P.C.A., Boersma, A.R., Kiel, J.H.A., Prins, M.J., Ptasinski, K.J., Janssen, F. 2004. Torrefaction for entrained flow gasification of biomass. In :2nd world conference and technology exhibition on biomass for energy, Industry and Climate protection. Rome, Italy.

Bergman, P.C.A., Boersma, A.R., Zwart, R.W.R., Kiel, J.H.A. 2005. Torrefaction for biomass co-firing in existing coal-fired power stations. BIOCOAL. Project no. 2020-02-12-14-001, Energy research Centre of the Netherlands (ECN), ECN Biomass, Utrecht, NL.

Bergman, P.C.A., Kiel, J.H.A. 2005. Torrefaction for biomass upgrading. In: European biomass conference, Energy research Centre of the Netherlands (ECN), ECN Biomass. Paris, France.

Bergström, D., Israelsson, S., Öhman, M., Dahlqvist, S.-A., Gref, R., Boman, C., Wästerlund, I. 2008. Effects of raw material particle size distribution on the characteristics of Scots pine sawdust fuel pellets. Fuel Processing Technology, 89(12), 1324-1329.

Bernhart, M., Fasina, O.O. 2009. Moisture effect on the storage, handling and flow properties of poultry litter. Waste management, 29(4), 1392-1398.

Bourgois, J., Bartholin, M.C., Guyonnet, R. 1989. Thermal treatment of wood: analysis of the obtained product. Wood Science and Technology, 23(4), 303-310.

Bridgeman, T.G., Jones, J.M., Shield, I., Williams, P.T. 2008. Torrefaction of reed canary grass, wheat straw and willow to enhance solid fuel qualities and combustion properties. Fuel, 87(6), 844-856.

Broese van Groenou, A. 1981. Compaction of ceramic powders. Powder Technology, 28(2), 221-228.

Butler, J.L., McColly, H.F. 1959. Factors affecting the pelleting of hay. Agricultural Engineering, 40 (8), 442–446.

Carpita, N., McCann, M. 2000. The cell wall. Biochemistry and molecular biology of plants, American Society of Plant Physiologists, Rockville, Maryland, pp. 52-108.

Cheremisinoff, N.P. 1980. Wood for energy production. Ann Arbor Science Publishers, Ann Arbor, Michigan.

Chow, S.Z., Pickles, K.J. 1971. Thermal softening and degradation of wood and bark. Wood and Fiber, 3(3), 166-178.

Cooper, A.R., Eaton, L.E. 1962. Compaction behavior of several ceramic powders. Journal of the American Ceramic Society, 45(3), 97-101.

Couhert, C., Salvador, S., Commandré, J.M. 2009. Impact of torrefaction on syngas production from wood. Fuel, 88(11), 2286-2290.

Curtis, L.J., Miller, D.J. 1988. Transport model with radiative heat transfer for rapid cellulose pyrolysis. Industrial & Engineering Chemistry Research, 27(10), 1775-1783.

Damstedt, B., Pederson, J.M., Hansen, D., Knighton, T., Jones, J., Christensen, C., Baxter, L., Tree, D. 2007. Biomass co-firing impacts on flame structure and emissions. In: Proceedings of the Combustion Institute. 31(2), 2813-2820.

Demirbas, A. 2000. Biomass resources for energy and chemical industry. Energy Education Science and Technology, 5(1), 21-45.

Demirbas, A. 2005. Potential applications of renewable energy sources, biomass combustion problems in boiler power systems and combustion related environmental issues. Progress in Energy and Combustion Science, 31(2), 171-192.

Demirbas, A., Meydan, F. 2004. Utilization of biomass as alternative fuel for external combustion engines. Energy Sources, 26(13), 1219-1226.

Demirbas, A., Sahin-Demirbas, A. 2004. Briquetting properties of biomass waste materials. Energy Sources, 26(1), 83-91.

Di Giacomo, G., Taglieri, L. 2009. Renewable energy benefits with conversion of woody residues to pellets. Energy, 34(5), 724-731.

Dinwoodie, J.M. 2000. Timber, its nature and behavior. Taylor & Francis, E & FN Spon, London.

Dobie, J.B. 1959. Engineering appraisal of hay pelleting. Agricultural Engineering, 40(2), 76-72.

Dominik, R., Antti, A., Karsten, R., Inge, S. 2008. Chapter 2. Forest energy resources and potentials: sustainable use of forest biomass for energy. Springer Netherlands, 12, 9-28.

Dutta, A., Dullea, L.V. 1990. A comparative evaluation of negatively and positively charged submicron particles as flow conditioners for a cohesive powder. AIChE Symposium Series, 86(276), 26–40.

Esteban, L.S., Carrasco, J.E. 2006. Evaluation of different strategies for pulverization of forest biomasses. Powder Technology, 166(3), 139-151.

Faborode, M.O., O'Callaghan, J.R. 1987. Optimizing the compression/briquetting of fibrous agricultural materials. Journal of Agricultural Engineering Research, 38(4), 245-262.

FAO. 2001. State of the world's forests-2001, Rome, Italy. <www.fao.org> (accessed 02.01.10).

Felfli, F.F., Luengo, C.A., Suárez, J.A., Beatón, P.A. 2005. Wood briquette torrefaction. Energy for Sustainable Development, 3, 19-22.

Ferro, D.T., Vigouroux, V., Grimm, A., Zanzi, R. 2004. Torrefaction of agricultural and forest residues. In: Cubasolar conference, Department for Research Cooperation: Sida-SAREC and the European Community: ALFA Programme. Guantánamo, Cuba.

Franke, M., Rey, A. 2006. Pelleting quality. World Grain, 78–79.

Freeman, M.C., O'Dowd, W.J., Brown, T.D., Hargis, R.A., James, R.A., Plasynski, S.I., Walbert, G.F., Lowe, A.F., Battista, J.J. 2000. Pilot-scale air toxics R&D assessment of creosotetreated and PCP-treated wood co-firing for pulverized coal utility boiler applications. Biomass and Bioenergy, 19(6), 447-456.

Furnas, C.C. 1931. Grading aggregates-I.-Mathematical relations for beds of broken solids of maximum density. Industrial & Engineering Chemistry, 23(9), 1052-1058.

Geldart, D. 1973. Types of gas fluidization. Powder Technology, 7(5), 285-292.

Geldart, D., Harnby, N., Wong, A.C. 1984. Fluidization of cohesive powders. Powder Technology, 37(1), 25-37.

Gérardin, P., Petric, M., Petrissans, M., Lambert, J., Ehrhrardt, J.J. 2007. Evolution of wood surface free energy after heat treatment. Polymer Degradation and Stability, 92(4), 653-657.

Gevers, P. 2002. Green energy: From wood or torrefied wood? In: Amer 9 unit, Department of chemical engineering and chemistry, Eindhoven University of Technology. Eindhoven, Netherlands.

Ghebre-Sellassie, I. 1989. Mechanism of pellet formation and growth. Pharmaceutical pelletization technology, 123-143.

Gilbert, P., Ryu, C., Sharifi, V., Swithenbank, J. 2009. Effect of process parameters on pelletization of herbaceous crops. Fuel, 88(8), 1491-1497.

Goring, D.A.I. 1963. Thermal softening of lignin, hemicellulose and cellulose. Pulp and Paper Magazine of Canada, 64(12), 517-27.

Granada, E., Lopez Gonzalez, L.M., Míguez, J.L., Moran, J. 2002a. Fuel lignocellulosic briquettes, die design and products study. Renewable Energy, 27(4), 561-573.

Gray, W.A. 1968. Compaction after deposition. In: the packing of solid particles. New York, NY, Marcel Dekker, Inc., pp. 89-107.

Grey, R.O., Beddow, J.K. 1969. On the Hausner Ratio and its relationship to some properties of metal powders. Powder Technology, 2(6), 323-326.

Groesbeck, C.N., McKinney, L.J., DeRouchey, J.M., Tokach, M.D., Goodband, R.D., Dritz, S.S., Nelssen, J.L., Duttlinger, A.W., Fahrenholz, A.C., Behnke, K.C. 2008. Effect of crude glycerol on pellet mill production and nursery pig growth performance. Journal of Animal Science, 86, 2228–2236.

Grønli, M.G. 1996. A theoretical and experimental study of the thermal degradation of biomass, Ph.D. dissertation, Norwegian University of Science and Technology. Trondheim, Norway.

Grover, P.D., Mishra, S.K. 1996. Biomass briquetting: technology and practices. in: Regional wood energy development program in Asia, Vol. 46, Food and Agriculture Organization of the United Nations. Bangkok, Thailand.

Guo, A., Beddow, J.K., Vetter, A.F. 1985. A simple relationship between particle shape effects and density, flow rate and Hausner Ratio. Powder Technology, 43(3), 279-284.

Hakkila, P., Parikka, M. 2002. Chapter 2: Fuel resources from the forest. In: bioenergy from sustainable forestry, Kluwer Academic Publishers. Boston, Massachusetts, pp. 19-48.

