

# **HYDROTHERMAL PRETREATMENT OF SOFTWOOD BIOMASS AND BARK FOR PELLETIZATION**

by

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## Abstract

Densification can resolve the logistical challenges encountered when large volumes of biomass are required for conversion processes to benefit from economies-of-scale. Despite the higher density of pellets, they easily disintegrate into fines due to impact or moisture sorption during handling and storage. Fines accumulation can lead to explosion, off-gassing and self-combustion, threatening the occupational health and safety of the workers. The current study investigates the use of several hydrothermal pretreatments to improve pellet quality in terms of mechanical strength and moisture sorption resistance, while lowering energy input during size reduction, drying and densification steps. Pretreatment of ground softwood particles (Pine, Spruce, Douglas fir whitewood and bark) with external saturated steam at 220°C for 5 min resulted in the higher calorific values, higher hydrophobicity and higher carbon percentage. These changes along with the dark brownish colour of steam treated material indicated a mild degree of torrefaction when compared to dry torrefaction at higher temperatures. Despite a slightly lower density, the mechanical strength of pellets made of steam treated particles increased considerably. Mechanical energy input for pelletization of treated material was higher than the untreated pellets when compressed under the same force for all species and bark samples.

Hydrothermal pretreatment of wet Douglas fir wood particles, by steam generated from the moisture inside the material, resulted in the same characteristics as those obtained from pretreatments by external steam. Increased treatment temperature increased the hydrophobicity compared to untreated pellets.

Sulfur-dioxide catalyzed steam pretreatment substantially reduced the particle size of Douglas fir woodchips, eliminating any further grinding requirement for pelletization. The SO<sub>2</sub>-catalyzed steam treated pellets had a higher density and exhibited a two-time higher mechanical strength compared to untreated pellets. Despite a higher moisture adsorption capacity than the untreated, treated pellets remained intact under highly humid (30°C, 90% RH) conditions. The high heating values, low ash content and good overall carbohydrate recovery of SO<sub>2</sub>-catalyzed steam treated pellets indicate their potential suitability for both biochemical and thermo-chemical applications.

## Preface

Chapters 1 and 2 are mainly based on the literature review prepared for three journal publications by the major author (Zahra Tooyserkani). The design and construction of steam treatment unit with the control system (Chapter 3) were done by Dr. Pak Sui Wilson Lam, the former PhD student in the Biomass and Bioenergy Research Group (BBRG) at UBC. The major author did the modifications (Chapter 3) on the steam treatment and pelletization units based on the requirements of the current study. The research supervisors, Dr. Sokhansanj, Dr. Bi and Dr. Lim provided guidelines and advice on the work from Chapter 1 to Chapter 8.

Chapter 4 is based on the laboratory experimental work. The major author developed experimental design, data collection, analysis, and manuscript preparation. The co-authors provided feedback and insight throughout this process, and edited the manuscript. These studies have been accepted as two journal papers: Tooyserkani, Z., Sokhansanj, S., Bi, X., Lim, C. J., Saddler, J., Lau, A., Melin, S., Lam, P. S., Kumar, L., 2012. Effect of steam treatment on pellet strength and the energy input in pelleting of softwood particles. *Transactions of ASABE*. 55 (6), 2265-2272; Tooyserkani, Z., Sokhansanj, S., Bi, X., Lim, C. J., Lau, A., Saddler, J., Kumar, L., Lam, P.S., Melin, S., 2013. Steam treatment of four softwood species and bark to produce torrefied wood. *Applied Energy*. 103, 514-521.

Chapter 5 is based on the collaborative work between BBRG and Forest Products Biotechnology/Bioenergy (FPB) group. The SO<sub>2</sub>-catalyzed steam pretreatments were conducted in FPB by Mr. Linoj Kumar and the pelletization and characterizations were done in BBRG Labs by the major author. The output of this collaboration was two publications: Kumar, L., Tooyserkani, Z., Sokhansanj, S., Saddler, J., 2012. Does densification influence the steam pretreatment and enzymatic hydrolysis of softwoods to sugars? *Bioresource Technology*. 121, 190–198; Tooyserkani, Z., Kumar, L., Sokhansanj, S., Saddler, J., Bi, X. T., Lim, C. J., Lau, A., Melin, S., 2013. SO<sub>2</sub>-catalyzed steam pretreatment enhances the strength and stability of softwood pellets. *Bioresource Technology*. 130, 59-68.

Chapter 6 and 7 are based on the experimental studies conducted by the major author (Zahra Tooyserkani), under supervision of Dr. Sokhansanj, Dr. Bi and Dr. Lim. The work was given as an oral presentation at the Canadian Society of Chemical Engineers (CSCHE, 2012) in Vancouver. A version of Chapter 6 has been prepared for publication and will be submitted soon. Another manuscript will be formed based on Chapter 7 for publication.

# Table of Contents

Abstract .....	ii
Preface .....	iii
Table of Contents .....	v
List of Tables .....	viii
List of Figures .....	x
Acknowledgements .....	xiii
Dedication .....	xv

<b>Chapter 1. Introduction .....</b>	<b>1</b>
1.1. Background .....	1
1.2. Objectives .....	4
1.3. Structure of the thesis .....	5

<b>Chapter 2. Background on hydrothermal pretreatment and densification of biomass .....</b>	<b>9</b>
2.1. Cellular structure, composition, properties of wood .....	9
2.2. Hydrothermal pretreatment .....	10
2.2.1. Thermodynamics of steam in a hydrothermal treatment .....	11
2.2.2. Liquid hot water pretreatment .....	12
2.2.3. Saturated steam pretreatment .....	13
2.2.4. Superheated steam pretreatment .....	14
2.2.5. Dry torrefaction .....	16
2.3. Pelletization .....	18
2.3.1. Pellet dimensions, bulk density and single pellet density .....	20
2.3.2. Moisture resistance .....	20
2.3.3. Durability and mechanical strength .....	20
2.3.4. Moisture content of feedstock .....	21
2.3.5. Particle size distribution .....	22
2.3.6. Biomass constituents .....	22
2.3.7. Type of pellet mill and die specification .....	23
2.3.8. Die temperature .....	24
2.3.9. Pelletization pressure and relaxation time .....	25
2.4. Concluding remarks .....	26

<b>Chapter 3. Description of experiments .....</b>	<b>31</b>
3.1. Introduction .....	31
3.2. Materials and methods .....	31
3.2.1. Materials .....	31
3.2.2. Sample preparation .....	32
3.2.3. Hydrothermal treatment setups .....	32
Treatment of ground dry biomass .....	33
Treatment of ground wet biomass .....	34
Treatment of woodchip samples .....	34
3.2.4. Measurements on ground samples .....	35
Moisture content and solid yield .....	35

Particle size distribution .....	36
Compositional analyses .....	36
Density measurements .....	37
Color .....	38
Scanning electron microscope (SEM) .....	39
3.2.5. Pelletization .....	39
3.2.6. Pellet property measurements .....	40
3.3. Concluding remarks .....	42

<b>Chapter 4. Steam treatment of softwood species and bark to produce durable torrefied pellets .....</b>	<b>51</b>
4.1. Introduction .....	51
4.2. Materials and methods .....	52
4.2.1. Materials .....	52
4.2.2. Equipment and procedure .....	52
4.3. Measurements on ground samples .....	53
4.3.1. Moisture content .....	53
4.3.2. Particle size distribution .....	53
4.3.3. Color .....	54
4.3.4. Bulk, tapped and particle density .....	55
4.3.5. Ash content and calorific value .....	56
4.3.6. Carbon percentage .....	57
4.3.7. Moisture adsorption .....	57
4.4. Pellet properties .....	59
4.4.1. Energy to produce pellets .....	59
4.4.2. Mechanical strength of pellets .....	60
4.5. Concluding remarks .....	62

<b>Chapter 5. SO<sub>2</sub>-catalyzed steam pretreatment for enhancing the strength and stability of softwood pellets .....</b>	<b>77</b>
5.1. Introduction .....	77
5.2. Materials and methods .....	78
5.2.1. Materials .....	78
5.2.2. Equipment and procedure .....	78
5.3. Effect of SO <sub>2</sub> -catalyzed steam pretreatment .....	79
5.3.1. Particle size distribution .....	79
5.3.2. Chemical composition .....	80
5.3.3. Mechanical properties of the pellets .....	80
5.3.4. Energy input to make pellets .....	81
5.3.5. Moisture sorption properties of pellets .....	82
5.4. Discussion on practical application of this research .....	84
5.5. Concluding remarks .....	85

<b>Chapter 6. Superheated steam drying and treatment of cellulosic biomass to improve the quality of pellets .....</b>	<b>94</b>
6.1. Introduction .....	94
6.2. Materials and methods .....	95
6.2.1. Materials .....	95

6.2.2. Equipment and procedure .....	95
6.3. Drying effect and material loss .....	97
6.4. Measurements on ground biomass .....	99
6.4.1. Particle size distribution .....	99
6.4.2. Calorific heating value and elemental analysis .....	99
6.5. Characterization of pelletized samples.....	100
6.5.1. Pellet density and mechanical strength .....	100
6.5.2. Mechanical energy input for pelletization .....	101
6.5.3. Stickiness of treated samples.....	101
6.5.4. Moisture adsorption of pellets.....	102
6.6. Concluding remarks.....	102
<b>Chapter 7. Analysis of mass and energy balances .....</b>	<b>113</b>
7.1. Introduction .....	113
7.2. Development of analysis method .....	113
7.2.1. Drying .....	114
7.2.2. Size reduction .....	116
7.2.3. Densification.....	117
7.2.4. Hydrothermal treatment .....	117
7.3. Energy inputs comparison .....	119
7.4. Concluding remarks.....	119
<b>Chapter 8. Conclusions and future work .....</b>	<b>123</b>
8.1. Overall conclusions.....	123
8.2. Recommendations for future studies.....	125
<b>References.....</b>	<b>126</b>
<b>Appendix A .....</b>	<b>138</b>

## List of Tables

Table 2.1 Quality requirements of the wood pellets (% dry weight) (Mosiera et al. 2005) .....	27
Table 3.1 List of valves in the experimental unit .....	43
Table 3.2 List of thermocouples and pressure transducers in the experiment unit.....	44
Table 4.1 Moisture content, geometric mean ( $d_{gm}$ ) and geometric standard deviation ( $S_{gm}$ ) of treated and untreated particles.....	64
Table 4.2 Color changes after steam treatment.....	65
Table 4.3 Bulk, tapped and particle solid densities of untreated and treated biomass.....	66
Table 4.4 Ultimate* and heat value* analysis of untreated and steam treated ground biomass .....	67
Table 4.5 Equilibrium moisture content ( $M_e$ ) and moisture adsorption constant (k) before and after treatment.....	68
Table 4.6 Matrix of correlation coefficient among percent differences between untreated and treated biomass properties. ....	69
Table 4.7 Comparing steam torrefaction with dry torrefactions on Pine and Spruce particles .....	70
Table 4.8 Energy input to make pellets and the required forces to crush pellets (pellets were made at 4000 N) .....	71
Table 4.9 Characteristics of Douglas-fir pellets made from treated and untreated biomass at three levels of compression forces .....	72
Table 5.1 Chemical composition of untreated and steam treated Douglas-fir chips and pellets (% dry weight) (numbers in the brackets represents standard deviations for n=3).....	86
Table 5.2 Mechanical properties of steam treated and untreated pellets (numbers in the brackets represents standard deviations for n=10).....	87
Table 5.3 Elemental analysis of samples (numbers in the brackets are standard deviations for n=3) .....	88
Table 6.1 Drying effect of the hydrothermal treatment (numbers in the brackets represents standard deviations for n=3) .....	104



Table 6.2 Thermo-chemical properties of samples (numbers in the brackets represents standard deviations for n=3) .....	105
Table 6.3 Mechanical properties of produced pellets and energy inputs for densification (numbers in the brackets represents standard deviations for n=10).....	106
Table 7.1 Direct energy Input per unit kilogram of produced pellets at 10 % m.c. (w.b.) to the biomass pelletization process with the laboratory data of different hydrothermal treatments .....	121
Table A. 1 Physical and chemical characteristics of samples before and after steam drying .....	140

## List of Figures

Figure 1.1 Pellet production capacity in Canada and the U.S. (Spelter and Toth, 2009) .....	6
Figure 1.2 Traditional pellet production unit operations .....	7
Figure 1.3 Pelletization process incorporating hydrothermal pretreatment.....	8
Figure 2.1 Compression curve (Sokhansanj et al., 2005).....	28
Figure 2.2 Ring-die pellet mill (Stelte et al., 2012) .....	29
Figure 2.3 Flat die pellet mill (Stelte et al., 2012).....	30
Figure 3.1 Hydrothermal pretreatment experimental set-up .....	45
Figure 3.2 Flow diagram of hydrothermal pretreatment experimental set-up.....	46
Figure 3.3 L, a, b coordinates of color in the Lab system .....	47
Figure 3.4 The pelletization set-ups consist of a cylinder piston arrangement. The cylinder is wrapped with electric heating tape; (a) a fixed piston-cylindrical die pelletizer assembly, (b) the posts guide the movement and alignment of the piston with respect to the die. The entire assembly is placed under MTI for making single pellet. ....	48
Figure 3.5 Mechanical strength test set-up. A single pellet is placed under two platens. The top platen is lowered and forced on the pellet until the pellet disintegrates.....	49
Figure 3.6 MTI generated plots of force vs. displacement. (a) The plot of compression curves for untreated material and (b) the lower plots of expulsion curves of pellets out of die for untreated material. The areas under these curves are computed to yield energy input for compression and energy input for pellet expulsion.....	50
Figure 4.1 Photos of untreated (left) and steam treated (right) samples.....	73
Figure 4.2 Particle size distribution for untreated ground whitewood and bark.....	74
Figure 4.3 Distribution of three size groups of particles before and after steam treatment.....	75
Figure 4.4 Specific energy to compact and extrude pellets made from untreated and treated biomass. ....	76

Figure 5.1 Appearance of raw material and pellets made in this study: (a) original Douglas fir woodchips, (b) SO <sub>2</sub> -catalyzed steam treated and dried woodchips, (c) SEM image of untreated Douglas fir particles with x5K magnification, (d) SEM image of SO <sub>2</sub> -steam treated Douglas fir particles with 5K magnification, (e) pellets made from untreated particles, (f) pellets made from SO <sub>2</sub> -steam treated particles. ....	89
Figure 5.2 Particle size distribution for untreated (gray) and SO <sub>2</sub> -catalyzed steam treated substrates (dark) before pelletization.....	90
Figure 5.3 MTI generated plots of force vs. displacement. The top plots are compression curves for (a) untreated and (b) SO <sub>2</sub> -catalyzed steam treated particles; the lower plots are the expulsion curves of pellets out of die for (c) untreated and (d) SO <sub>2</sub> -catalyzed steam treated pellets. The areas under these curves are computed to yield energy input for compression and energy input for pellet expulsion. ....	91
Figure 5.4 (a) Pellet moisture content vs. time when placed in the humid chamber (30°C – 90%). Treated pellets reached to higher equilibrium moisture content than the untreated sample. (b) Moisture adsorption rate constant. Treated pellets reached equilibrium moisture content in longer time. ....	92
Figure 5.5 Moisture sorption tests: (a) untreated pellet right after immersing in water, (b) treated pellet after one week immersing in water, (c) appearance of an untreated pellet reached to equilibrium moisture content in humid chamber (30°C – 90% RH) after 4 h, (d) unchanged appearance of a treated pellet reached to equilibrium moisture content after 24 h.....	93
Figure 6.1 Thermodynamic curves for pure water, (a) liquid/vapor phase equilibrium boundaries, (b) saturation region.....	107
Figure 6.2 Equilibrium pressure vs. temperature curves for the experimental reactor .....	108
Figure 6.3 Size reduction effect of hydrothermal treatments at different treatment temperatures.....	109
Figure 6.4 Expulsion curves for saturated steam treated samples at different treatment temperatures .....	110
Figure 6.5 Expulsion curves for superheated steam treated samples at different treatment temperatures .....	111
Figure 6.6 Moisture uptake rates of pellets made of samples treated at different conditions.....	112
Figure 7.1 Unit operations and process flow in a pellet production plant (Lam, 2011) .....	122

Figure A. 1 Schematic diagram of superheated steam drying; open system .....	141
Figure A. 2 Steam drying kinetics for Pine sample .....	142

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## Dedication

*I would like to dedicate this thesis to my life's  
best friend, my husband, Mani.*

# Chapter 1. Introduction

## 1.1. Background

World energy consumption has been projected to increase by 47% from 2010 to 2035 (Energy Information Agency, 2012). People are becoming increasingly concerned with using less expensive and more environmentally friendly energy sources (World Watch Institute, 2007). Renewable energy is the world's fastest-growing source of marketed energy, currently increasing by an average of 3.0 percent per year, compared to an average of 1.6 percent per year increase for total world energy consumption (Energy Information Agency, 2012). Renewable energy is derived from natural resources which include wind, geothermal heat, sunlight, water, and biomass. In 2010, 16.7% of total global energy consumption came from renewable sources. Of this total, an estimated 8.5% came from traditional biomass alone (REN21, 2012). The use of biomass such as wood residues and agricultural crops as lignocellulosic-based biofuels in place of fossil fuels can reduce the dependence on oil, reduce greenhouse gas emissions, increase farm income and create jobs in the rural areas (DOE, 2005). One of the challenges with any future biomass-to-fuels/chemicals process will be achieving access to the substantial amounts of biomass that will be required to benefit from the economics of scale that are inherent in the traditional oil based refinery process.

Raw cellulosic feedstocks are typically bulky ( $75 - 200 \text{ kg/m}^3$ ) and have a high moisture content ( $\sim 50\%$ ) (Mani et al., 2006b). These two undesirable characteristics alone make raw biomass costly and difficult to be stored, transported and fed into a reactor. Earlier published research (Sokhansanj et al., 2005; Mani et al., 2006a) has shown that one way to improve the economics of transporting biomass over long distances is to pelletize the material. The high bulk density ( $600\text{-}800 \text{ kg/m}^3$ ), low moisture content ( $5 - 8\%$ ) and uniform shape and size make wood pellets an attractive feedstock for the biofuel/bioenergy processes. Pelletization is a mass and energy densification process. Biomass pellets have lower emissions, improved burning



efficiency and higher energy density during combustion than using the low bulk density and fluffy biomass. One typical example of pellets application is the co-firing with coal as feedstock. Due to these benefits, wood pellet production and export have experienced a rapid growth, as demonstrated by the ever increasing global production and trade in wood pellets (Bradley et al., 2011). In 2010, 37 Canadian pellet plants operated at about 65% of their capacity, producing about 1.3 million metric tons (t) pellets per year. Canadian pellet production increased in 2011 with almost 1.9 million t of pellets being produced and exported to Europe, USA and Japan for heat and power generation (WPAC, 2012). The U.S. is experiencing an even steeper growth in the production capacity and export of wood pellets (Spelter and Toth, 2009) (Figure 1.1). British Columbia (BC) accounts for about 65% of Canadian capacity and production, while Alberta, Quebec, New Brunswick, Nova Scotia, and Newfoundland collectively account for 35%. Pellet plants in BC tend to be large whereas those in Eastern Canada are much smaller. Wood pellet plants in British Columbia and the Maritimes mainly export their product to Europe over ocean due to their coastal port access. The pellet quality must be maintained during transport in order to meet the European standard of the imported biofuels (WPAC, 2012).

It is recognized that, despite a considerable increase in the mass and energy densities achieved by densification, the pellet durability still need to be further enhanced for their effective handling and storage (Lehtikangas, 2001; Lam et al., 2011). Improved mechanical strength and higher stability reduce the generation of fines and minimize the loss of material during transport, storage and subsequent handling. Broken pellets and dust aggravate problems associated with health and dust explosion in pellet plants (Vinterback, 2004; Tumululu et al., 2010). Wood pellets tend to adsorb moisture from the surrounding humid air or when exposed to rain. Moistened pellets readily disintegrate and provide an environment for microbial activities and subsequent decay (Rupar and Sanati, 2005). Anaerobic conditions lead to local heat generation and production of toxic off-gases. Local heat generated may ignite the volatiles inside the pellets to cause fire, and the off-gas accumulations inside the storage silos are toxic to the workers. Thus, the affinity of wood pellets to water is a serious concern for an exporting country like Canada where wood pellets travel long distances often over oceans. Therefore, minimizing the disintegration of pellets upon moisture adsorption and

improving the mechanical strength are as important as increasing the energy density of the biomass. All these objectives have to be met with minimum energy input during size reduction, drying and subsequent densification steps for a continued growth of the industry. Each of the unit operations along the pellet production process (Figure 1.2) plays an important role on the quality of produced pellets and the energy consumption of the whole system. The drying step is the most energy consuming operation, followed by densification step (Mani et al., 2006a).

Pellet durability reflects the binding strength of the material. Kaliyan and Morey (2006) reviewed literature on factors affecting the durability and its relation with conventional definitions for the strength of densified biomass. In their study, the more durable pellets were mechanically stronger with respect to compressive forces. Compaction of bulk of solids is a complex interaction between particles, their constituents and applied forces (Mani et al., 2006). Composition of raw material, moisture content, particle size and process temperature are among important parameters in making durable pellets (Sokhansanj et al., 2005). Earlier work (Lehtikangas, 2001; Angle's et al., 2001; Kaliyan and Morey, 2006) reported that lignin acts as an effective binding agent that contributes to the strength of the pellets. It is also likely that the surface lignin distribution improves the hydrophobicity of the steam pretreated material (Angle's et al., 2001; Donohoe et al., 2008; Lam, 2011).

A key to successful densification of lignocellulosic material is the access to natural binding agents within the biomass (Mani et al., 2006; Sokhansanj et al., 2005; Kaliyan and Morey, 2006). Modern pelletization plants apply a treatment prior to compression to alter the physio-chemical structure of cellulosic biomass in order to activate these natural bindings in the plant (Figure 1.3). That's why we call this treatment as a "pretreatment" process all through this thesis. Different pretreatments prior to pelletization have been proposed to improve the mechanical strength, hydrophobicity and energy density of wood pellets (Shaw et al., 2009; Lam et al., 2011; Reza et al., 2012). However, these studies showed the increased moisture content of produced solid fraction up to two times after treatment (Saddler et al., 1983; Brownell et al., 1986; Lam et al., 2011; Reza et al., 2012). This additional moisture demands excessive drying energy (Mani et al., 2006a). So, a hydrothermal pretreatment that uses internal moisture in the biomass may make the economy of the whole system attractive.

While already a preferred feedstock for combustion to produce heat and power from biomass, wood pellets can also, potentially, be used as a feedstock for bioconversion to produce fuel and chemicals via biochemical pathways. Rijal et al. (2012) investigated the influence of pelletization, dilute acid and aqueous ammonia pretreatments of switchgrass on bioconversion. They found that pelletization significantly increased the sugar yield from ammonia pretreated biomass whereas pelletization had only a marginal improvement on dilute acid pretreated biomass. Theerarattananoon et al. (2012) also studied the effects of pelleting conditions on chemical composition and sugar yield of corn stover, big bluestem, wheat straw, and sorghum stalk pellets. They showed that changes in pelleting parameters and dilute acid pretreatment can influence the sugar yields. None of the previous published research has investigated the suitability of wood pellets as feedstocks for liquid biofuel production. So, it is worth to study whether wood pellets could be processed with similar ease as woodchips during a typical bioconversion process, involving a steam pretreatment and subsequent enzymatic hydrolysis, to give comparable fermentable sugar yields.

## **1.2. Objectives**

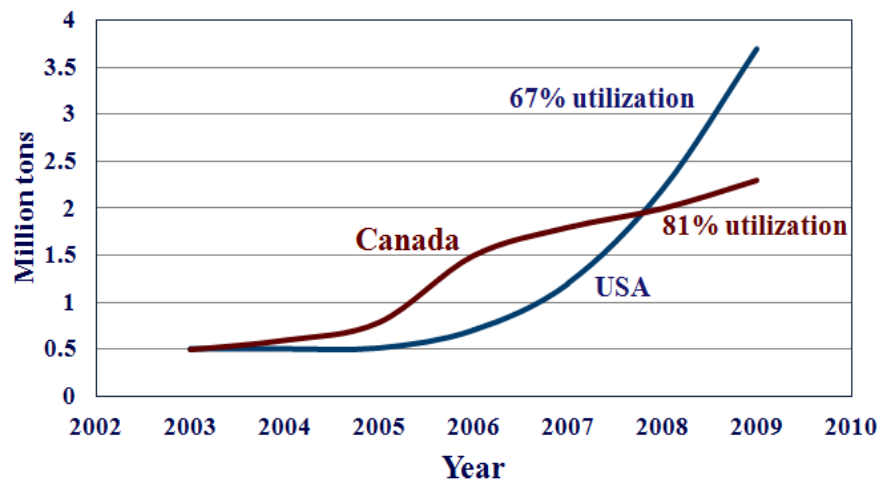
The overall goal of the research program are to (1) investigate hydrothermal pretreatments that would improve the mechanical strength and stability of wood pellets; (2) pellets made from the treated and untreated feedstock are subjected to enzymatic hydrolysis to assess their conversion to sugars and bioethanol. The reported research in this thesis focuses on goal number 1. To meet this goal, a number of experimental hydrothermal pretreatments have been applied to a specific woody biomass. The quality properties of pellets made from pretreated and untreated feedstock have been studied. These quality factors consisted of density, hardness, hydrophobicity of pellets.

The specific objectives of this study are to,

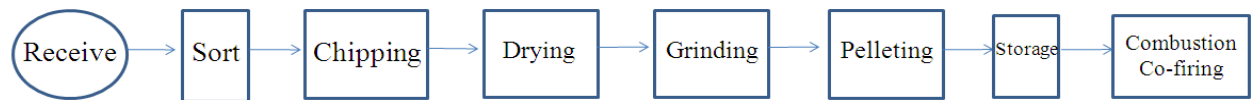
1. Investigate the compositional and physical properties of three most abundant species of woody residues (Pine, Spruce, Douglas fir whitewood and bark) in British Columbia.
2. Investigate the influence of applying saturated and dry steam and the use of  $\text{SO}_2$ -catalyst for production of durable pellets from softwood (Douglas fir) particles.