Harnby, N., Hawkins, A.E., Vandame, D. 1987. The use of bulk density determination as a means of typifying the flow characteristics of loosely compacted powders under conditions of variable relative humidity. Chemical Engineering Science, 42(4), 879-888.

Hartley, I.D., Wood, L.J. 2008. Hygroscopic properties of densified softwood pellets. Biomass and Bioenergy, 32(1), 90-93.

Hasting, W.H., Vernon, M., Higgs, W.D. 1978. Feed milling processes. in: FAO/UNDP Training course in fish feed technology. Seattle, Washington.

Hatakka, A. 2001. Biodegradation of lignin. Biopolymers, 1, 129-180.

Hausmann, F. 1967. Briquetting wood waste by the Fred Hausmann method. in: Proceedings of 14th biennial briquetting conference. Cape Cod, MA, pp. 75.

Hausner, H.H. 1967. Friction conditions in a mass of metal powder. International Journal of Powder Metallurgy, 3(4), 7-13.

Hausner, H.H. 1972. The role of interparticulate friction in powder technology. in: 1st International conference on compaction and consolidation of particulate matter. London, UK pp. 7-12.

Heffner, L.E., Pfost, H.B. 1973. Gelatinization during pelleting. Feedstuffs, 45, 23-32.

Hill, B., Pulkinen, D.A. 1988. A study of the factors affecting pellet durability and pelleting efficiency in the production of dehydrated alfalfa pellets. A special report, Saskatchewan Dehydrators Association, Tisdale, SK, Canada, 25.

Hilton, J.W., Cho, C.Y., Slinger, S.J. 1981. Effect of extrusion processing and steam pelleting diets on pellet durability, pellet water absorption, and the physiological response of rainbow trout (Salmo gairdneri R.). Aquaculture, 25(2-3), 185-194.

Holm, J.K., Henriksen, U.B., Hustad, J.E., Sorensens, L.H. 2006. Toward an understanding of controlling parameters in softwood and hardwood pellets production. Energy Fuels, 20(6), 2686-2694.

Holm, J.K., Henriksen, U.B., Wand, K., Hustad, J.E., Posselts, D. 2007. Experimental verification of novel pellet model using a single pelleter unit. Energy Fuels, 21(4), 2446-2449.

Hon, D.N.S. 1989. Adhesives from renewable resources. American Chemical Society Symposium Series #385, Washington, D.C.

Humphreys, F.R., Ironside, G.E. 1974. Charcoal from New South Wales species of timber. Forestry Commission of NSW Technology, 23, 41.

IEA. 2009. CO_2 emission from fuel combustion 2009 - Highlights, International Energy Agency, Paris, France. <http://www.iea.org/publications/free_new_Desc.asp?PUBS_ID=2143> (accessed 11.01.2009).

Johnson, T. 2010. Biomass power for utility applications: Southern Company's Experience, Southern Company. Georgia.

Kaliyan, N., Vance Morey, R. 2009. Factors affecting strength and durability of densified biomass products. Biomass and Bioenergy, 33(3), 337-359.

Kastberg, S., Nilsson, C. 2000. Combustion optimization study of biomass powder. in: Proceedings of 1st world conference on biomass for energy and industry. Seville, Spain, pp. 890-892.

Kerr, A.J., Goring, D.A.I. 1975. Ultrastructural arrangement of the wood cell wall. Cellulose Chemistry Technology, 9, 563-73.

Kiel, J.H.A., Verhoeff, F., Gerhauser, H., Meuleman, B. 2008. BO_2-technology for biomass upgrading into solid fuel-pilot-scale testing and market implementation. In: 16th European biomass conference & exhibition. Valencia, Spain, pp. 2-6.

Kocaefe, D., Poncsak, S., Doré, G., Younsi, R. 2008a. Effect of heat treatment on the wetability of white ash and soft maple by water. European Journal of Wood and Wood Products, 66(5), 355-361.

Kollmann, F., Fengel, D. 1965. Changes in the chemical composition of wood by thermal treatment. Holz Roh Werkst, 12, 461-468.

Köser, H.J.K., Schmalstieg, G., Siemers, W. 1982. Densification of water hyacinth—basic data. Fuel, 61(9), 791-798.

Koufopanos, C.A., Papayannakos, N., Maschio, G., Lucchesi, A. 2009. Modelling of the pyrolysis of biomass particles. Studies on kinetics, thermal and heat transfer effects. The Canadian journal of chemical engineering, 69(4), 907-915.

Lam, P.S., Sokhansanj, S., Lim, J.C., Bi, X.T., Sowlati, T., Mani, S., Melin, S. 2009. Steam treated sawdust pelleting and systems energetic. In: ASAE Paper no: 096648, ASABE. St. Joseph, MI.

Larfeldt, J., Leckner, B., Melaaen, M.C. 2000. Modeling and measurements of the pyrolysis of large wood particles. Fuel, 79(13), 1637-1643.

Lehtikangas, P. 1999. Quality properties of fuel pellets from forest biomass, Ph.D. dissertation, The Swedish University of Agricultural Sciences. Uppsala, Sweden.

Lehtikangas, P. 2000. Storage effects on pelletised sawdust, logging residues and bark. Biomass and Bioenergy, 19(5), 287-293.

Lehtikangas, P. 2001. Quality properties of pelletised sawdust, logging residues and bark. Biomass and Bioenergy, 20(5), 351-360.

Leuenberger, H. 1982. The compressibility and compactibility of powder systems. International Journal of Pharmaceutics, 12(1), 41-55.

Leuenberger, H., Rohera, B.D. 1986. Fundamentals of powder compression. I. The compactibility and compressibility of pharmaceutical powders. Pharmaceutical Research, 3(1), 12-22.

Li, J., Gifford, J. 2001. Evaluation of Woody Biomass Torrefaction. Forest Research, Rotorua, New Zealand.

Li, Q., Rudolph, V., Weigl, B., Earl, A. 2004. Interparticle van der Waals force in powder flowability and compactibility. International journal of pharmaceutics, 280(1-2), 77-93.

Li, Y., Liu, H. 2000. High-pressure densification of wood residues to form an upgraded fuel. Biomass and Bioenergy, 19(3), 177-186.

Lipinsky, E.S., Arcate, J.R., Reed, T.B. 2002. Enhanced wood fuels via torrefaction. Fuel Chemistry Division Preprints, 47(1).

Lu, H., Ip, E., Scott, J., Foster, P., Vickers, M., Baxter, L.L. 2008. Effects of particle shape and size on devolatilization of biomass particle. Fuel, 89(5), 1156-1168.

MacBain, R. 1984. Pelleting animal feed. American Feed Manufacturer's Association, Arlington, Virginia.

Mackay, D.M., Roberts, P.V. 1982. The dependence of char and carbon yield on lignocellulosic precursor composition. Carbon, 20(2), 87-94.

Mani, S. 2009. Integrating biomass torrefaction with thermo-chemical conversion processes. In: Proceedings of the 2009 AIChE Annual meeting. Paper No 160229. Nashville, TN.

Mani, S., Tabil, L.G., Sokhansanj, S. 2006. Effects of compressive force, particle size and moisture content on mechanical properties of biomass pellets from grasses. Biomass & Bioenergy, 30(7), 648-654.

Mani, S., Tabil, L.G., Sokhansanj, S. 2004a. Evaluation of compaction equations applied to four biomass species. Canadian Biosystems Engineering, 46(3), 3.55-3.61.

Mani, S., Tabil, L.G., Sokhansanj, S. 2004b. Grinding performance and physical properties of wheat and barley straws, corn stover and switchgrass. Biomass and Bioenergy, 27(4), 339-352.

Mani, S., Tabil, L.G., Sokhansanj, S. 2003. An overview of compaction of biomass grinds. Powder Handling and Processing, 15(3), 160-168.

Mansouri, N.E.E., Salvadó, J. 2006. Structural characterization of technical lignins for the production of adhesives: application to lignosulfonate, kraft, soda-anthraquinone, organosolv and ethanol process lignins. Industrial Crops & Products, 24(1), 8-16.

Meier, D., Faix, O. 1999. State of the art of applied fast pyrolysis of lignocellulosic materials-A review. Bioresource Technology, 68(1), 71-78.

Miles, T.R., Miles Jr, T.R. 1980. Densification systems for agricultural residues. In: Thermal conversion of solid wastes and biomass. American Chemical Society. Washington DC, pp. 179-191.

Millard, D.J. 1959. Relationship between strength and porosity for coal compacts. British Journal of Applied Physics, 10, 287-290.

Mohsenin, N., Zaske, J. 1976. Stress relaxation and energy requirements in compaction of unconsolidated materials. Journal of Agricultural Engineering Research, 21(2), 193-205.

Moreyra, R., Peleg, M. 1980. Compressive deformation patterns of selected food powders. Journal of Food Science, 45(4), 864-868.

Narayanan, K.V., Natarajan, E. 2007. Experimental studies on co-firing of coal and biomass blends in India. Renewable Energy, 32(15), 2548-2558.