### **1.3. Structure of the thesis**

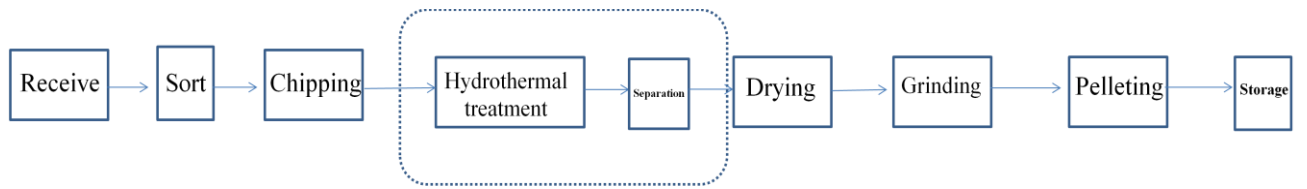
This thesis consists of 8 chapters. Chapter 1 is the introduction to wood pellet, its importance as a new bioenergy product, its susceptibility to handling and the objectives of the research to improve the quality of pellets. Chapter 2 provides a brief background on the production of wood pellets, a brief analysis on thermodynamics of steam treatment, and a review of previously published research on application of steam pretreatment to improve pellets quality. Chapter 3 explains the details of experimental set-up and the design of experiments. Chapter 4 deals with treatment of three species of softwood and bark with steam followed by their pelletization. Chapter 5 introduces the application of SO<sub>2</sub>-catalyzed steam pretreatment to woodchips and the effect of SO<sub>2</sub> impregnation on disintegrating woodchips to smaller particles. Chapter 6 outlines experiments on superheated steam drying and its effect on the quality of pellets made of dried and treated material at various treatment temperatures. In chapter 7, the mass and energy balances are developed and energy inputs in each major unit operation of pellet production plant are reported. Chapter 8 lists conclusions and recommendations for future work.



**Figure 1.1 Pellet production capacity in Canada and the U.S. (Spelter and Toth, 2009)**



***Figure 1.2 Traditional pellet production unit operations***



***Figure 1.3 Pelletization process incorporating hydrothermal pretreatment***

## **Chapter 2. Background on hydrothermal pretreatment and densification of biomass**

### **2.1. Cellular structure, composition, properties of wood**

The physical structures, major chemical compositions, and chemical structures of wood are extremely important for studying thermal chemical behavior of wood (Orfao and Figueiredo, 2001). Wood is composed of microfibrils, bundles of cellulose molecules ( $C_6$  polymers) surrounded by hemicelluloses (predominantly  $C_5$  polymers but including  $C_6$  species). Between the microfibrils, lignin consisting of phenyl-propane molecules is deposited.

The highly crystalline cellulose polymers consist of long chains of glucose molecules (normally 8000-10000 glucose molecules), with a general formula of  $(C_6H_{10}O_5)_n$  (Sjostrom, 1993). Cellulose is insoluble in water. Hemicellulose has an order of degree of polymerization (DOP) about 200 – 300, lower than cellulose, with a general formula of  $(C_5H_8O_4)_n$ . Unlike cellulose, amorphous and branched structure of hemicellulose favors the OH groups to be more reactive to water/dilute acid (Salisbury and Ross 1992). The most abundant hemicelluloses are xylan. Lignin is also a highly amorphous phenolic polymer of indeterminate molecular weight. Due to the random nature of the polymerization reaction, there is no definitive structure to the lignin, although the frequency of individual bond types is well established. Lignin is responsible for providing stiffness and mechanical strength to the cell wall and also serves to bond individual cells together in the middle lamella region. Although lignin is relatively rigid at room temperature, it undergoes glass transition at around 140°C. The presence of moisture in the cell wall opens up the structure of the lignin and additionally serves as a plasticizer for the lignin network.

Normally, a tree consists of 3-8% bark, 3-8% needles (leaves), 7-15% branches, and 65-80% trunk (Melin, 2006). Softwoods are referred to gymnosperm trees



(evergreens), which account for about 80% of the timber production source in the world. Hardwoods are referred to the wood from angiosperm (deciduous) trees. Conifers such as Pine, Spruce and Fir belong to softwoods. Typically, Pine consists of 40% cellulose, 28% hemicellulose, 28% lignin, and 4% extractives, and the outer bark of pine has more lignin, up to 48% (Lehtikangas, 2001). A growing tree has approximately 50% water content with variations from 35 to 65% between winter and summer. The wood extractives have the highest heating value in the wood, and lignin has higher heating value than cellulose and hemicellulose. Typically, the higher heating value (HHV) of cellulose is 17-18 GJ/t; 16-17 GJ/t for hemicelluloses; 25-26 GJ/t for lignin, and 33-38 GJ/t for extractives (Lehtikangas, 2001). There is a slight difference in heating values of different species and different parts of a tree.

## **2.2. Hydrothermal pretreatment**

Hydrothermal treatment is a pretreatment process that subjects a feedstock to thermal treatment at relatively low temperatures of 180–240°C in a water or steam environment (Garrote et al., 1999). It usually involves high pressures ranging from 150 to 500 psi (1.034 – 3.447 MPa) to heat up biomass rapidly, and with or without rapid decompression (explosion) to rupture the rigid structure of the biomass. In some cases, the addition of acidic gases or dilute acid as catalyst, e.g. SO<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>, is useful for enhancing the hydrolysis rate of hemicelluloses of softwood and corn fiber during the steam explosion treatment (Boussaid et al., 2000; Shevchenko et al, 2001; Bura et al., 2002; Kumar et al. 2010). Hydrothermal pretreatment has some advantages over other pretreatments involving chemicals, e.g.

1. It is carried out in a water or steam environment, so the use of synthetic chemicals is minimized;
2. Hemicelluloses can be hydrolyzed to monomeric sugars with low byproduct generation;
3. The physicochemical alteration provoked by treatments on lignin and cellulose facilitates a further processing of these fractions;

Hydrothermal treatment is a general term and does not specify the state of water or steam. The studies on the processing of lignocellulosic material by water or steam have been referred to in the literature as autohydrolysis (Lora and Wayman, 1978;

Conner, 1984; Carrasco, 1989), hydrothermolysis (Bonn et al., 1983; Hörmeyer et al., 1988; Kubikova et al., 1996), hydrothermal treatment (Overend and Chornet, 1987; Yan et al., 2009), steam pretreatment or explosion (Puls and Dietrichs, 1981; Ramos et al., 1992; Lam et al., 2011), wet torrefaction (Yan et al., 2009; Yan et al., 2010; Acharjee et al., 2011) and hydrothermal carbonization (Libra et al., 2011; Rizhikovs et al., 2011; Reza et al., 2012). All these studies are based on the same kind of reactions and are referred to as “hydrothermal treatments” in this work.

In hydrothermal treatments high pressure saturated steam or high pressure hot liquid water have been mostly applied and, to the knowledge of the author, superheated steam has never been used for pretreatment applications prior to pelletization. Also, the drying effect of a superheated steam environment has not been considered in pellet production. In the following sections, first the differences between different states of steam are explained from thermodynamic point of view, and then the application of each of these pretreatment media is briefly reviewed and the effects on the major components of lignocellulosic materials are identified.

### **2.2.1. *Thermodynamics of steam in a hydrothermal treatment***

In a boiler, energy from the fuel is transferred to liquid water in order to create steam. At first, cold water gets warmer and receives energy in the form of “sensible heat”, right until the boiling point.

Once the boiling point is reached, the temperature of water ceases to rise and stays the same until all the water is vaporized. The water transforms from a liquid state to a vapor state when it receives energy in the form of a “latent heat of vaporization”. As long as there is some liquid water left, the steam’s temperature remains the same as the liquid water’s. Steam is then called saturated steam.

When all the water is vaporized, any subsequent addition of heat raises the steam’s temperature. Steam heated beyond the saturated steam level is called superheated steam. Unlike saturated steam, a drop in temperature will not result in condensation of the superheated steam as long as the temperature is still greater than the saturation temperature at the processing pressure. This property of superheated

steam makes it suitable for dehydrating a wet substance and has been applied in Chapter 6.

### **2.2.2. *Liquid hot water pretreatment***

In liquid hot water pretreatment, the solid material is surrounded by water during the reaction, which is kept in a liquid state by allowing the pressure to rise with the steam pressure in pressurized reactors. Depending on the objective, this pretreatment has been performed over various temperature ranges and called differently; solvolysis which is mostly carried out prior to enzymatic hydrolysis for biochemical conversions at 180-240°C (Yu et al., 2010; Boussarsar et al., 2009; Sarkar et al., 2012) or hydrothermal carbonization, also called wet torrefaction, carried out in the absence or low concentration of oxygen at 220-260°C (Yan et al., 2009; Yan et al., 2010; Funke and Ziegler, 2009; Hu et al., 2010; Acharjee et al., 2011; Libra et al., 2011; Rizhikovs et al., 2011; Reza et al., 2012). Yan et al. (2009) treated Loblolly pine grounds in hot compressed water (water to biomass ratio of 5:1 on weight basis) at 200–260°C and pressure up to 700 psi (4.82 MPa). They showed that the wet torrefaction could significantly increase carbon percentage from 50% up to 72% and decrease oxygen content from 43% down to 23%, depending on the process temperature. The increase in carbon percentage was much higher in wet torrefaction at 260°C for 15-30 min residence time, compared to dry torrefaction (with nitrogen) at 300°C after a desired isothermal reaction period of about 80 min. Reza et al. (2012) followed the same treatment procedure as Yan et al. (2009) and showed that hydrophobicity, mechanical strength, energy and mass density of pellets made from hydro-treated material increased.

For both applications, the pH of water is affected by temperature. At 220°C the pH of pure water is nearly 5.0 (Weil et al., 1998). Hot water has an unusually high dielectric constant that enables ionic substances (acetyl groups of the hemicellulose with glycosidic linkages) to dissociate. Water is able to dissolve all of the hemicelluloses at high temperatures. Hot water cleaves hemi-acetal linkages and liberates acids during biomass hydrolysis (Antal, 1996). Reaction temperature (and pressure) determines the product distribution. With process temperatures of up to 220°C and corresponding pressures up to approximately 20 bar, very little gas (1–5%) is generated, and most

organics (Char and coke) remain as or are transformed into solids. At higher temperatures, up to approximately 400°C, and with the use of catalysts, more liquid hydrocarbons are formed and more gas is produced (Libra et al., 2011). Between 40% and 60% of the total biomass is dissolved in the process (in the presence of liquid hot water), with all of the hemicelluloses being removed. Variability in results was related to the biomass species of high lignin content, which impede the recovery of hemicellulose sugars.

### **2.2.3. Saturated steam pretreatment**

Steam pretreatment is a short time vapor-phase cooking of biomass at temperatures ranging from 180 – 240°C followed with or without decompression (DeLong 1981). The high pressure saturated steam ranging from 1 to 3.5 MPa (150 to 500 psi) heats up biomass rapidly. This high pressure ruptures the rigid cellular structure of the biomass. In some cases, acidic gases or dilute acids e.g. SO<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>, are used as catalysts to enhance hydrolysis of hemicelluloses of softwood and corn fiber during steam pretreatment (Boussaid et al., 2000; Shevchenko et al, 2001; Bura et al., 2002; Kumar et al., 2010). Steam pretreatment increases accessible sites for cellulose for the enzymatic hydrolysis followed by fermentation for ethanol production (Sendelius et al., 2005; Shevchenko et al., 2001; Bura et al., 2002; Bura et al., 2003). The major operation parameters of steam explosion are the reaction temperature (T) and the residence time (t). A severity index (log R<sub>0</sub>) was developed by Overend and Chornet (1987) to represent the degree of steam pretreatment,

$$\log R_0 = \log \int \exp \left( \frac{T - 100}{14.75} \right) dt \quad 2-1$$

where t is the residence time (minute), T is the reaction temperature (°C). This equation does not include the moisture content and particle size of the feedstock that also highly affect the kinetics of physical and chemical changes of the biomass by steam explosion.

Non-catalyzed steam treatment of the sawdust prior to pelletization has previously been shown to improve the mechanical strength and hydrophobicity of wood pellets (Shaw et al., 2009; Adapa et al., 2010; Lam et al., 2011; Biswas et al., 2011). Earlier work (Shaw et al., 2009) has shown that pellets made from steam-exploded poplar wood resisted higher breaking forces than did the untreated pellets. Biswas et al. (2011) reported the pellets produced from steam exploded short rotation woody crop (Salix woodchips) treated at 220°C and 228°C for 6 and 12 minutes increased in density, and resistance to impact and abrasion. In a related work, Lam et al. (2011) concluded that pellets made from ground Douglas fir particles, treated with high pressure steam at 220°C for 5 minutes were harder and more dimensionally stable than pellets made from untreated Douglas fir. However, grinding the woodchips followed by a steaming and a subsequent densification operation demanded higher amounts of energy, thus limiting the economic attractiveness of the overall process (Lam, 2011).

Previous published research indicates that the moisture content of produced solid fractions increases up to two times after steam treatment (Saddler et al., 1983; Brownell et al., 1986; Lam et al., 2011; Reza et al., 2012). This could lead to doubling the drying energy. Saddler et al. (1983) found out that the final moisture content of steam treated aspen wood increased with the initial moisture content e.g., for an initial moisture content of 50% (wet basis) or greater the void volume of aspen wood was filled by condensate before steam temperature was reached. Further heat transfer is controlled by the slower process of surface condensation and conduction into the cooler particle interiors. This leads to uneven cooking of wood, higher steam consumption in wood treatment and the higher moisture associated with treated wood (Brownell et al., 1986).

#### **2.2.4. *Superheated steam pretreatment***

Superheated steam (SS) is steam that has been given additional sensible heat to raise its temperature above the saturation point at a given pressure. The main advantages of superheated steam drying (SSD) compared to hot air drying are reduced net energy consumption due to higher heat transfer, recovering or recycling of exhaust steam, and improved food hygiene (Mujumdar et al., 2000; Devahastin et al., 2002). Drying with superheated steam produces an oxygen free environment, which eliminates

the possibility of fire or explosions in the system and can lead to improved product quality by eliminating scorching. The lack of oxygen can also eliminate oxidative reactions from occurring within the product. Major limitations can be the potential damage to heat sensitive components due to the high product temperature and complexity of the system (Pronyk et al., 2004). Most industrial applications so far are related to products that are not heat sensitive; e.g., municipal sludge.

Both experimental and theoretical studies have shown that the drying rate of a wood lumber using superheated steam is higher than that of the hot moist air when the drying temperature is above 185–205°C with the same circulation velocity (Pang, 1998), in spite of the initial gain in moisture on the surface of material due to steam condensation. Also other researchers (Sheikholeslami and Watkinson, 1990) have suggested that at any pressure during drying there is an inversion temperature; above which the effect of rise in specific heat due to the moisture addition to drying media is higher than the effect of reduction in thermal gradient. So, at temperatures lower than inversion point the evaporation decreases with increasing humidity while at temperatures above it a reverse relationship prevails. Sheikholeslami and Watkinson (1990) suggested an inversion temperature of 164°C at atmospheric pressure for hog fuel drying and higher values for higher pressures.

Hasibuan and Wan Daud (2009) studied quality changes of superheated steam-dried fibers from palm empty fruit bunches (EFB) and found that the strength of the superheated steam-dried EFB fibers was higher than that of moist and hot air-dried EFB fibers. Superheated steam drying successfully removed the silica particles from the EFB fibers at temperatures of at least 200°C and a steam velocity of at most 0.49 m/s (Silica has a higher solubility in superheated steam than in saturated steam). Bahrin et al. (2012) studied the effect of superheated steam treatment on EFB in terms of physiochemical property changes and enzymatic hydrolysis enhancement. The experiments were carried out at different temperatures (140-210°C) and durations (20-90 min). Their results showed that as the superheated steam temperature and time increased more small particles were produced. They concluded that superheated steam would enhance the accessibility required for enzymatic hydrolysis especially when shifted to temperatures above 180°C.

Miyamoto et al. (2008) used superheated steam to improve bedding for laboratory animals. High-temperature and high-pressure dry steam removed both harmful organic components and aromatic hydrocarbons that can affect metabolism of animals. The treatment increased the number of acidic functional groups on the bedding surface and gave it the high adsorptive efficiency of ammonia gas. Based on this study, the authors suggested that the formation of acidic functional groups is initiated by the promotion of dehydration below 200°C on the wood surface.

Esteves et al. (2008) heated eucalypt wood in an oven for 2–24 h at 170–200°C and in an autoclave with superheated and saturated steam for 2–12 h at 190–210°C. Hemicelluloses degraded first. Lignin degraded at a slower rate. Cellulose was only slightly affected under severe treatment conditions. The extractive content increased first with heat treatment and decreased later on. Almost all of the original extractives disappeared and new compounds were formed at extended treatment time.

### **2.2.5. *Dry torrefaction***

Torrefaction is a pyrolytic process that subjects a feedstock to thermal treatment at relatively low temperatures of 250–350°C in a reduced or absence of oxygen environment. Torrefaction can convert diverse lignocellulosic biomass feedstocks into an energy-dense and homogeneous solid biofuels (Phanphanich and Mani, 2011). The main principle of torrefaction from a chemical point of view is the removal of elemental oxygen to lower O/C ratio compared to the original biomass (van der Stelt et al., 2011). Reaction mechanisms of torrefaction are only partly understood due to the high degree of feedstock complexity and number of possible reaction mechanisms. Bond cleavage, decarboxylation, decarbonylation, dehydration, demethoxylation, condensation and aromatization are some of the characteristic mechanisms (Libra et al., 2011). The reaction temperature largely governs which reaction dominates. However, owing to the non-uniform temperature profiles within pyrolysis reactors, it is common for many of the aforementioned reaction mechanisms to occur in parallel. The highest (peak) temperature reached during the process has a critical influence on the pyrolytic reactions and the properties of the char product. Decomposition of specific compounds can also be characterized by temperature. Hemicelluloses mainly decompose between 200°C and 300°C, while cellulose decomposes at higher temperatures (300–400°C). By

contrast, lignin is the most stable component, gradually decomposes between 180 and 600°C (Groenli et al., 2002).

In comparison, during wet torrefaction feedstock decomposition is dominated by reaction mechanisms similar to those in dry pyrolysis, which include hydrolysis, dehydration, decarboxylation, aromatization and recondensation (Funke and Ziegler, 2009; Peterson et al., 2008). However, the hydrothermal degradation of biomass is initiated by hydrolysis, which exhibits a lower activation energy than most of the dry pyrolytic decomposition reactions. This has been shown by calorimetric measurements (Mok et al., 1992). Therefore, the principal biomass components are less stable under hydrothermal conditions. This means that reactions take place at lower temperatures. Although it has been observed that both time and temperature influence product characteristics (Landais et al., 1994), temperature remains the decisive process parameter (Funke and Ziegler, 2009; Ruyter, 1982). Bobleter (1994) noted that a manipulation of the water pH has a significant impact on the reaction mechanism of cellulose in water.

Torrefied biomass has been compacted to produce the second generation biomass pellets to address the problems of low heating value per unit volume. Torrefied pellets exhibit a number of other desirable properties like hydrophobicity and low off-gas emissions, when compared to the current regular pellets (Gilbert et al., 2009; Stelte et al., 2011a; Li et al., 2012; Duncan et al., 2012; Shang et al., 2012; Peng et al., 2012). The downside of torrefaction is its detrimental effect on natural binding capacity of the treated biomass to form pellets.

Gilbert et al. (2009), Stelte et al. (2011a), and Peng et al. (2012) confirmed that pellets produced from torrefied biomass were not as durable as untreated pellets. It was also shown that torrefaction increased friction in the channels of the press mill resulting in generation of excessive heat and burning of biomass. Pellets from torrefied wood were more brittle and less strong compared to untreated pellets.



## 2.3. Pelletization

Pelletization is a mechanical densification of biomass. The first patented biomass densification process was registered in 1880 by Mr. William Harold Smith in Chicago, Illinois (Smith, 1880). It describes a process where sawdust is heated up to 150°C, put in a strong mold and is compressed using a steam hammer. Pelletization became a commercial, large scale process in the second half of the last century, and was used to improve the handling properties of biomass both for energy production and animal feedstock. In North America, wood pellets came into existence in the 1970s with the primary purpose to resolve the energy crisis. The European markets started later, with Sweden running at the forefront beginning about 1980 and then soon spread all over the Europe. This development was initially driven by increasing prices for fossil fuels and good availability of residues from sawmills and pulp and paper industry. Political decisions aiming to reduce carbon dioxide emissions and a general environmental consciousness became important factors too (Bauen et al., 2009; Peksa-Blanchard et al., 2007).

Several published research explored the area of densification of woody and agricultural residues. They employed different types of processing methods and proposed different mechanisms about particles binding. According to Rumpf (1962) and Pietsch (2002) bonding forces between particles in compacted bodies can be classified into 1) attraction forces between solid particles, 2) mechanical interlocking, 3) interfacial forces and capillary pressure, 4) adhesion and cohesion, and 5) solid bridges (Figure 2.1). These bonding mechanisms have been identified and assumed also to be valid for densified forage and wood residues (Tabil et al., 1996; Mohsenin and Zaske, 1976).

Mani et al. (2004) have analyzed compression curves of various grasses (barley straw, wheat straw, switchgrass and corn stover) and interpreted them. They studied the compaction models developed by Kawakita-Ludde and Cooper-Eaton for studying the compaction mechanism of pharmaceutical and cellulosic materials. These equations that relate pellet density to applied compressive forces fitted well with the compression data of biomass grinds.

Piestch (2002) described the formation of pellets using the following phases. Loose bulk solid material fills up a container. Pressure is applied to the bulk. Initially the pressure builds up slowly because particles rearrange in a way that they fill empty voids. Air in the pores between the particles is removed upon pressing. Particles get closer to each other. Short range bonding forces, i.e. van der Waals forces and electrostatic forces, make particles adhere to one another as the pressure increases. After a certain point no closer packing can be obtained and particles are pressed against each other, undergoing elastic and plastic deformation and fiber interlocking (Piestch, 2002). In case of plant cells that contain a large inner volume (vacuole) filled with air (dried biomass) the cell structure breaks up and the vacuole is compressed. At the same time, cell wall compounds (i.e. lignin and hemicelluloses) are expected to be released from the cell and to interact with surrounding particles (Odogherty, 1989). Due to the high temperature and pressure lignin softens and flows, resulting in inter-diffusion and entanglement of polymer chains between adjacent fibers. This phenomenon has earlier been described as “solid bridge” formation (Kaliyan and Morey, 2010) and is important for the pellet strength (Stelte et al., 2011b). The density increases with pressure until it reaches a maximum which, in the case of plant biomass, can be expected to be close to the density of the plant cell wall.

The quality of the biomass pellets affects not only the ease of handling, but also the end-user application performance. Table 2.1 shows the important factors and their required values in the pellet quality. A pellet not only must be durable for safe handling during transportation and storage, but also needs to be efficiently convertible to chemicals or directly combusted to produce heat and power. Pellet quality is controlled by the feedstock characteristics, pelletizing conditions and system design of the pellet mill. Pelletization conditions include die temperature, pretreatment conditioning, pressure, feeding speed and retention/relaxation time. The design parameters of densification units include types of densification unit, die shape, and die specifications. The following sections first describe the pellet quality properties and then explain the role of each of the influencing factors on these properties.

### **2.3.1. Pellet dimensions, bulk density and single pellet density**

The mass and dimension of a pellet determine the density of a single pellet. The pellets are usually 6-8 mm in diameter and with a length of 2-4 times the diameter (12-30 mm). The unit particle densities of pellets are 0 to 1150 to 1250 kg/m<sup>3</sup>. The bulk density ranges in 650 to 750 kg/m<sup>3</sup>. There is a standard for defining physical dimensions and bulk density of biomass pellets set up by the European Committee for Standardization, CEN (TC335) (Alakangas et al., 2006).

### **2.3.2. Moisture resistance**

Hygroscopicity of biomass pellets defines adsorbing capacity of pellets for moisture. A moistened pellet tends to disintegrate into fines under high humidity. Materials are lost as fines and less material can be transported. High surface area of the small fines also favors the susceptibility of the microbial attack during storage (Lehtikangas, 2000). The microbial anaerobic digestion degrades the soluble and storage carbohydrates and leads to generation of local heat and toxic off-gassing, e.g. terpenes (Rupar and Sanati, 2005). Local heat generated ignites the volatiles in a bulk of stored pellets to cause self-ignition during storage. Accumulations of off-gases inside the storage silos are lethal to the workers during exposure. High moisture content of the pellets also reduces burning efficiency at the power plant. Therefore, hydrophobic pellets are desired to be tailor made for safe handling, storage and final usage.

### **2.3.3. Durability and mechanical strength**

The durability is reported as percentage of the total weight of a pellet sample after tumbling and removal of the fine fraction using a sieve size (normally 3.2 mm in diameter for a 6 mm diameter pellet) (ASABE S269.4, 2003). It is also an index to measure the resistance of pellets to break down into fines during transporting. Pellets with high durability are desired for safe handling and transportation as the fines may accumulate in conveyors and silos during processing. Fines lead to dust explosion and dust inhalation which threatens safety and health of workers in the pelleting plant and storage silos. Fines are also more susceptible for fungal attack which creates a risk of

off-gassing and finally self-ignitions inside the silos (Lehtikangas, 2000; Rupar and Sanati, 2005).

Hardness or mechanical strength is defined (in metallurgy) as the resistance of material to permanent deformation or breakage. Kaliyan and Morey (2006) reviewed major factors affecting strength and durability of pellets. In their study, the more durable pellets were mechanically stronger with respect to compressive forces. They suggested four major parameters affecting the durability and hardness of pellets; moisture content of feedstock, particle size distribution of grinds, binders (natural lignin and extractives content of the biomass feedstock), and compaction conditions including pressure, compression time and temperature. The other factors included raw material and the mixing of biomass feedstocks.

#### **2.3.4. *Moisture content of feedstock***

The effect of raw material moisture content on the pelletization and product quality has been the subject of numerous studies (Odogherty and Wheeler, 1984; Rhen et al., 2005; Mani et al., 2006b; Arshadi et al., 2008; Kaliyan and Morey, 2009a; Nielsen et al., 2009; Nielsen et al., 2010; Filbakk et al., 2011; Serrano et al., 2011; Carone et al., 2011; Stelte et al., 2011c)

Optimum moisture of feedstock for pellets production is lower in the case of wood than herbaceous. Usually moisture content of feedstock should not exceed 12% (wet basis). Nielsen et al. (2009) have shown that an increase in moisture content for pine and beech resulted in a decrease of the energy requirement for different components of the pelletizing process but the durability of pellets decreased. The moisture acts as a lubricant so as to reduce the wall friction and also decrease the glass transition temperature of the materials for better binding. Therefore, the optimum water content can act as both a binding agent and a lubricant during pelletization to produce good quality biomass pellets.