Ndiema, C.K.W., Manga, P.N., Ruttoh, C.R. 2002. Influence of die pressure on relaxation characteristics of briquetted biomass. Energy Conversion and Management, 43(16), 2157-2161.

Nevalainen, H., Jegoroff, M., Saastamoinen, J., Tourunen, A., Jäntti, T., Kettunen, A., Johnsson, F., Niklasson, F. 2007. Firing of coal and biomass and their mixtures in 50 kW and 12

MW circulating fluidized beds-Phenomenon study and comparison of scales. Fuel, 86(14), 2043-2051.

Newitt, P.D.M., Conway-Jones, J.M. 1958. A contribution to the theory and practice of granulation. Chemical Engineering Research and Design, 36(a), 422-442.

Nimlos, M.N., Looker, E., Evans, R.J. 2003. Biomass torrefaction studies with a molecular beam mass spectrometer, Vol. 48, American Chemical Society, Division of Fuel Chemistry Preprints, pp. 590.

Nunes, A.P., Pourquie, J. 1996. Steam explosion pretreatment and enzymatic hydrolysis of eucalyptus wood. Bioresource Technology, 57(2), 107-110.

Obernberger, I., Thek, G. 2004. Physical characterisation and chemical composition of densified biomass fuels with regard to their combustion behaviour. Biomass and Bioenergy, 27(6), 653-669.

Ollet, A.L., Kirby, A.R., Parker, R., Smith, A.C. 1993. A comparative study of the effects of water content on the compaction behaviour of some food materials. Powder Technology, 75(1), 59-65.

Orth, H.W., Löwe, R. 1977. Influence of temperature on wafering in a continuous extrusion process. Journal of Agricultural Engineering Research, 22(3), 283-289.

Ouwens, C.D., Küpers, G. 2003. Lowering the Cost of Large-Scale, Biomass Based Production of Fischer-Tropsch Liquids. 2003. Jyväskylä, Finland: Eindhoven University of Technology.

Pach, M., Zanzi, R., Björnbom, E. 2002. Torrefied biomass as substitute for wood and charcoal. In: sixth Asia-Pacific international symposium on combustion and energy utilization, Kuala Lumpur. pp. 285-290.

Parikka, M. 2004. Global biomass fuel resources. Biomass and Bioenergy, 27(6), 613-620.

Payne, J.D. 1978. Improving quality of pellets feeds. Milling Feed and Fertiliser, 162(5), 34-41.

Peleg, M., Mannheim, C.H. 1973. Effect of conditioners on the flow properties of powdered sucrose. Powder Technology, 7(1), 45-50.

Peleg, M., Moreyra, R. 1979. Effect of moisture on the stress relaxation pattern of compacted powders. Powder Technology, 23(2), 277-279.

Pentananunt, R., Rahman, A., Bhattacharya, S.C. 1990. Upgrading of biomass by means of torrefaction. Energy, 15(12), 1175-1179.

Pérez, J., Munoz-Dorado, J., De la Rubia, T., Martínez, J. 2002. Biodegradation and biological treatments of cellulose, hemicellulose and lignin: an overview. International Microbiology, 5(2), 53-63.

Perlack, R.D., Wright, L.L., Turhollow, A.F., Graham, R.L., Stokes, B.J., Erbach, D.C. 2005. Biomass as feedstock for a bioenergy and bioproducts industry: the technical feasibility of a billion-ton annual supply. Oak Ridge National Lab, Tennessee.

Persson, K., Olofsson, I., Nordin, A. 2007. Biomass Refinement by Torrefaction, Energy Technology and Thermal Process Chemistry, Umeå University. Umeå, Sweden.

PFI. 2010. Pellet Fuel Institute, Arlington, Virginia. <www.pelletheat.org> (accessed 9.28.09).

Pietsch, W. 1991. Size enlargement by agglomeration. John Wiley & Sons.

Pimchuai, A., Dutta, A., Basu, P. 2010. Torrefaction of agriculture residue to enhance combustible properties. Energy & Fuels, 3458-3470.

Pizzi, A., Mittal, K.L. 2003. Handbook of adhesive technology, Marcel Dekker Inc New York.

Prins, M.J., Ptasinski, K.J., Janssen, F. 2006. More efficient biomass gasification via torrefaction. Energy, 31(15), 3458-3470.

Pyle, O. 1976. Process for producing solid industrial fuel. In: US patent no. 3,938,965,1976.

Rastogi, S., Dhodapkar, S.V., Cabrejos, F., Baker, J., Weintraub, M., Klinzing, G.E., Yang, W.C. 1993. Survey of characterization techniques of dry ultrafine coals and their relationships to transport, handling and storage. Powder Technology, 74(1), 47-59.

Raveendran, K., Ganesh, A. 1998. Adsorption characteristics and pore-development of biomass-pyrolysis char. Fuel, 77(7), 769-781.

Raveendran, K., Ganesh, A., Khilar, K.C. 1996. Pyrolysis characteristics of biomass and biomass components. Fuel, 75(8), 987-998.

Reed, T., Byrant, B. 1978. Densified biomass: a new form of solid fuel. SERI-35, Solar Energy Research Institution, Golden, CO.

Reed, T.B. 2002. Process and apparatus for making a densified torrefied fuel. In: US patent no. 2003/0221363 A1.

Reed, T.B., Trezek, G., Diaz, L. 1980. Biomass densification energy requirements. In: Thermal conversion of solid wastes and biomass. American Chemistry Society. Washington DC. pp. 169-177.

Repellin, V., Govin, A., Rolland, M., Guyonnet, R. 2010. Energy requirement for fine grinding of torrefied wood. Biomass and Bioenergy, 34(7), 923-930.

Rhen, C., Gref, R., Sjöström, M., Wästerlund, I. 2005. Effects of raw material moisture content, densification pressure and temperature on some properties of Norway spruce pellets. Fuel Processing Technology, 87(1), 11-16.

Rhén, C., Öhman, M., Gref, R., Wästerlund, I. 2007. Effect of raw material composition in woody biomass pellets on combustion characteristics. Biomass and Bioenergy, 31(1), 66-72.

Ritchie, R.W. 2004. Wood Pellet Handbook and Buyer's Guide, Ralph Ritchie Press. Springfield, Oregon.

Roberts, A.F., Clough, G. 1963. Thermal decomposition of wood in an inert atmosphere. Elsevier. pp. 158-166.

Rowell, R., Lange, S., Davis, M. 2000. Steam stabilization of aspen fiberboards. pp. 425-438.

Rowell, R.M., Banks, W.B. 1985. Water repellency and dimensional stability of wood. USDA Forest Service General Technical Report FPL 50.

Rowell, R.M., Susott, R.A., DeGroot, W.F., Shafizadeh, F. 1984. Bonding fire retardants to wood. Part I. Thermal behavior of chemical bonding agents. Wood and Fiber Science, 16(2), 214-223.

Rudnick, A., Hunter, A.R., Holden, F.C. 1963. An analysis of the diametral-compression test. Material Research & Standards, 3, 283-289.

Rumpf, H. 1962. The strength of granules and agglomerates. In: Agglomeration, (Ed.) Knepper WA, John Wiley. New York, pp. 379–418.

Runkel, R.O.H. 1951. Zur Kenntnis des thermoplastischen Verhaltens von Holz. European Journal of Wood and Wood Products, 9(2), 41-53.

Saastamoinen, J., Aho, M., Moilanen, A., Sørensen, L.H., Clausen, S., Berg, M. 2010. Burnout of pulverized biomass particles in large scale boiler-Single particle model approach. Biomass and Bioenergy, 34(5), 728-736.

Sanderman, W., Augustin, H. 1963. Chemical investigations on the thermal decomposition of wood. Part I: Stand of research. Holz Als Roh-Und Werkstoff, 21, 256-265.

Schell, D.J., Harwood, C. 1994. Milling of lignocellulosic biomass. Applied Biochemistry and Biotechnology, 45(1), 159-168.

Seville, J.P.K., Willett, C.D., Knight, P.C. 2000. Interparticle forces in fluidization: a review. Powder Technology, 113(3), 261-268.

Shafizadeh, F. 1978. Combustion, combustibility, and heat release of forest fuels. AIChE Symposium Series, 177(74), 76-82.

Sharma, R.K., Wooten, J.B., Baliga, V.L., Martoglio-Smith, P.A., Hajaligol, M.R. 2002. Characterization of Char from the Pyrolysis of Tobacco. Journal of Agricultural and Food Chemistry, 50(4), 771-783.

Shaw, M.D. 2008. Feedstock and process variables influencing biomass densification, MS. dissertation, Department of Agricultural and Bioresource Engineering, University of Saskatchewan Saskatoon, Saskatchewan.

Shaw, M.D., Karunakaran, C., Tabil, L.G. 2009. Physicochemical characteristics of densified untreated and steam exploded poplar wood and wheat straw grinds. Biosystems Engineering, 103(2), 198-207.

Shaw, M.D., Tabil, L.G. 2007. Compression and relaxation characteristics of selected biomass grinds. in: ASAE paper no. 076183. Minneapolis, MN. ASAE, 2950 Niles Road, St. Joseph, MI.

Shepperson, G., Marchant, W.T.B. 1978. Production of grass and alfalfa cubes using an experimental ring die press. In: Proceedings 2nd International Green Crop Drying Conference. Saskatoon, SK, pp. 264–270.

Shotton, E., Ridgway, K. 1974. Physical pharmaceutics. Clarendon Press.

Silverstein, R.M., Bassler, G.C., Morrill, T.C. 1991. Spectrometric identification of organic compounds. Wiley, New York.

Sitkel, G. 1986. Mechanics of agricultural materials. Elsevier Science Publisher Co. Inc., New York.

Smith, I.E., Probert, S.D., Stokes, R.E., Hansford, R.J. 1977. The briquetting of wheat straw. Journal of Agricultural Engineering Research, 22(2), 105-111.

Smith, W.B. 2004. Forest resources of the United States: 2002. North Central Forest Experiment Station, Forest Service, US Department of Agriculture.

Smith, W.B., Vissage, J.S., Darr, D.R., Sheffield, R.M. 2001. Forest resources of the United States, 1997. USDA Forest Service North Central Research Station.

Sokhansanj, S., Mani, S., Bi, X., Zaini, P., Tabil, L. 2005. Binderless pelletization of biomass. In: ASAE paper no. 056061, ASABE. St. Joseph, MI.

Sokhonsanj, S., Crerar, W. 1999. Development of a durability tester for pelleted and cubed animal feed. SAE Technical Paper Series–1999-01-2830. Society of Automotive Engineers Inc., Warrendale, PA.

Sonja, N.O., Mike, T., Smith, W.B. 2010. The National Report on Sustainable Forests–2010. U.S. Forest resource facts and historical trends. United States Department of Agriculture. Washington, D.C. .

Srivastava, A.C., Bilanski, W.K., Graham, V.A. 1981. Feasibility of producing large-size hay wafers. Canadian Agricultural Engineering, 23(2), 109-112.

Stamm, A.J. 1956. Thermal degradation of wood and cellulose. Industrial & Engineering Chemistry, 48(3), 413-417.

Stamm, A.J. 1964. Wood and cellulose science. The Ronald Press Co., New York.

Stamm, A.J., Harris, E.E. 1953. Chemical processing of wood. Soil Science, 76(2), 165.

Svarovsky, L. 1987. Powder testing guide: methods of measuring the physical properties of bulk powders. The British Materials Handling Board by Elsevier Applied Science, London and New York.

Tabil, L., Sokhansanj, S. 1996a. Process conditions affecting the physical quality of alfalfa pellets. Applied Engineering in Agriculture, 12(3), 345-350.

Tabil, L.G., Sokhansanj, S. 1996b. Compression and compaction behavior of alfalfa grinds - part 1: compression behavior. Powder Handling & Processing, 8(1), 17-23.

Thomas, M., van der Poel, A.F.B. 1996. Physical quality of pelleted animal feed 1. Criteria for pellet quality. Animal Feed Science and Technology, 61(1-4), 89-112.

Thomas, M., van Zuilichem, D.J., van der Poel, A.F.B. 1997. Physical quality of pelleted animal feed. 2. contribution of processes and its conditions. Animal Feed Science and Technology, 64(2-4), 173-192.

Thomas, P.H., Bowes, P.C. 1961. Some aspects of the self-heating and ignition of solid cellulosic materials. British Journal of Applied Physics, 12, 222-229.

Timoshenko, S.P., Goodier. JN. 1951. Theory of elasticity. Mc Graw-Hill, New York.

Tjeerdsma, B.F., Boonstra, M., Pizzi, A., Tekely, P., Militz, H. 1998. Characterisation of thermally modified wood: molecular reasons for wood performance improvement. European Journal of Wood and Wood Products, 56(3), 149-153.

Turner, R. 1995. Bottomline in feed processing: Achieving optimum pellet quality. Feed Management, 46, 30-33.

Uslu, A., Faaij, A.P.C., Bergman, P.C.A. 2008. Pre-treatment technologies, and their effect on international bioenergy supply chain logistics. Techno-economic evaluation of torrefaction, fast pyrolysis and pelletisation. Energy, 33(8), 1206-1223.

Van Loo, S., Koppejan, J. 2008. The handbook of biomass combustion and co-firing. Earthscan/James & James.

Van Soest, P.J., Robertson, J.B. 1980. Systems of analysis for evaluating fibrous feeds. Standardization of analytical methodology for feeds (ed. WJ Pigden, CC Balch and M. Graham), 49-60.

Varhegyi, G., Antal, M.J. 1997. Kinetic modeling of biomass pyrolysis* 1. Journal of Analytical and Applied Pyrolysis, 42(1), 73-87.

Vernois, M. 2000. Heat treatment of wood in France-state of the art. Centre Technique du Bois et de l'Ameublement.

Vesterinen, P., Alakangas, E. 2001. Export & import possibilities and fuel prices of biomass in 20 European countries-Task 2. AFB network, VTT Energy.

Walsh, M. 2008. US cellulosic biomass feedstock supplies and distribution, M & E Biomass, University of Tennessee.

White, R.H. 1987. Effect of lignin content and extractives on the higher heating value of wood. Wood and fiber science, 19(4), 446-452.

Williams, P.T., Besler, S. 1993. Thermogravimetric analysis of the components of biomass. Advances in thermochemical biomass conversion, 2, 771-783.

Winowiski, T. 1985. Optimizing pelleting temperature. Feed Management, 36, 28–33.

Wong, A.C.-Y. 2002. Use of angle of repose and bulk densities for powder characterization and the prediction of minimum fluidization and minimum bubbling velocities. Chemical Engineering Science, 57(14), 2635-2640.

Wong, C.Y. 2000. Characterization of the flowability of glass beads by bulk densities ratio. Chemical Engineering Science, 55(18), 3855-3859.

Wood, S.M., Layzell, D.B. 2003. A Canadian biomass inventory: Feedstocks for a biobased economy. Canadian BIOCAP Foundation.

Wouters, I.M.F., Geldart, D. 2004. Characterizing semi-cohesive powders using angle of repose. Particle & Particle Systems Characterization, 13(4), 254-259.

Xiumin, J., Chuguang, Z., Che, Y., Dechang, L., Jianrong, Q., Jubin, L. 2002. Physical structure and combustion properties of super fine pulverized coal particle. Fuel, 81(6), 793-797.

Yaman, S. 2004. Pyrolysis of biomass to produce fuels and chemical feedstocks. Energy Conversion and Management, 45(5), 651-671.

Yang, H., Yan, R., Chen, H., Lee, D.H., Zheng, C. 2007. Characteristics of hemicellulose, cellulose and lignin pyrolysis. Fuel, 86(12-13), 1781-1788.

Yang, H., Yan, R., Chin, T., Liang, D.T., Chen, H., Zheng, C. 2004. Thermogravimetric Analysis- Fourier Transform Infrared Analysis of Palm Oil Waste Pyrolysis. Energy Fuels, 18(6), 1814-1821.

Yerazunis, S., Bartlett, J.W., Nissan, A.H. 1962. Packing of binary mixtures of spheres and irregular particles. Nature, 195, 33-35.

Yu, A.B., Standish, N., Lu, L. 1995. Coal agglomeration and its effect on bulk density. Powder Technology, 82(2), 177-189.

Yvan, S. 1985. Process for converting ligneous matter of vegetable origin by torrefaction, and product obtained thereby. In: US patent no. 4,553,978.

Zandersons, J., Gravitis, J., Zhurinsh, A., Kokorevics, A., Kallavus, U., Suzuki, C.K. 2004. Carbon materials obtained from self-binding sugar cane bagasse and deciduous wood residues plastics. Biomass and Bioenergy, 26(4), 345-360.

Zanzi, R., Ferro, D.T., Torres, A., Soler, P.B., Björnbom, E. 2004. Biomass torrefaction. In: 2nd world conference and technology exhibition on biomass for energy, industry and climate protection. Rome, Italy, pp. 859–62.

APPENDIX A - STRUCTURAL AND FUNCTIONAL CHARACTERIZATION

A1: SEM study

A study in changes of wood cell wall after exploded to torrefaction was observed on the surface morphology of the torrefied pine chips using scanning electron microscope (SEM Inspect F, FEI Company, OR). First, torrefied wood chips at various temperatures, including the untreated sample (225ºC, 250ºC, 275ºC, and 300ºC) were cut cross-sectional by an electric saw into approximately 1cm x 1cm pieces. The wood pieces were then attached on top of the holders using a conductive tape as a connector. Then they were gold-palladium coated using the SPI-Module sputter coater for 60 s under 2 Mbar argon pressure and 15 mA DC to enhance the electrical conductivity of the wood samples. The coated samples were then examined and imaged using the SEM. The images were taken from the top surface view (at low magnification of 100) and the cell wall close up perspective (at high magnification of 2,000 and 8,000). Individual cell wall images were taken at three different locations on the piece of wood.