### **2.3.5. Particle size distribution**

Studies have been made about the impact of particle size on the compaction properties of biomass (Mani et al., 2006b; Filbakk et al., 2011; Serrano et al., 2011; Jensen et al., 2011; Stelte et al., 2011c). Stelte et al. (2011c) have shown that the friction in the press channel of a pellet mill increases with decreasing particle size for beech particles. Kaliyan and Morey (2009) showed that decreasing particle size for corn stover grinds results in an increased briquette density. Similar results were observed by Mani et al. (2006b) who found out that particle size significantly affects the pellet density for pellets made from barley straw, corn stover and switchgrass, but not in case of wheat straw. Smaller particles with a larger surface area per volume increase particle to particle contact area, thus facilitating a closer packing, resulting in denser and more durable pellets (Mani et al., 2006b). A study made by Serrano et al. (2011) indicated opposite results when they used an industrial pellet mill instead of laboratory scale single pellet press units. Bergström et al. (2008) have suggested that, under high forces (more than 3000 N), raw material particle size distribution had a minor effect on physical and thermo-chemical characteristics of produced pellets formed from Scots Pine sawdust. These results were of practical importance as if oversized particles (more than 6 mm) were sieved off, the grinding process could be eliminated resulting in a cost reduction (Bergström et al., 2008).

The disadvantage of producing fine grinds is to consume more energy in size reduction for production of higher quality pellets. It was found that the specific energy consumption of the corn stover grind increased from 0.8 to 1.3 MJ/t when the particle size decreased from 0.8 to 0.66 mm while that of switchgrass grinds increased from 2.5 to 4.3 MJ/t when the particle size decreased from 0.64 to 0.56 mm at 25°C (Kaliyan and Morey, 2006).

### **2.3.6. Biomass constituents**

The lignin of the biomass contributes to the bonding and stabilization during pelletizing. The lignin softens and melts and it exhibits thermosetting properties when the biomass is heated (van Dam et al., 2004). The lignin supports the bonding of particles in high pressure and high temperature densification. The content and structural

arrangement of lignin and hemicellulose affect the strength of biomass pellets (Back and Salmen, 1982). Lehtikangas (2001) reported that the durability of the pelletized sawdust, logging residues and bark is closely related to the lignin content of the biomass. The higher the lignin contents of the biomass, the higher the durability of the pellets.

The species of biomass and storage time determine the lignin content. It was found (Stelte et al., 2011b) that the lignin content increased from 38 % to 41 % when bark was stored for 3 months. Sawdust has the lowest lignin content of around 28 % when fresh and increased to 30% after stored for 6 months. There is a loss of organic substances during storage by leaching which results in an increase in lignin content. It has been shown that high extractive contents lower the friction in the press channel of a pellet mill (Nielsen et al., 2010; Stelte et al., 2011b; Stelte et al., 2012) and that high concentrations of extractives on the biomass particle surface can reduce the mechanical strength of densified biomass products (Bikerman, 1967; Stelte et al., 2011b; Stelte et al., 2012).

### **2.3.7. *Type of pellet mill and die specification***

Pellets are produced in a pellet mill that generally consists of a die with cylindrical press channels and rollers that force the biomass to flow into and through the channels. Due to the friction between the steel surface and the biomass in the press channel, a high back pressure is built up and heat is generated due to wall friction between feed material and the die wall. The majority of commercial pellet mills are of two configurations: ring die (Figure 2.2) and flat die (Figure 2.3). Ring die is a more common type of pellet mill used in commercial unit (Figure 2.2). Either the die or the rollers can be rotating, and due to that movement the biomass particles are squeezed into the openings of the press channel. Cut off knives mounted on the swing cover cut the pellets when they extruded from the die. The advantage of the ring die type pellet mill allows a higher production throughput compared to other types of presses (e.g. piston and screw presses), while maintaining the power consumption in the range of 15-40 kWh/ton (Grover and Mishra, 1996).

According to Tumuluru et al.'s review (2010), die geometry refers to the size and shape of the die. The die geometry determines the pellet dimensions as well as density

and durability. The L/D ratio (length to diameter of the pellet) is a metric for the degree of compression during pelletization. High L/D ratios provide high pellet die resistance as feed moves through the hole. Low L/D ratios provide less resistance. Each material has an L/D ratio requirement to form the material into a pellet. The durability of the pellets improved when a smaller die with higher L/D ratios was used (Tabil and Sokhansanj, 1996). In general, the die with a smaller diameter is easier to exert a high pressure on biomass feed materials to produce durable pellets.

### **2.3.8. *Die temperature***

Die temperature is determined by the frictional heat generated during expulsion and pelletization. It is not a controlled parameter in the real commercial pelletization process, although it may be indirectly controlled by the following factors. The frictional heat depends on the material species, particle size, moisture content of the feed and the speed of feeding (i.e. material feeding rate).

The durability and density of the pellets are highly influenced by the die temperature. Tumuluru et al. (2010) reported that the durability of pellets increased with die temperature.

The use of glass transition temperature ( $T_g$ ) to determine the processing temperature is also a key to produce durable pellets (Kalyan and Morey, 2009a; Stelte et al., 2011b). A higher die temperature than the glass transition temperature ( $T_g$ ) produces durable pellets. However, the die temperature should not be too high to dry the feedstock and to cause frequent blocking of materials inside the die (i.e. reducing the throughput capacity or even unable to produce).

It should be noted that different species of wood contain different amounts and types of lignin, in which they exhibit different  $T_g$ . The  $T_g$  of different species of wood ranges between 50–100°C depending on the moisture content. Hardwood lignin has fewer phenolic hydroxyl groups, and a substantially more methoxyl groups (Sjöström, 1983) than softwood, resulting in a significantly lower softening temperature of hardwood lignin than softwood lignin (Olsson and Salmen, 1992). This helps to explain why different wood species require different die temperatures to produce high quality pellets.

For example, hardwood pellets are stronger than softwood pellets, regardless of the low lignin content of hardwood (Stelte et al., 2011b). The higher strength of beech pellets compared to spruce can be explained in the same way. At lower  $T_g$  the wood fibers are more easily deformed to form the strong bonding under high pressure during pelletization at a lower compression temperature.

### **2.3.9. Pelletization pressure and relaxation time**

The pressure the biomass is exposed to during pelletizing has a significant impact on the product density and durability as well as on the process energy consumption and has therefore been a subject of various studies (Odogherty and Wheeler, 1984; Mani et al., 2006b; Gilbert et al., 2009; Kaliyan and Morey, 2009a; Adapa et al., 2009; Stelte et al., 2011c; Carone et al., 2011). Maximum applied pressures range from 50 MPa to 600 MPa. There is a general tendency that the pellet density does increase only incrementally at pressures above 50 to 100 MPa (Mani et al., 2006b; Adapa et al., 2009; Stelte et al., 2011c). The mechanical properties, compressive strength (Gilbert et al., 2009) and durability (Kaliyan and Morey, 2009b; Carone et al., 2011) improve with increasing pressure and follow a saturation curve, indicating that the plant cell wall density is the upper limit that can be reached (Stelte et al., 2011c). Building up pressure by motor power either in a pellet mill or briquetting press consumes energy and it seems clear that, above a certain threshold which is somewhere above 100 MPa, additional energy input into the process mainly results in excess heat instead of density and stability increase of the pellets.

Retention/relaxation time refers to the holding durations the biomass remains inside the die. It is usually around 5–30 seconds. During this time, it allows enough time for the biomass particles to densify without a significant spring back. The relaxation time has a significant effect on the final density of the pellet during low pressure compaction. At high pressure compaction, the relaxation time did not show a significant effect on pellet density.

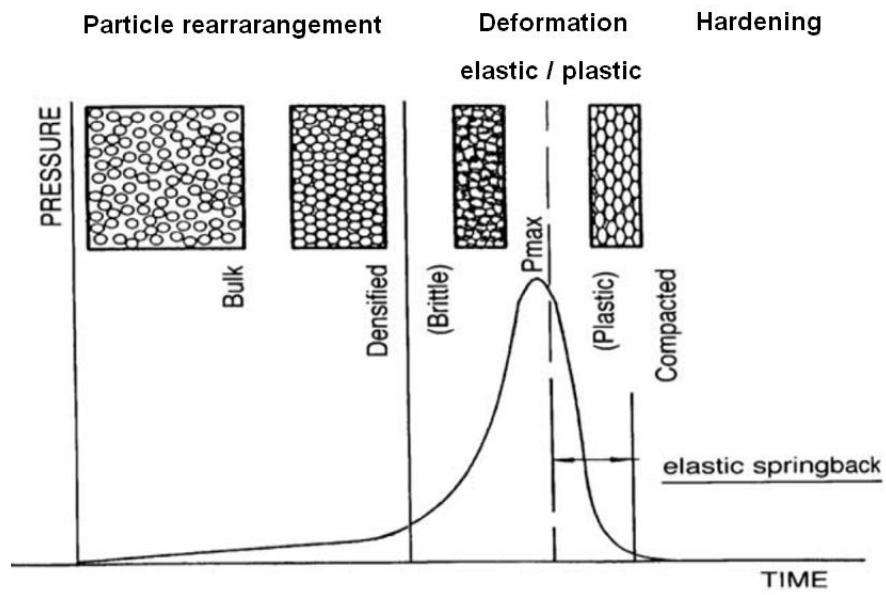


## **2.4. Concluding remarks**

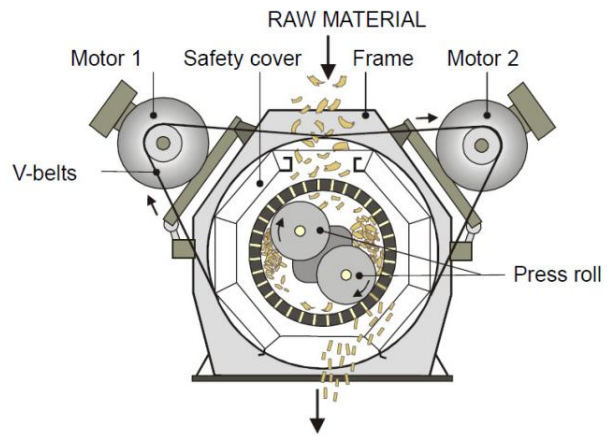
In this chapter, the structure and composition of woody biomass was briefly described. The concept of hydrothermal treatment was introduced. This critical literature review along with the background on quality properties of pellets and influencing factors on these properties would help familiarization with the subject matter and with the experimental data and discussions to be presented in the following chapters.

**Table 2.1 Quality requirements of the wood pellets (% dry weight) (Mosiera et al. 2005)**

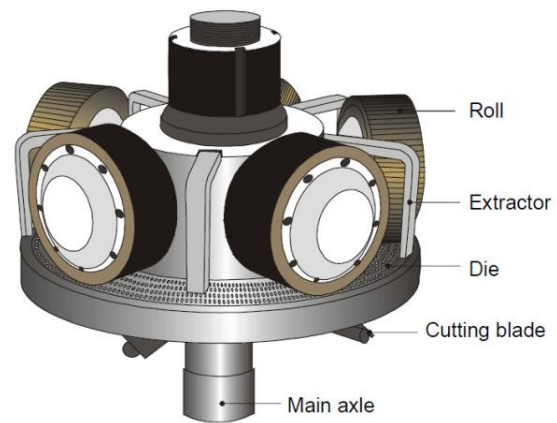
Parameter	Effect	CEN Standards for wood pellets
Moisture content	Storability, spoilage, calorific value, self ignition, drying cost	Moisture < 10 wt%
Ash content	Heating value, milling and pelleting equipment, combustion	< 0.7 wt% of dry matter
Calorific heating value	Fuel utilization, plant design	$\geq 4.7$ kWh/kg (i.e. 16.9MJ/kg)
Particle size distribution	Unit density of pellets, pellet quality including hydrophobicity	N/A
Sulphur and Chlorine content	Toxic emission, melting point of ash, formation of deposits in the furnace during combustion, corrosive to the furnace wall	< 0.05 wt % of dry matter for Sulphur
Extractives content	Binding quality, durability, hardness, ignition, storability, emissions	N/A
Klason lignin content	Binding quality, durability, hardness	N/A
Length (L) and diameter (D)	Combustion properties, specific heat conductivity, rate of gasification, fuel feeding properties	- D: $6 \pm 0.5$ mm and $L < 5 \times$ diameter or - D: $8 \pm 0.5$ mm and $L < 4 \times$ diameter - Maximum 20 wt% of the pellets may have a length of $7.5 \times$ diameter
Bulk density	Transportation load and cost	$> 600$ kg/m <sup>3</sup>
Durability	Handling and transport	- 97.5 wt% of a pellet batch of 100 g shall be uncrushed after testing - Percentage of fines among pellets sieved through < 3.15 mm sieve shall not exceed 1 or 2 wt % at factory gate
Hardness	Resistance to deformation and abrasion, change of structure, properties under pressure	N/A



**Figure 2.1 Compression curve (Sokhansanj et al., 2005)**



**Figure 2.2 Ring-die pellet mill (Stelte et al., 2012)**



***Figure 2.3 Flat die pellet mill (Stelte et al., 2012)***

## Chapter 3. Description of experiments

### 3.1. Introduction

Application of steam for drying of wood pieces has been practiced commercially; but the steam treatment is usually performed at the atmospheric pressure. At atmospheric pressure, the moisture inside the material evaporates at about 100°C. Our preliminary experiments conducted at the University of Manitoba (Appendix A) showed that atmospheric steam could not change the chemical composition of woody materials. Pressurized superheated steam enables the moisture inside biomass to remain in the liquid phase inside particles up to high temperatures required for the degradation of hemicellulose components. Several pressurized steam set-ups and tests are described in this chapter.