The results of the SEM images of cut wood in Figure A1 showed that untreated samples experienced the most difficulty in grinding as shown in the apparent fibrous and tenacious structure. This was explained by the fact that untreated sample only loses water during physical drying; therefore, cell wall components still remained undamaged (Lipinsky et al., 2002). Torrefied wood, on the other hand, became less splinter structure. The splinter characteristic was observed to diminish with the increase of torrefaction temperature. This indicates the ease in grinding after torrefaction process. It should be noted that, obtained torrefied chips at various temperature had fairly similar chip average size with original. Similarly, the size of the wood cell wall (perimeter) from the SEM images was observed to not significantly change. The finding was in agreement with Baileys & Blankenhorn (1982) as they claimed that wood shrinkage began above 300ºC. Furthermore, Curtis & Miller (1988) reported the solid char only became porous but still retained its original shape during pyrolysis. At the observed maximum torrefaction temperature (300ºC), torrefied wood clearly showed no fibrous structure, and the gap within a cell wall was solid. It should be noted that, though pores of the solid wood are believed to be enlarged (Koufopanos et al., 2009), the results from SEM can not reveal the claim.

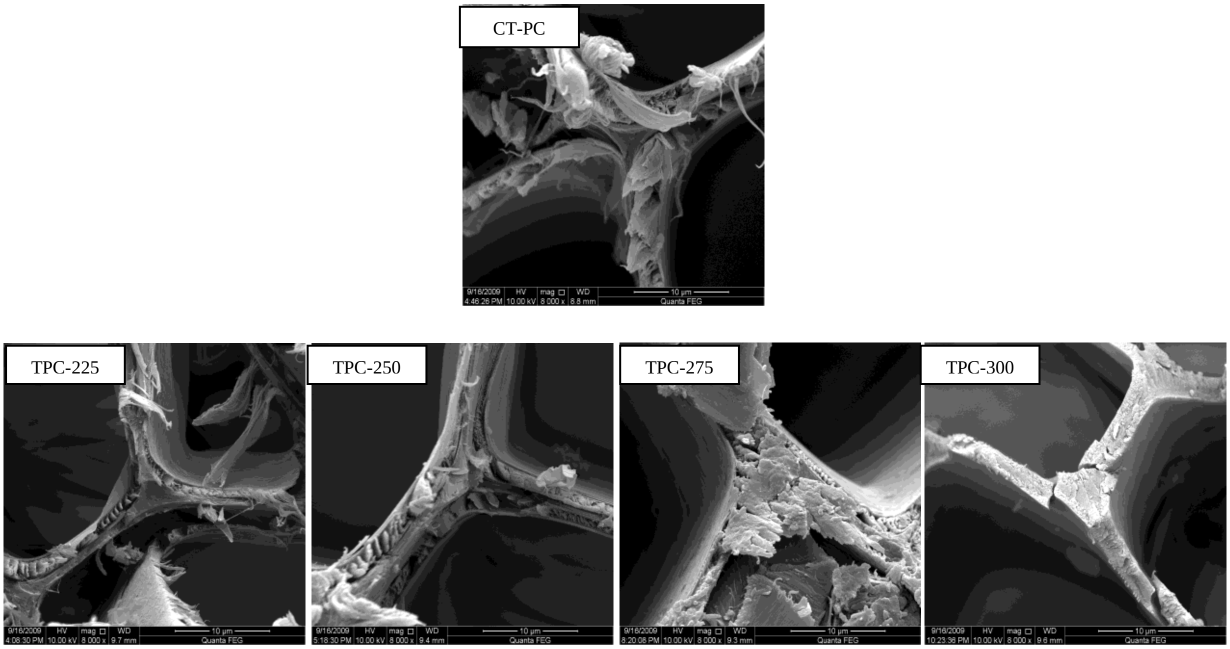

Figure A.1: The SEM images of destructive structure of wood cell wall at various torrefaction temperatures after size reduction procedure.

A2: FT-IR study

FT-IR (Fourier transform infrared spectroscopy) imaging was introduced to support the hygroscopic property investigation of torrefied wood. The analysis utilizes the infrared regions of the electromagnetic spectrum, particularly to examine differences in the chemical structure of untreated and pretreated feedstocks. Approximately 10 mg of biomass grinds (CT-, T-225, T-250, T-275, and T-300) was homogeneously milled to mix with 190 mg of potassium bromide. The diffuse reflectance (DRIFT) spectrum mode was selected to express the infrared absorption of the wood at various studied temperatures, recorded as Kubelka-Munck transformed spectra against KBr background.

The spectral changes of heated woods are observed from the reduction of the hydroxyl absorptions. In all cases examined, wood hydroxyl absorbed in the range of 2700 to 3800 cm^{-1} (Silverstein et al., 1991). The Figure A2 shows that hydroxyl groups decrease with increase of torrefaction temperature, compared to the untreated wood. However, beyond torrefaction temperature of 250ºC over the wave number of 3100 to 3700; the change does not markedly vary. This result is analogous to those of Bourgois (1989) who studied the torrefied pine sawdust in the range of 240-290ºC, 30 min residence time. They found that improve in water resistance was greatly only in the initial stages of pyrolytic process, but the development in hydrophobic character was minimal when temperature was raised. However, the author did not mention a clear cut off temperature.

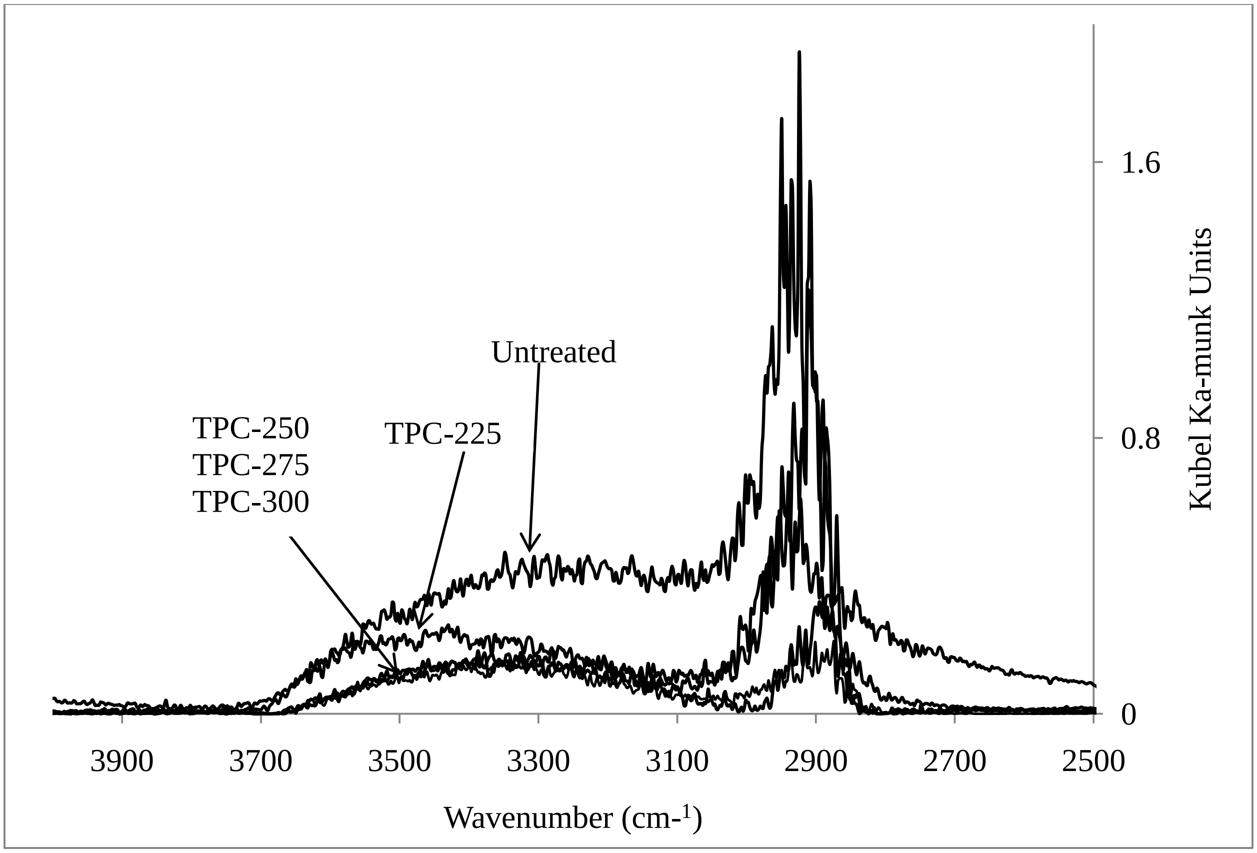

Figure A.2: The diffuse reflectance (DRIFTS) spectrum of torrefied wood pellets. The sample was diluted in 5% in KBr.