### 3.2. Materials and methods

#### 3.2.1. *Materials*

Both woodchips and ground samples were prepared for these sets of experiments. The biomass material tested in this research consisted of three white softwood species, Douglas fir (*Pseudotsugamenziesii*), Pine (*Pinus contorta*), Spruce (*Picea glauca*) and one sample of bark from Douglas fir (D. Fir). These trees constitute the majority of species of the forests in British Columbia (BC), Canada. Large pieces of Pine and Spruce lumber were provided by the Centre for Advanced Wood Processing, Faculty of Forestry at the University of British Columbia. These samples originally came from Williams Lake forests, in the central region of BC. Branches of recently cut Douglas fir were provided by Malcolm Knapp Research Forest, located in Maple Ridge, BC.

### **3.2.2. Sample preparation**

The large freshly cut wood pieces were brought to the lab and debarked manually, split using a band saw (Craftsman 14" band saw, Sears Canada Inc.), and then chipped and screened to an approximate size of 20 × 20 × 5 mm chips. The white woodchips and bark samples were dried naturally in the laboratory environment to lower the moisture content from 50% (moisture contents MC are expressed in wet mass basis or stated otherwise) to about 20% MC by spreading wood pieces on wire mesh trays in a stack in the lab. All MC in this research are measured using the convection drying oven method according to the ASABE standard S358.2 (ASABE, 2008a). Half of the dried woodchips were then ground in a hammer mill (Model 10HMBL, Glen Mills Inc., Clifton, NJ) with a screen size of 1.6 mm. The MC of ground samples and woodchips was adjusted to the desired MC for each test, either by drying high moisture material in the convection oven (THELCO laboratory PRECISION oven, Thermo Electron Corporation) set at 80°C or spraying distilled water on the over-dried samples. The amount of material conditioned was about 800 g for each species. The conditioned samples were kept inside sealed plastic bags and stored inside the cold room at 4°C before pretreatments or physical, chemical, or thermal analyses.

### **3.2.3. Hydrothermal treatment setups**

Steam pretreatments were carried out in a modified closed batch reactor setup (Figure 3.1) that has previously been developed at the Clean Energy Research Centre (CERC) laboratory, University of British Columbia (Lam, 2011). The process flow diagram of the whole setup is depicted in Figure 3.2. The unit consists of a 2 L steam generator, generating saturated steam, and a 1 L pressure vessel reactor (Model 316L SS Double-Ended DOT-Compliant Sample Cylinder, Swagelok) for steaming biomass samples. The heat for the steam generator was supplied by a 3 zone tubular furnace (Lindberg/Blue M, STF55666C). The 1 L reactor was equipped with a 12.7 mm diameter ball valve, controlled by an electrical actuator for rapid discharging of the treated biomass into ambient pressure. A surface mounted thermocouple connected to a temperature controller regulated the power input to the heater wrapped around the reactor. The details and functions of valves in the experiment unit are summarized in Table 3.1. Temperatures and pressures were measured by 1.6 mm diameter K-type

thermocouples (Omega, Stamford, USA) and digital pressure transducers (Omega, Stamford, USA), respectively. Thermocouples and pressure transducers are summarized in Table 3.2. Data were acquired and saved by LabView 8.2 software (National Instruments, Austin, Texas, USA). The data acquisition card used is PCI DAS-08. The data logging rate for was selected as 1 Hz (1 data point per second). Temperature and pressure were measured based on the logged voltage signals and converted to degree Celsius and pound per square inch, respectively.

### **Treatment of ground dry biomass**

In each experiment, 300 mL of distilled water were used to generate saturated steam. 2 L of distilled water were loaded into the water tank and pumped into the steam boiler by a water supply pump. Before loading the water, ball valves B-4 and B-6 were opened to purge the remaining water. The opening of B-4 valve facilitates faster water drainage as trapped air can vent through that valve. Ball valve (B-2) has to be always kept closed during water purging and loading. Prior to biomass loading, ball valve (B-1) is closed. 25 g biomass powder was loaded through the ball valve B-3 into the 1 L reactor.

Steam was generated inside the boiler and the temperature ( $T_1$ ) kept increasing to the target temperature, e.g., 200°C after an hour. When the temperature of the generated steam ( $T_1$ ) reached 150°C, the temperature controller was switched on to maintain the reactor at set temperature. The ramping rate of the temperature controller was set to allow the target reactor temperature ( $T_4$ ) of 200°C being reached simultaneously when the temperature ( $T_1$ ) of steam generated in the steam generator reached 200°C. This helped to prevent the prolonged heating of the biomass inside the reactor before steaming. When the steam temperature reached the target reaction temperature, ball valve (B-2) was opened to allow the saturated steam transferred to the reactor chamber to treat the 25 g sample for a pre-specified period of time.

The control of the ball valve (B-1) for rapid opening to discharge the steam to cook biomass was done by the Labview control program. Two switches were used to control the signal through the digital port to open/close the ball valve (B-1). When both output signals are high (1), the ball valves will open. When one of the output signal is high (1) and the second output signal is low (0), the ball valve will close.



Treated samples were discharged into ambient conditions (101.13 kPa, 23°C) by opening the ball valve after 5 min of treatment. The pressure of the chamber was rapidly decreased to ambient gauge pressure within 3 s. Treated samples were collected in a plastic bag inside the collection chamber and kept at 6°C in a refrigerator for further analysis. The preliminary run showed that the experiments were repeatable at the same processing condition.

### **Treatment of ground wet biomass**

As the objective of these experiments is to dry and treat the biomass simultaneously, the ball valve (B-2) was kept closed (no transfer of saturated steam from the boiler to the reactor). In each experiment, specific amount of wet biomass (around 50 g or 17 g) with about 50% MC was loaded to the reactor (not preheated before). Based on the amount of loadings and moisture content, we could calculate the amount and specific volume ( $\text{cm}^3/\text{g}$ ) of water present in a closed fixed volume of the vessel, considering the occupied volume by biomass itself. The top inlet was sealed after loading. The heater around the pressure vessel heated up the content of the reactor till the inside temperature reached the set temperature (180°C -280°C). Once the temperature was reached, the biomass kept at the set temperature for 5 min and then the content of the reactor discharged suddenly into a cloth mesh bag (Spectra Nylon mesh, 20 $\mu\text{m}$  opening, USA) at the ambient temperature and pressure. The cloth opening mesh size was chosen in such a way that it allowed the passage of steam molecules but not the solid particles. So, the drying effect could be calculated by comparing the final MC vs. the initial MC. The MC of collected material was measured immediately after collection (ASABE, 2008a). The treated materials were kept in sealed plastic containers at 6°C for further analysis.

### **Treatment of woodchip samples**

Prior to steam pretreatment, the woodchips were impregnated by adding a specified amount (about 12 g) of  $\text{SO}_2$  (4% wt/wt of the substrate) to a sealable plastic bag containing 300 g dry weight of chips (Bruno et al., 2009; Ewanick et al., 2007). Once the desired amount of  $\text{SO}_2$  entered the bag, the bag was immediately sealed and left for approximately 12 h before steam treatment. After 12 hours, the bags were opened under the fume hood to let the residual  $\text{SO}_2$  escape for 60 minutes. The amount of  $\text{SO}_2$

retained in the biomass was calculated by weighing the substrates with absorbed SO<sub>2</sub>. Steam pretreatment was conducted in a 2 L StakeTech (Stake Tech-Norvall, Ontario, Canada) steam gun at 200°C for 5 min. This treatment regime had previously been shown to be effective for Douglas fir woodchips (Lam et al., 2011; Kumar et al., 2010). A higher ratio of biomass to steam (1.0:1.5 w/w) was used to reduce moisture uptake by the solid in order to minimize post drying of the solids fraction. The higher ratio of biomass to steam was achieved by increasing the amount of biomass aliquots in each batch run from 50 g to 220 g dry weight of the chips. This higher solid-steam ratio is a deviation from previous studies (Ewanicket al., 2007; Kumar et al., 2010) where the objective has been to maximize sugar recovery. Instead of having slurry and two fractions of the water soluble (WS) and insoluble (WI), only one wet solid fraction with MC of about 60% was recovered after steam treatment. No washing of treated material was done in order to keep the moisture as low as possible. The optimum MC for pelletization was reported to be between 9-15% depending on different feedstock (Mani et al., 2006a; Relova et al., 2009). The treated materials were kept in sealed plastic containers at 6°C for further analysis.

#### **3.2.4. *Measurements on ground samples***

The following paragraphs describe the methods used to determine physical and compositional properties of the treated and untreated samples.

##### **Moisture content and solid yield**

Moisture contents of the samples were analyzed according to ASABE standard S358.2 (ASABE, 2008a). Around 1 g of each sample was used for MC measurement. Triplicate samples were oven dried at 103°C for 24 hours and MC was reported in wet basis. We assumed that the residual moisture after 24 hours is negligible and the loss of volatiles does not affect the mass loss significantly during MC measurement. The solid yield was calculated based on the dry mass recovered vs. the initial dry mass for each loading.

## Particle size distribution

The analysis of size distribution for both treated and untreated particles was conducted by sieving in accordance with the ASAE standard S319.4 (ASAE, 2008b). Prior to a sieving analysis, samples were conditioned to  $10 \pm 0.5\%$  MC. Roughly 20 g of the analyzed sample was placed on top of a stack of sieves on a Ro-Tap shaker (Tyler Industrial Products, Cleveland, OH). The sieve series selected were based on the range of particles in the sample (Mani et al., 2006b). Sieve mesh numbers used were 20, 30, 40, 50, 70, 100, 140, and 200 corresponding to nominal US sieve openings of 0.841, 0.595, 0.420, 0.297, 0.210, 0.149, 0.105, and 0.074 mm, respectively (ASAE, 2008b). The duration of sieving was 10 min, which was previously determined through trials to be optimal (Mani et al., 2006b). The mass retained on each sieve and in the pan was weighed on an electronic balance to 0.01 g precision. The sieving test was repeated three times for each sample and the weighted mean diameter ( $d_m$ ) of particles was calculated. The geometric mean diameter ( $d_{gm}$ ) and geometric standard deviation ( $S_{gm}$ ) of particle diameters were calculated according to the Standard S319.4 (ASAE, 2008b).

## Compositional analyses

Raw material and treated material were analyzed in triplicate for insoluble (Klason) lignin, hemicellulose and cellulose contents using the modified Tappi T-222 om-88 method as previously described as the NREL-LAP method (Sluiter et al., 2008a). The hydrolysate from this analysis was retained and analyzed for hemicelluloses sugars and cellulose using a HPLC (ICS-2500) equipped with an AS50 auto sampler, an ED50 electrochemical detector, a GP50 gradient pump, and an anion exchange column (Dionex, CarboPac PA1). Deionized water at 1 mL/min was used as an eluent, and post column addition of 0.2 M NaOH ensured optimization of baseline stability and detector sensitivity. After each analysis, the column was washed with 1 M NaOH. Twenty  $\mu\text{L}$  of each sample was injected after filtration through a 0.45  $\mu\text{m}$  syringe filter (Chromatographic specialties, Brockville, Canada). Standards were prepared with seven serial dilutions containing sufficient arabinose, galactose, glucose, xylose, and mannose to encompass the same range of concentrations as the samples. Fucose (0.2 g/L) was added to all samples and standards as an internal standard.

The ash content of each sample was measured in triplicate using the NREL method (Sluiter et al., 2008b). For ash content measurement, about 0.5-1.0 g of completely dried powdered samples were used. The higher heating value (HHV) of solid samples was determined in an oxygen bomb calorimeter (Model 6600, Moline, IL) fitted with continuous temperature recording. A small mass of 0.6-1.2 g ground sample was densified manually in the Parr pelleter and placed in the instrument chamber. The measurements were repeated three times (three different pellets). The carbon, hydrogen, nitrogen and sulfur contents of both treated and untreated samples were determined on dry basis using a CHNS analyzer (Model 2400 series II, PerkinElmer Company, MA USA). Assuming that only oxygen is present in the woody material aside from these elements, we calculated the oxygen content by subtracting the sum of these measured components from 100%. The elemental analyses were repeated twice for each untreated and treated material.

### **Density measurements**

Bulk density was calculated following the method previously used by Mani et al. (2006b) for ground cellulosic materials. A glass cylinder with a volume of 25 mL and inside diameter of 25.4 mm (about 50 times larger than the maximum of average particle sizes among the samples) was used. A funnel was filled with the biomass powder. The biomass powder was poured freely into the cylinder from a height of 200 mm. Overflow excess material was stroke off gently from the top of the cylinder by a rubber-coated steel rod (Mani et al., 2006b). The ratio of mass of the sample divided by the occupied volume of sample in the glass cylinder was calculated as the bulk density (loose bulk density). For tapped density, the loosely filled glass cylinder was tapped on the laboratory bench 15 times, while any produced free volume on top was again filled up with the material (Lam et al., 2008). Bulk and tapped densities were determined in triplicates for each sample. The particle solid density was determined using a Quantachrome Multipycnometer (Quantachrome, Boyton Beach, FL, USA). The analysis was done by measuring the pressure difference when a known quantity of pressurized nitrogen flows from a reference volume into the sample cell. The volume of solid particles in the sample cell then is calculated based on the following equation,

$$V_p = V_c - V_R \left[ \frac{P_1}{P_2} - 1 \right] \quad 3-1$$

where  $V_p$  is the true volume of biomass grinds ( $m^3$ ),  $V_c$  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 reading after including  $V_c$  (Pa). The density (bulk and particle) was calculated from dividing mass over volume ( $V_p$  in case of particle solid density).

Inter particle porosity ( $\varepsilon_0$ ) provides packing information of the biomass grinds inside a known container and is determined by:

$$\varepsilon_0 = 1 - \frac{\rho_b}{\rho_p} \quad 3-2$$

where  $\varepsilon_0$  is packing porosity (decimal),  $\rho_b$  is bulk density of ground ( $kg/m^3$ ),  $\rho_p$  is particle density of the ground ( $kg/m^3$ ). Particle density and porosity for each species were measured three times.

## Color

The color of each sample was measured in triplicate using Spectrophotometer CM-5 (Konica-Minolta). The color was characterized using a three-dimensional (L a b) color scale as shown in Figure 3.3. The scale L ranges from 0 for black to +100 for white; the scale a ranges from -50 for green to +50 for red; and the scale b ranges from -50 for blue to +50 for yellow. The color coordinate values for each sample before and after steam treatment were measured. A differential color composite  $\Delta E$  was calculated as an indicator of color deviation between treated and untreated samples,

$$\Delta E = \sqrt{(L_2 - L_1)^2 + (a_2 - a_1)^2 + (b_2 - b_1)^2} \quad 3-3$$

where subscripts 1 and 2 represent sample 1 (untreated) and sample 2 (treated).

### **Scanning electron microscope (SEM)**

SEM observations of the ultra-structure and surface were carried out on samples. The powder samples were mounted on specimen stubs and coated with gold under vacuum. All photographs were taken at 10 to 20 kV accelerating voltage by using a field emission scanning electron microscope, Hitachi S4700 (Hitachi, Japan) in UBC bio-imaging facility.

#### **3.2.5. Pelletization**

Two different pelletization set-ups have been used in this study. Figure 3.4a and b are pictures of both set-ups. The first assembly consisted of three parts (Figure 3.4a): (1) a piston with 6.30 mm diameter and 90 mm in length, (2) a cylinder with 6.35 mm inside diameter and 70 mm long, (3) a heating tape wrapped around the outer body of the cylinder, and temperature control system. The piston was bolted onto the crosshead of an MTI (Measurement Technology Inc., Roswell, GA) model 50K universal mechanical testing machine. The open bottom of the cylinder was closed during compression by placing a removable block under the cylinder. The body of the cylinder was heated and maintained at about 100°C. The cavity in the cylindrical die was filled with  $0.9 \pm 0.02$  g of the ground and steam treated biomass using a spatula.

The MTI was preset to the different maximum forces on the piston, 2000, 4000 and 6000 N. The downward measured displacement speed was set at 6.7 mm/min. The bulk biomass in the cylinder was compressed to the preset maximum force and held for 30 s to arrest the spring back effect of the biomass. To eject a pellet from the die, the block under the cylinder was removed from the underneath of the pellet and the crosshead's downward motion was activated at a speed of 10 mm/min. The piston pushed the formed pellet out of the cylinder.

The second assembly was also consisted of three parts (Figure 3.4b): (1) a piston with 6.32 mm diameter and 90 mm in length, bolted onto a rectangular top surface with four holes on the four corners, (2) an open end cylinder with 6.35 mm inside diameter and 70 mm length, attached to a rectangular bottom surface with four poles on the four corners, (3) a heating tape wrapped around the outer body of the cylinder.

The open bottom of the cylinder was closed during compression by placing a removable block under the cylinder. A 12 or 24 mm solid cylindrical spacer placed in the die to rest on the block. The spacer came out of the compression channel by removing the block from the bottom of the die. The body of the cylinder was heated and maintained at about 70°C. The cavity in the cylindrical die was filled with approximately 0.9 g of biomass using a spatula. The crosshead of a MTI (Measurement Technology Inc., Roswell, GA, model 50K universal) mechanical testing machine pressed on the center of the top surface, so that the four holes were engaged with the four poles and the piston was aligned against the cylindrical die. The MTI was preset to a maximum force of 4000 N on the piston. The downward measured displacement speed was set at 10 mm/min. The bulk biomass in the cylinder was compressed to the preset maximum force and held for 30 s to arrest the spring back effect of the biomass. To eject a pellet from the die, the block under the cylinder was removed from the underneath of the pellet and the crosshead's downward motion was reactivated at a speed of 10 mm/min. The piston pushed the formed pellet out of the cylinder. The produced pellet was cooled to room temperature and stored inside a sealed glass bottle for further measurements. In most cases, 20 pellets were made from each steam treated and untreated samples.

### **3.2.6. *Pellet property measurements***

The density of each pellet was measured by dividing its mass by the pellet volume. The volume was calculated by measuring pellet diameter and length using a digital caliper. To evaluate the mechanical strength, each time, one pellet was placed between two steel circular platens under the MTI crosshead (Figure 3.5). The compression was diametrical. The load vs. displacement data to a complete crushing of a pellet was recorded. The maximum force for breakage of pellets was recorded.

Force vs. displacements data during compaction of pellets in the die and during expulsion out of the die was recorded every two seconds. The area under force vs. displacement curves were integrated to yield mechanical energy (J) input required to make a pellet (excluding external heat input) (Figure 3.6),

$$E = \sum_{i=1}^n F_i \cdot \Delta L_i \quad 3-4$$

F is force (N) at distance  $i$  interval,  $\Delta L$  is deformation at distance  $i$  interval. The total displacement used in the calculation was from origin to that when the maximum of the force applied to make a pellet was reached. The total displacement used to expel a pellet from the die was 12 or 24 mm, the length of the spacer. The energy for compression of a pellet and the energy for expulsion of the pellet were normalized by dividing the calculated energy values by the density of pellets. The results are reported in J/(g/cm<sup>3</sup>) or J.cm<sup>3</sup>/g. This normalization compensates for variation in volume and mass of each pellet.

The higher heating value (HHV) of solid samples was determined in an oxygen bomb calorimeter (Model 6600, Moline, IL) fitted with continuous temperature recording. A small mass 0.6-1.2 g of densified sample was placed in the instrument chamber. The measurements were repeated three times (on three different pellets).

Moisture adsorption rate of pellets was measured by placing three untreated and treated pellets in a controlled environment chamber (Model LHU-113, ESPEC Corp., Japan). The pellet samples were completely dried initially. The chamber temperature was set at 30°C with a relative humidity (RH) of 90%. The increase in mass of the sample was monitored and recorded every 10 min for the first hour and every 30 min afterwards. The weight recording was continued until it reached a constant value (Lam et al., 2011). The MC calculated from this final mass was considered as the equilibrium MC ( $M_e$ ) of the material. The kinetics of moisture sorption is represented using the ASABE standard S448.1 formulation for thin-layer drying (ASAE, 2001),



$$\frac{M - M_e}{M_i - M_e} = e^{-kt} \quad 3-5$$

M is instantaneous MC (decimal, dry basis),  $M_e$  is equilibrium MC (decimal, dry basis), and  $M_i$  is initial MC (decimal, dry basis). Coefficient k is the adsorption rate constant ( $\text{min}^{-1}$ ), and t is exposure time (min) (ASAE, 2001). For adsorption,  $M_i = 0$ , above equation reduces to

$$M = M_e(1 - e^{-kt}) \quad 3-6$$

Constant  $k$  in this equation is the adsorption rate constant.

### 3.3. Concluding remarks

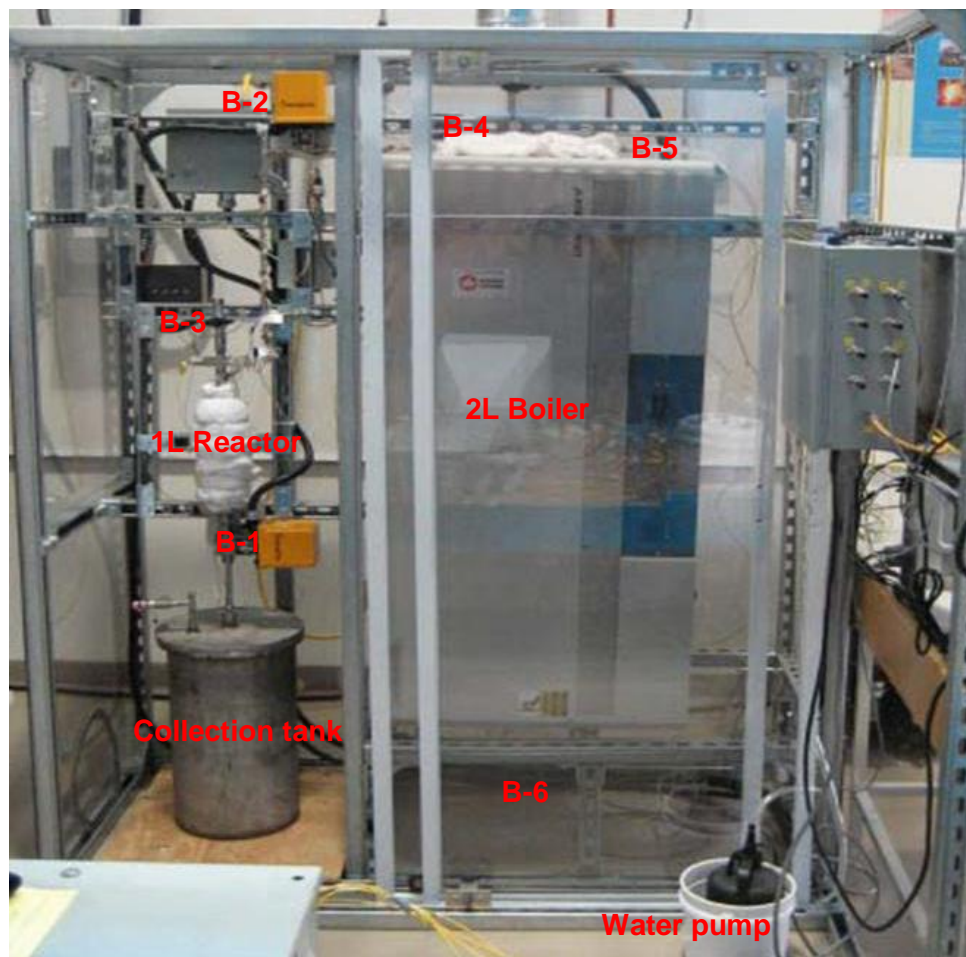
In this chapter, the details of experimental equipment and procedures were described. The biomass test material was subjected to several hydrothermal pretreatments. Characterization procedures of untreated and treated samples were explained. Equations for data reduction and analysis were outlined. All this information is applicable in the next chapters and referred to, later on.

**Table 3.1 List of valves in the experimental unit**

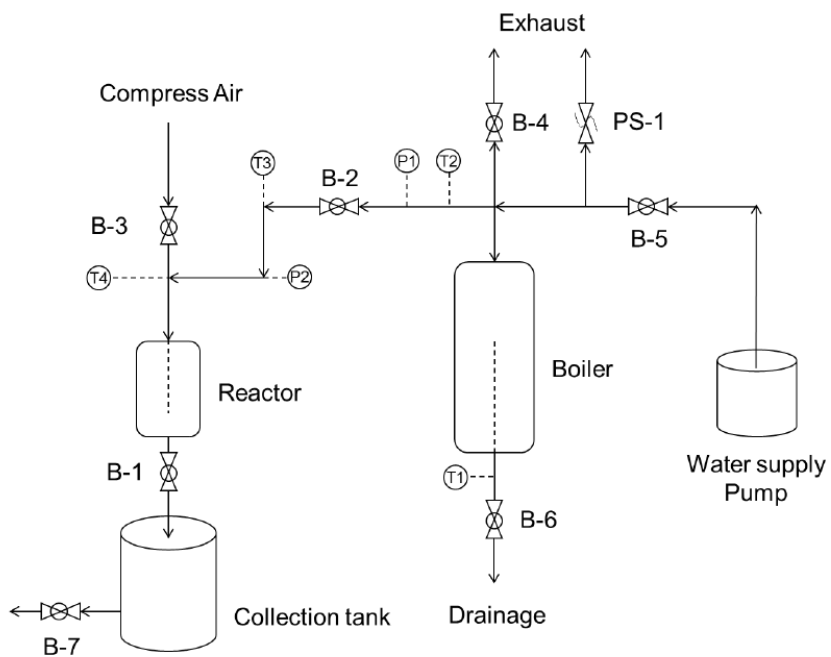
Component	Code	Operation mode	Function
Ball valve	B-1	Electric actuated – Computer control	Close: Maintain steam in the reactor Open: Allow rapid decompression of biomass and steam and extrude out to the collection tank
Ball valve	B-2	Electric actuated – Switch	Close: Allow steam treatment in steam boiler Open: Allow saturated steam to pass to the reactor
Ball valve	B-3	Manual	Close: Always close if not purging the reactor Open: Open if purging
Ball valve	B-4	Manual	Close: Always close during steam generation and water loading in the boiler Open: Open if after small amount of water loading to remove trapped air
Ball valve	B-5	Manual	Close: Always closed if not loading the water Open: Facilitate the water loading into the boiler
Ball valve	B-6	Manual	Close: Always closed during water loading and steam generation Open: Open only when drainage
Ball valve	B-7	Manual	Close: Always closed Open: Open only for gas sampling
Pressure relief valve	PS-1	Automatic	Threshold pressure pre-set value: 750 PSI