APPENDIX B – ANOVA TABLES

Table B1.1: Analysis of variance (ANOVA) table for factors affecting the specific energy required for compression of pellets (MJ/t).

Source	df	SS	MS	F-value	Probability
Intercept	1	416539.30	416539.30	1915.54	<.0001
Torrefied temperature *(T)*	3	14987.03	4995.68	13065.30	<.0001
Moisture content *(M)*	2	6224.71	3112.35	8139.83	<.0001
Compressive force *(F)*	2	16837.18	8418.59	22017.40	<.0001
*T*M*	6	284.51	47.42	124.01	<.0001
*T*F*	6	340.68	56.78	148.50	<.0001
*M*F*	4	184.99	46.25	120.95	<.0001
*T*M*F*	12	9.90	0.82	2.16	0.0168
Error	144	55.06	0.38		
Total	180	455463.36			

Table B1.2: Effect of torrefaction temperature, moisture content, and compressive force on the specific energy required for compression pellets.

Torrefaction temperature (Cº)	Specific energy required for compression of pellets (MJ/t)
22	36.07^{D}
225	44.10^{C}
250	51.46^{B}
275	60.79^{A}
Moisture content (%wb)	Specific energy required for compression of pellets (MJ/t)
3.5	55.89^{A}
7	46.74^{B}
10.5	41.68^{C}
Compressive force (kN)	Specific energy required for compression of pellets (MJ/t)
8	36.27^{C}
13	48.09^{B}
18	59.96^{A}

Means with the same letters are not significantly different at 5% level.

Table B2.1: Analysis of variance (ANOVA) table for factors affecting the initial density of pellet.

Source	df	SS	MS	F-value	Probability
Intercept	1	625536447.80	625536447.80	94537.80	<.0001
Torrefied temperature *(T)*	3	1325705.00	441901.60	17810.40	<.0001
Moisture content *(M)*	2	1546906.00	773452.90	31173.20	<.0001
Compressive force *(F)*	2	55149.15	27574.58	1111.37	<.0001
*T*M*	6	237355.10	39559.19	1594.39	<.0001
*T*F*	6	16746.46	2791.08	112.49	<.0001
*M*F*	4	104956.00	26239.01	1057.54	<.0001
*T*M*F*	12	18499.97	1541.66	62.14	<.0001
Error	489	12132.80	24.81		
Total	525	628853898.28			

Table B2.2: Effect of torrefaction temperature, moisture content, and compressive force on the initial pellet density (kg/m3).

Torrefaction temperature (Cº)	Initial pellet density (kg/m3)
22	1150^{A}
225	1124^{B}
250	1088^{C}
275	1011^{D}
Moisture content (%wb)	Initial pellet density (kg/m3)
3.5	1127^{A}
7	1107^{B}
10.5	992^{C}
Compressive force (kN)	Initial pellet density (kg/m3)
8	1065^{C}
13	1104^{B}
18	1105^{A}

Means with the same letters are not significantly different at 5% level.

Table B3.1: Analysis of variance (ANOVA) table for factors affecting the relaxed density of pellets.

Source	df	SS	MS	F-value	Probability
Intercept	1	196213535.50	196213535.50	39822.90	<.0001
Torrefied temperature *(T)*	3	293575.47	97858.49	9686.39	<.0001
Moisture content *(M)*	2	352159.03	176079.51	17429.00	<.0001
Compressive force *(F)*	2	31267.50	15633.75	1547.49	<.0001
*T*M*	6	161726.89	26954.48	2668.05	<.0001
*T*F*	6	7016.04	1169.34	115.75	<.0001
*M*F*	4	20331.77	5082.94	503.13	<.0001
*T*M*F*	12	11284.13	940.34	93.08	<.0001
Error	143	1444.68	10.10		
Total	179	197092341.01			

Table 3.2: Effect of torrefaction temperature, moisture content, and compressive force on the relaxed density of pellets (kg/m^3).

Torrefaction temperature (Cº)	Relaxed density of pellets (kg/m3)
22	1091^{A}
225	1067^{B}
250	1049^{C}
275	981^{D}
Moisture content (%wb)	Relaxed density of pellets (kg/m3)
3.5	1065^{B}
7	1089^{A}
10.5	986^{C}
Compressive force (kN)	Relaxed density of pellets (kg/m3)
8	1028^{B}
13	1057^{A}
18	1057^{A}

Means with the same letters are not significantly different at 5% level.

Table B4.1: Analysis of variance (ANOVA) table for factors affecting the longitudinal expansion of pellets (%).

Source	df	SS	MS	F-value	Probability
Intercept	1	2312.14	2312.14	203.57	<.0001
Torrefied temperature *(T)*	3	396.93	132.31	607.56	<.0001
Moisture content *(M)*	2	2578.73	1289.37	5920.68	<.0001
Compressive force *(F)*	2	1.25	0.62	2.87	0.0585
*T*M*	6	466.71	77.78	357.18	<.0001
*T*F*	6	6.89	1.15	5.27	<.0001
*M*F*	4	3.46	0.87	3.97	0.0038
*T*M*F*	12	20.26	1.69	7.75	<.0001
Error	257	55.97	0.22		
Total	293	5842.34			

Table B4.2: Effect of torrefaction temperature, moisture content, and compressive force on the longitudinal expansion of pellets.

Torrefaction temperature (Cº)	Longitudinal expansion of pellets (%)
22	4.91^{A}
225	3.04^{B}
250	1.92^{C}
275	1.92^{C}

Moisture content (%wb)	Longitudinal expansion of pellets (%)
3.5	5.32^{A}
7	1.16^{B}
10.5	-1.00^{C}

Compressive force (kN)	Longitudinal expansion of pellets (%)
8	2.66^{B}
13	3.02^{A}
18	2.72^{B}

Means with the same letters are not significantly different at 5% level.

Table B5.1: Analysis of variance (ANOVA) table for factors affecting the diametral expansion of pellets (%).

Source	df	SS	MS	F-value	Probability
Intercept	1	75.93	75.93	270.53	<.0001
Torrefied temperature *(T)*	3	8.80	2.93	216.05	<.0001
Moisture content *(M)*	2	32.78	16.39	1207.30	<.0001
Compressive force *(F)*	2	0.24	0.12	8.84	0.0002
*T*M*	6	2.74	0.46	33.64	<.0001
*T*F*	6	1.48	0.25	18.22	<.0001
*M*F*	4	6.44	1.61	118.59	<.0001
*T*M*F*	12	3.27	0.27	20.09	<.0001
Error	169	2.29	0.01		
Total	205	133.97			

Table B5.2: Effect of torrefaction temperature, moisture content, and compressive force on the diametral expansion of pellets (%)

Torrefaction temperature (Cº)	Diametral expansion of pellets (%)
22	0.93^{A}
225	0.57^{B}
250	0.42^{D}
275	0.50^{C}

Moisture content (%wb)	Diametral expansion of pellets (%)
3.5	1.16^{A}
7	0.55^{B}
10.5	0.17^{C}

Compressive force (kN)	Diametral expansion of pellets (%)
8	0.59^{B}
13	0.58^{B}
18	0.66^{A}

Means with the same letters are not significantly different at 5% level.

Table B6.1: Analysis of variance (ANOVA) table for factors affecting the tensile strength of pellets.

Source	df	SS	MS	F-value	Probability
Intercept	1	868.68	868.68	1068.85	<.0001
Torrefied temperature *(T)*	3	60.48	20.15	410.27	<.0001
Moisture content *(M)*	2	32.73	16.36	333.10	<.0001
Compressive force *(F)*	2	2.25	1.12	22.94	<.0001
*T*M*	6	35.64	5.93	120.88	<.0001
*T*F*	6	1.09	0.18	3.71	0.0019
*M*F*	4	2.10	0.53	10.69	<.0001
*T*M*F*	12	3.43	0.29	5.81	<.0001
Error	138	6.78	0.05		
Total	174	1013.18			

Table B6.2: Effect of torrefaction temperature, moisture content, and compressive force on the tensile strength of pellets (MPa)

Torrefaction temperature (Cº)	Tensile strength of pellets (MPa)
22	1.50^{D}
225	1.90^{C}
250	2.98^{A}
275	2.54^{B}
Moisture content (%wb)	Tensile strength of pellets (MPa)
3.5	2.39^{B}
7	2.62^{A}
10.5	1.65^{C}
Compressive force (kN)	Tensile strength of pellets (MPa)
8	2.06^{B}
13	2.30^{A}
18	2.35^{A}

Means with the same letters are not significantly different at 5% level.

Table B7.1: Analysis of variance (ANOVA) table for factors affecting the durability of pellets (%).

Source	df	SS	MS	F-value	Probability
Intercept	1	96110.92	96110.92	111.79	<.0001
Torrefied temperature *(T)*	3	61550.30	20516.77	2398.21	<.0001
Moisture content *(M)*	2	4736.13	2368.07	276.80	<.0001
Compressive force *(F)*	2	3263.46	1631.73	190.73	<.0001
*T*M*	6	8398.38	1399.73	163.61	<.0001
*T*F*	6	2891.81	481.97	56.34	<.0001
*M*F*	4	1086.34	271.59	31.75	<.0001
*T*M*F*	12	1463.14	121.93	14.25	<.0001
Error	68	581.74	8.56		
Total	104	180082.2			

Table B7.2: Effect of torrefaction temperature, moisture content, and compressive force on the durability of pellets (%).

Torrefaction temperature (Cº)	Durability of pellets (%)
22	5.70^{C}
225	4.92^{C}
250	61.51^{A}
275	45.70^{B}
Moisture content (%wb)	Durability of pellets (%)
3.5	33.69^{B}
7	35.51^{A}
10.5	20.96^{C}
Compressive force (kN)	Durability of pellets (%)
8	21.94^{B}
13	34.24^{A}
18	35.15^{A}

Means with the same letters are not significantly different at 5% level.

Table B8.1: Analysis of variance (ANOVA) table for factors affecting the water uptake of pellets (after 10s) (%).

Source	df	SS	MS	F-value	Probability
Intercept	1	220317.10	220317.10	826.09	<.0001
Torrefied temperature *(T)*	3	15721.09	5240.36	694.56	<.0001
Moisture content *(M)*	2	5777.63	2888.82	382.89	<.0001
Compressive force *(F)*	2	229.07	114.53	15.18	<.0001
*T*M*	6	19591.24	3265.21	432.77	<.0001
*T*F*	6	721.13	120.19	15.93	<.0001
*M*F*	4	87.89	21.97	2.91	0.0238
*T*M*F*	12	699.27	58.27	7.72	<.0001
Error	138	1041.19	7.54		
Total	174	264185.61			

Table B8.2: Effect of torrefaction temperature, moisture content, and compressive force on the water uptake of pellets (after 10s) (%).

Torrefaction temperature (Cº)	Water uptake of pellets (after 10s) (%)
22	50.75^{A}
225	22.90^{D}
250	31.48^{C}
275	36.14^{B}
Moisture content (%wb)	Water uptake of pellets (after 10s) (%)
3.5	43.61A
7	31.23B
10.5	31.50B
Compressive force (kN)	Water uptake of pellets (after 10s) (%)
8	34.00^{B}
13	35.94^{A}
18	36.86^{A}

Means with the same letters are not significantly different at 5% level.

Table B9.1: Analysis of variance (ANOVA) table for factors affecting the water uptake of pellets (after 30s) (%).

Source	df	SS	MS	F-value	Probability
Intercept	1	1513684.32	1513684.32	992.68	<.0001
Torrefied temperature *(T)*	3	222651.90	74217.31	3581.18	<.0001
Moisture content *(M)*	2	21692.61	10846.31	523.36	<.0001
Compressive force *(F)*	2	1017.21	508.60	24.54	<.0001
*T*M*	6	10511.37	1751.90	84.53	<.0001
*T*F*	6	2080.48	346.75	16.73	<.0001
*M*F*	4	783.60	195.90	9.45	<.0001
*T*M*F*	12	1281.90	106.83	5.15	<.0001
Error	138	2859.95	20.72		
Total	174	1776563.34			

Table B9.2: Effect of torrefaction temperature, moisture content, and compressive force on the water uptake of pellets (after 30s) (%).

Torrefaction temperature (Cº)	Water uptake of pellets (after 30s) (%)
22	151.03^{A}
225	75.72^{C}
250	89.52^{B}
275	56.15^{D}
Moisture content (%wb)	Water uptake of pellets (after 30s) (%)
3.5	106.15^{A}
7	93.19^{B}
10.5	79.31^{C}
Compressive force (kN)	Water uptake of pellets (after 30s) (%)
8	89.99^{C}
13	93.17^{B}
18	96.77^{A}

Means with the same letters are not significantly different at 5% level.

Table B10.1: Analysis of variance (ANOVA) table for factors affecting the increase of water uptake from 10s to 30s (%).

Source	df	SS	MS	F-value	Probability
Intercept	1	579028.62	579028.62	493.47	<.0001
Torrefied temperature *(T)*	3	146602.90	48867.65	1888.37	<.0001
Moisture content *(M)*	2	9138.92	4569.46	176.58	<.0001
Compressive force *(F)*	2	280.92	140.46	5.43	0.0054
*T*M*	6	43286.30	7214.38	278.78	<.0001
*T*F*	6	642.71	107.12	4.14	0.0007
*M*F*	4	392.25	98.06	3.79	0.0059
*T*M*F*	12	1209.59	100.80	3.90	<.0001
Error	138	3571.20	25.88		
Total	174	784153.41			

Table B10.2: Effect of torrefaction temperature, moisture content, and compressive force on the

Torrefaction temperature (Cº)	Increase of water uptake from 10s to 30s (%)
22	100.28^{A}
225	52.82^{C}
250	58.05^{B}
275	20.01^{D}
Moisture content (%wb)	Increase of water uptake from 10s to 30s (%)
3.5	62.54^{A}
7	61.96^{A}
10.5	47.81^{B}
Compressive force (kN)	Increase of water uptake from 10s to 30s (%)
8	55.99^{B}
13	57.23^{B}
18	59.91^{A}

Means with the same letters are not significantly different at 5% level.

APPENDIX C – DATA TABLES

Table C1: Specific energy required for compression of pellets (MJ/t).

MC (% wb)	Force (kN)	Specific energy required for compression pellets (MJ/t)			
		Torrefaction temperature (ºC)			
		CT	225	250	275
3.5	8	30.45 (0.44)	38.44 (0.39)	46.05 (0.37)	54.41 (1.08)
	13	41.18 (0.40)	51.68 (1.18)	59.97 (0.85)	70.89 (0.68)
	18	52.06 (0.45)	64.92 (0.46)	74.49 (1.09)	86.16 (1.68)
7	8	26.43 (0.33)	32.57 (0.26)	37.55 (0.31)	44.79 (0.22)
	13	35.63 (0.34)	43.86 (0.30)	49.37 (0.30)	58.07 (0.42)
	18	44.51 (0.55)	54.46 (0.29)	61.56 (0.21)	72.11 (1.09)
10.5	8	23.01 (0.30)	27.25 (0.24)	33.85 (0.41)	40.43 (0.37)
	13	30.92 (0.37)	36.92 (0.61)	44.55 (0.40)	54.03 (0.25)
	18	40.43 (0.28)	46.81 (0.41)	55.78 (0.36)	66.22 (0.98)

Table C2: Initial pellet density.

MC (% wb)	Force (kN)	Initial pellet density (kg/m^3)			
		Torrefaction temperature (ºC)			
		CT	225	250	275
3.5	8	1148 (5)	1123 (5)	1091 (5)	995 (5)
	13	1177 (5)	1177 (5)	1151 (5)	1073 (5)
	18	1181 (5)	1191 (5)	1170 (5)	1092 (5)
7	8	1170 (5)	1126 (5)	1063 (5)	985 (5)
	13	1180 (5)	1157 (5)	1083 (4)	1026 (5)
	18	1175 (6)	1150 (5)	1089 (5)	1032 (5)
10.5	8	1090 (5)	963 (5)	986 (5)	935 (5)
	13	1079 (5)	933 (4)	981 (5)	938 (5)
	18	1093 (4)	910 (8)	952 (3)	925 (4)

Table C3: Relaxed density of pellets (kg/m^3).

MC (% wb)	Force (kN)	Relaxed density of pellets (kg/m^3)			
		Torrefaction temperature (°C)			
		CT	225	250	275
3.5	8	1032 (2)	1076 (2)	1049 (1)	955 (3)
	13	1071 (2)	1105 (4)	1117 (1)	1043 (1)
	18	1050 (2)	1131 (2)	1136 (1)	1019 (2)
7	8	1139 (2)	1106 (0)	1062 (2)	976 (2)
	13	1145 (2)	1148 (1)	1084 (2)	1025 (3)
	18	1146 (2)	1141 (2)	1074 (2)	1022 (2)
10.5	8	1074 (3)	969 (6)	977 (1)	918 (3)
	13	1071 (2)	957 (3)	976 (3)	938 (1)
	18	1089 (1)	949 (13)	967 (4)	935 (5)

Table C4: Longitudinal expansion of pellets (%).

MC (% wb)	Force (kN)	Longitudinal expansion of pellets (%)			
		Torrefaction temperature (ºC)			
		CT	225	250	275
3.5	8	11.37 (0.58)	5.56 (0.36)	3.57 (0.49)	3.55 (0.49)
	13	10.55 (0.55)	5.92 (0.42)	3.94 (0.35)	3.31 (0.43)
	18	11.24 (0.45)	5.77 (0.50)	3.11 (0.44)	4.24 (0.39)
7	8	2.27 (0.08)	1.03 (0.09)	0.49 (0.11)	0.88 (0.06)
	13	2.87 (0.18)	0.89 (0.06)	0.47 (0.13)	0.69 (0.05)
	18	2.01 (0.20)	1.21 (0.06)	0.33 (0.05)	0.81 (0.12)
10.5	8	-1.03 (0.18)	-1.66 (0.31)	-0.86 (0.26)	0.08 (0.17)
	13	-0.61 (0.20)	-1.74 (0.28)	-0.81 (0.11)	-0.66 (0.12)
	18	-0.22 (0.17)	-3.59 (2.87)	-1.12 (0.13)	-0.56 (0.10)

Table C5: Diametral expansion of pellets (%).

MC (% wb)	Force (kN)	Diametral expansion of pellets (%)			
		Torrefaction temperature (ºC)			
		CT	225	250	275
3.5	8	1.07 (0.09)	1.17 (0.07)	0.69 (0.11)	0.59 (0.05)
	13	1.83 (0.06)	1.14 (0.10)	0.79 (0.07)	0.57 (0.07)
	18	2.18 (0.07)	1.34 (0.06)	1.09 (0.06)	1.48 (0.00)
7	8	0.81 (0.10)	0.64 (0.05)	0.35 (0.05)	0.43 (0.07)
	13	0.76 (0.05)	0.41 (0.06)	0.39 (0.05)	0.49 (0.14)
	18	0.87 (0.00)	0.60 (0.18)	0.49 (0.11)	0.33 (0.10)
10.5	8	0.54 (0.10)	0.10 (0.14)	0.53 (0.06)	0.20 (0.06)
	13	0.48 (0.12)	-0.14 (0.28)	0.16 (0.06)	0.41 (0.10)
	18	0.21 (0.06)	-0.03 (0.47)	-0.53 (0.10)	0.06 (0.07)

Table C6: Tensile strength of pellets (MPa).

MC (% wb)	Force (kN)	Tensile strength of pellets (MPa)			
		Torrefaction temperature (ºC)			
		CT	225	250	275
3.5	8	0.71 (0.10)	1.89 (0.12)	3.16 (0.39)	2.39 (0.27)
	13	0.79 (0.07)	2.13 (0.23)	3.91 (0.18)	3.36 (0.20)
	18	0.69 (0.08)	2.34 (0.31)	4.30 (0.21)	2.98 (0.32)
7	8	2.08 (0.17)	2.37 (0.26)	2.89 (0.41)	2.52 (0.17)
	13	2.06 (0.22)	2.46 (0.35)	3.31 (0.24)	3.05 (0.17)
	18	2.05 (0.16)	2.40 (0.17)	3.36 (0.12)	3.08 (0.14)
10.5	8	1.48 (0.17)	0.93 (0.13)	2.22 (0.30)	1.84 (0.15)
	13	1.74 (0.08)	0.70 (0.36)	1.97 (0.21)	1.83 (0.13)
	18	1.91 (0.19)	0.84 (0.21)	1.75 (0.11)	1.78 (0.23)

Table C7: Durability of pellets (%).

MC (% wb)	Force (kN)	Durability of pellets (%)			
		Torrefaction temperature (ºC)			
		CT	225	250	275
3.5	8	2.98 (0.36)	1.96 (0.67)	49.30 (7.47)	26.26 (2.54)
	13	2.21 (0.14)	3.68 (0.66)	78.79 (3.80)	69.73 (0.68)
	18	1.27 (0.40)	5.34 (1.37)	83.97 (2.89)	78.73 (3.84)
7	8	3.59 (1.10)	4.32 (0.99)	63.74 (3.40)	39.38 (1.31)
	13	8.03 (2.60)	3.74 (0.53)	78.86 (1.77)	66.17 (0.46)
	18	5.96 (1.19)	5.26 (1.08)	77.81 (0.45)	69.23 (1.60)
10.5	8	6.26 (0.95)	8.11 (0.04)	36.37 (4.69)	16.44 (0.15)
	13	11.82 (6.76)	8.01 (0.01)	46.95 (0.60)	24.12 (8.09)
	18	9.12 (1.10)	7.98 (0.00)	37.79 (0.48)	21.26 (4.53)

Table C8: Water uptake of pellets (after 10s) (%).

MC (% wb)	Force (kN)	Water uptake of pellets (after 10s) (%)			
		Torrefaction temperature (ºC)			
		CT	225	250	275
3.5	8	75.23 (5.75)	23.35 (0.99)	30.94 (3.29)	43.40 (1.08)
	13	89.02 (3.50)	20.78 (1.38)	27.65 (5.87)	36.81 (0.84)
	18	84.34 (5.08)	19.48 (0.38)	39.34 (2.36)	32.93 (1.02)
7	8	36.99 (2.54)	18.69 (1.23)	24.45 (1.70)	35.03 (0.77)
	13	41.81 (7.48)	20.23 (2.35)	31.40 (1.54)	34.51 (0.86)
	18	47.35 (6.07)	21.74 (1.12)	30.25 (1.67)	34.44 (1.48)
10.5	8	23.34 (1.77)	26.70 (2.38)	32.07 (1.79)	36.39 (0.58)
	13	29.05 (1.34)	31.14 (1.26)	33.99 (1.50)	35.12 (0.65)
	18	27.81 (2.53)	31.58 (0.58)	33.20 (1.69)	36.63 (1.09)

Table C9: Water uptake of pellets (after 30s) (%).

MC (% wb)	Force (kN)	Water uptake of pellets (after 30s) (%)			
		Torrefaction temperature (ºC)			
		CT	225	250	275
3.5	8	149.17 (7.85)	81.03 (2.85)	112.91 (3.26)	79.98 (1.61)
	13	154.19 (11.07)	82.78 (3.08)	119.00 (6.38)	73.18 (1.29)
	18	156.02 (7.24)	83.87 (1.65)	123.23 (3.12)	58.42 (1.02)
7	8	147.46 (7.31)	72.27 (2.44)	80.47 (2.12)	51.85 (1.04)
	13	161.03 (7.36)	79.57 (4.41)	86.57 (3.88)	52.27 (0.53)
	18	179.76 (9.31)	76.22 (1.66)	91.85 (1.01)	52.48 (2.49)
10.5	8	131.11 (6.38)	62.36 (2.94)	60.41 (3.95)	45.33 (1.32)
	13	141.11 (6.82)	66.80 (4.18)	65.31 (2.49)	44.54 (0.65)
	18	141.42 (4.26)	66.68 (1.68)	65.93 (1.33)	47.28 (1.79)

Table C10: Increase of water uptake from 10s to 30s (%).

MC (% wb)	Force (kN)	Increase of water uptake from 10s to 30s (%)			
		Torrefaction temperature (ºC)			
		CT	225	250	275
3.5	8	73.94 (9.50)	57.68 (2.52)	81.98 (2.07)	36.57 (1.73)
	13	65.17 (10.76)	62.00 (2.01)	91.35 (10.76)	36.37 (1.66)
	18	71.68 (8.12)	64.39 (1.97)	83.89 (1.39)	25.48 (1.69)
7	8	110.47 (8.58)	53.58 (1.55)	56.03 (3.41)	16.83 (1.00)
	13	119.23 (8.83)	59.33 (2.51)	55.17 (3.50)	17.76 (1.09)
	18	132.41 (12.06)	54.48 (1.49)	61.60 (2.00)	18.04 (1.63)
10.5	8	107.77 (7.04)	35.65 (2.16)	28.33 (2.84)	8.94 (0.93)
	13	112.06 (7.20)	35.66 (3.21)	31.33 (2.53)	9.42 (0.78)
	18	113.60 (4.37)	35.10 (1.10)	32.72 (1.48)	10.65 (2.20)

APPENDIX D – EXAMPLE OF SAS CODE FOR THREE-WAY ANOVA

```
OPTIONS LINESIZE=78;
OPTIONS PAGESIZE=66;
OPTIONS FORMDLIM='*';
DATA STAT;
INPUT T M F Y @@;
CARDS;
22    3.5   8000  1147.573489
22    3.5   8000  1147.340259
22    3.5   8000  1138.982267
22    3.5   8000  1151.698988
22    3.5   8000  1146.209966
22    3.5   8000  1152.785379
22    3.5   8000  1146.940731
22    3.5   8000  1148.587976
22    3.5   8000  1152.976064
22    3.5   8000  1143.557934
22    3.5   8000  1139.18201
22    3.5   8000  1153.408174
22    3.5   8000  1153.825442



275   10.5  18000 922.1283513
275   10.5  18000 927.3276
275   10.5  18000 924.7281659
275   10.5  18000 921.1144218
275   10.5  18000 920.136174
275   10.5  18000 933.1155638
275   10.5  18000 923.4843011
275   10.5  18000 924.5776322
275   10.5  18000 926.7411119
275   10.5  18000 930.7918357
275   10.5  18000 927.3052266
275   10.5  18000 921.5714054
;
PROC GLM;
CLASS T M F;
MODEL Y =/;
RUN;

PROC GLM;
CLASS T M F;
MODEL Y = T M F T*M T*F M*F T*M*F;
MEANS T*M*F;
MEANS T M F/DUNCAN;
RUN;
```