**Table 3.2 List of thermocouples and pressure transducers in the experiment unit**

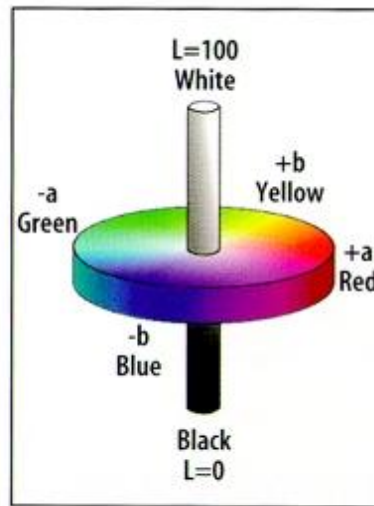
Component	Code	Type	Function
Thermocouple	T <sub>1</sub>	1/16" diameter, 36" length, K-type, Ceramic end	Measure the temperature of the steam inside the generator
Thermocouple	T <sub>2</sub>	Surface mounted type, K-type, Operation temperature maximum 350°C	Measure the surface temperature of the steam-line in the generator section and provide feedback control to maintain the steam-line temperature
Thermocouple	T <sub>3</sub>	Surface mounted type, K-type, Operation temperature maximum 350°C	Measure the surface temperature of the steam-line in the reactor section and provide feedback control to maintain the steam-line temperature
Thermocouple	T <sub>4</sub>	1/16" diameter, 18" length, K-type	Measure the reaction temperature inside the reactor
Pressure transducer	P <sub>1</sub>	¼" MPT, Digital, 0 – 1000 psi	Measure the pressure of the steam generated in generator
Pressure transducer	P <sub>2</sub>	¼" MPT, Digital, 0 – 1000 psi	Measure the pressure of the steam in the reactor during steaming



**Figure 3.1** *Hydrothermal pretreatment experimental set-up*

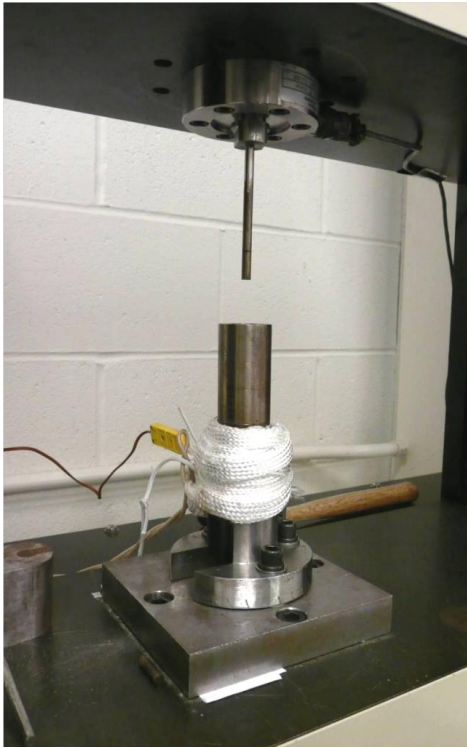


**Figure 3.2 Flow diagram of hydrothermal pretreatment experimental set-up**

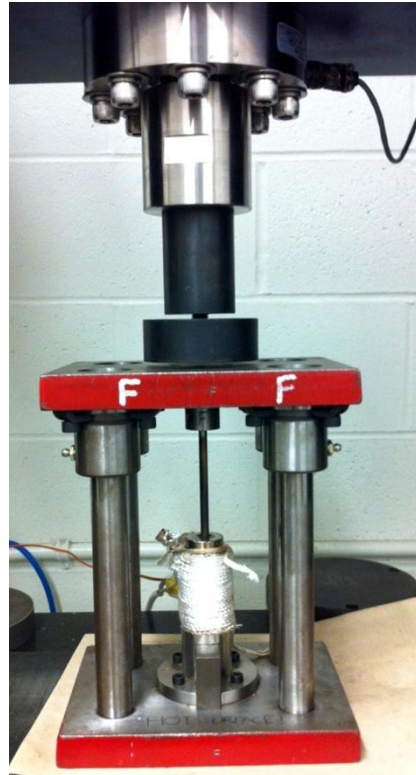


*Lab model*

**Figure 3.3  $L$ ,  $a$ ,  $b$  coordinates of color in the Lab system**

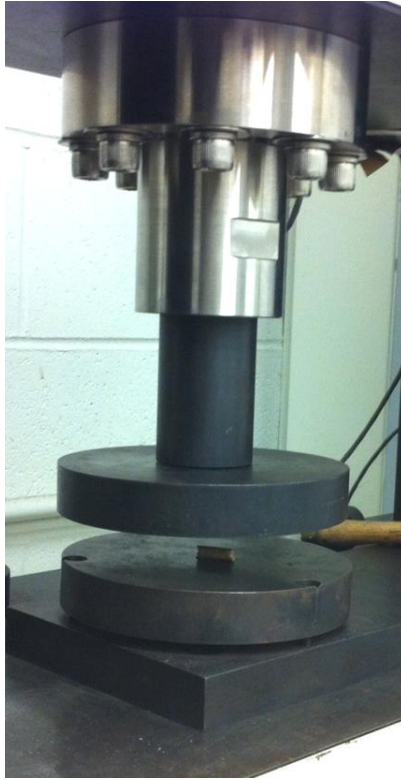


(a)



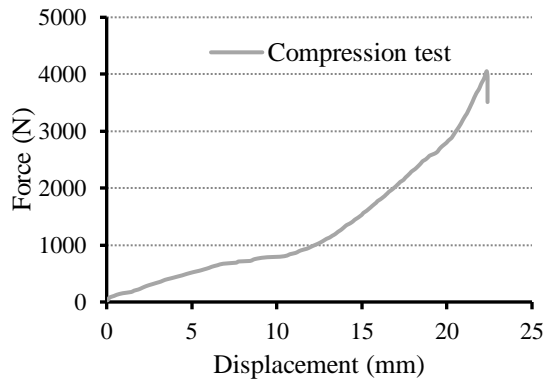
(b)

**Figure 3.4** The pelletization set-ups consist of a cylinder piston arrangement. The cylinder is wrapped with electric heating tape; (a) a fixed piston-cylindrical die pelletizer assembly, (b) the posts guide the movement and alignment of the piston with respect to the die. The entire assembly is placed under MTI for making single pellet.

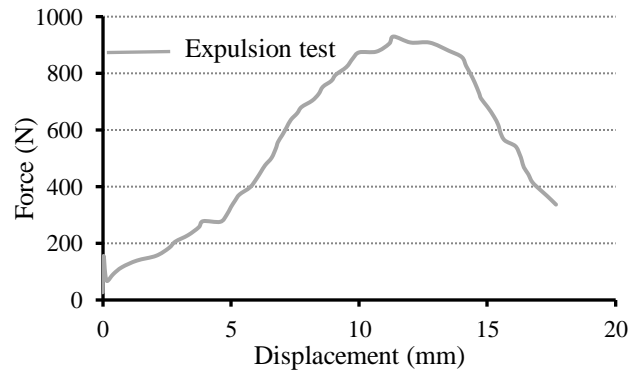


***Figure 3.5 Mechanical strength test set-up. A single pellet is placed under two platens. The top platen is lowered and forced on the pellet until the pellet disintegrates.***





(a)



(b)

**Figure 3.6 MTI generated plots of force vs. displacement. (a) The plot of compression curves for untreated material and (b) the lower plots of expulsion curves of pellets out of die for untreated material. The areas under these curves are computed to yield energy input for compression and energy input for pellet expulsion.**

## **Chapter 4. Steam treatment of softwood species and bark to produce durable torrefied pellets**

### **4.1. Introduction**

The available volume of saw mill residue, the traditional source of feedstock for wood pellets, has decreased recently due to the slowdown in housing market and the increased production capacity of pellet plants (Bradley, 2011). An increasing number of pellet producers are using a greater proportion of forest residues (a blend of different wood particles and bark) to make up the deficit in raw material. Unfortunately the non homogeneity of the feedstock results in low mechanical stability of pellets. In addition to a low mechanical strength, the low energy density of wood pellet as compared to coal is a serious issue for an exporting country like Canada where wood pellets travel long distances. Therefore improving energy density and strength of pellets are two key factors for a continued growth of the industry. Torrefaction is a pyrolytic process that subjects a feedstock to thermal treatment and can convert diverse lignocellulosic biomass feedstocks into an energy-dense and homogeneous solid biofuel (Phanphanich and Mani, 2011). The downside of torrefaction is its detrimental effect on natural binding capacity of the treated biomass to form pellets (Gilbert et al., 2009; Stelte et al., 2011a). On the other hand, saturated steam pretreatment has increased the binding quality of woody material (Shaw et al., 2009; Lam et al., 2011; Biswas et al., 2011). Knowing the positive effect of steam treatment on the binding characteristics of D. Fir particles, this research is an extension of previous studies of Lam et al. (2011) to three species of softwood Pine, Spruce, and D. Fir bark. The objective is to understand whether steam treatment of ground wood particles has differing effects on physical and compositional characteristics of ground particles that would affect the degree of carbonization (torrefaction) of softwood particles. The mechanical strength of pellets made from steam treated biomass and specific energy used to make pellets from these treated wood species are investigated in this chapter.

## **4.2. Materials and methods**

### **4.2.1. *Materials***

The biomass material tested in this research consisted of three white softwood species, Pine (*Pinus contorta*), Spruce (*Picea glauca*), and Douglas fir (*Pseudotsuga menziesii*); and one sample of bark from Douglas fir (D. Fir). These trees constitute the major makeup of species of the forests in British Columbia (BC), Canada. Large pieces of Pine and Spruce lumber were provided by the Centre for Advanced Wood Processing, Faculty of Forestry at the University of British Columbia. These samples originally came from Williams Lake forests in BC. Samples of D. fir white wood and bark were provided by Malcolm Knapp Research Forest, located in Maple Ridge, BC. The freshly cut stem wood pieces were brought to the lab and debarked manually.

### **4.2.2. *Equipment and procedure***

Steam treatments were carried out in a 1 liter treatment vessel. The treatment setup has previously been developed and calibrated at the Clean Energy Research Centre Laboratory, University of British Columbia (Lam, 2011). Approximately 25 g of each sample of ground wood was fed to the preheated reactor whose body temperature was maintained at 220°C. The saturated steam at 220°C, with a flow rate of 1 cm<sup>3</sup>/s from the 2 L boiler, was fed to the treatment vessel for treatment of the particles for 5 minutes. The treated sample was released at once through a gate valve into a collection container and cooled down before placing it into a plastic bag for further analysis. The moisture content of the solids was measured three times immediately after their release from the treatment vessel. Other physical (particle size distribution, color, bulk and particle densities, moisture adsorption capacity) and compositional characteristics (Ash and elemental contents and calorific heating value) of untreated and treated ground particles were measured and compared after conditioning of the material to the required moisture content for each test. Pellets made of treated and untreated samples were prepared by the piston-die single pelletizer (10 pellets for each wood species sample) under 4000 N force load. Different mechanical properties of these pellets were measured and compared. Figure 4.1 shows the appearance of ground wood and pellets made from untreated (Left) and treated (Right) biomass.

## **4.3. Measurements on ground samples**

### **4.3.1. *Moisture content***

The initial moisture content of the raw wood species averaged consistently at 11% (d.b.) with standard deviation of 0.1% (Table 4.1). The moisture content of treated biomass increased, because of the condensation of steam, exiting the reactor along with the treated material, inside the plastic bags. A portion of the treated material adhered to the inside wall of collection bags. This collection procedure was followed for all samples. The treated samples were dried inside the oven set at 50°C, till the MC was reached to about 11% (d.b.).

### **4.3.2. *Particle size distribution***

Table 4.1 lists the mean and standard deviation of particle sizes before and after treatments. Although all samples were ground using the same screen size (1.6 mm), the final mean particle size of material before treatment varied substantially (Table 4.1). The mean particle diameter of untreated Pine at 0.50 mm was the largest. Untreated bark particles (D. Fir bark) at around 0.23 mm were of the smallest dimension. From the geometric standard deviation values, it appeared that pine particles had a wider size distribution than other materials.

Figure 4.2 presents the particle size distribution of the particles before treatment. Among species, pine fractions in the two large size categories (more than 0.35 mm) were the highest. Bark fractions in these categories were the smallest. The fraction of small size particles (particles between pan and 0.25 mm) was the least for pine and the largest for bark. Spruce and D. Fir particles had similar mass fractions.

The variability among fractions of the mass for white wood samples was less than 0.5 g whereas the variability among bark fractions was between 0.5 g to 1 g. We concluded that the repeatability of sieving procedure was adequate and thus we present one typical run on each species. Figure 4.3 shows the mass fraction of three groups of sizes for the particles before and after steam treatment. For the size category >0.5 mm, the mass fractions decreased as a result of steam treatment. For size category between

0.5 mm and 0.1 mm, a slight increase in mass fractions indicated that a portion of particles in size category >0.5 mm of the untreated material comminuted to smaller ones. The mass fractions in the pan for the untreated species were all low except for the bark that was more than 10%. A larger fraction of steam treated species was present in the pan. Fragmentation of the particles was more for pine and spruce samples. Lam (2011) explained that particles fragment as a result of sudden pressure drop upon exit from the steam reactor. Lam (2011) speculated that the fine particles burst out from the surface of the wood particles due to explosion effect, resulting in the formation of groups of small size particles. The reduction in size was largest for pine from 0.50 mm to 0.37 mm, or roughly 25% in size reduction. The higher size reduction for Pine samples could be due to the fact that Pine had more of the larger particles in its initial untreated sample. Boussaid et al. (2000) found similar results from steam treatment of D. Fir woodchips. After steam treatment, one sample of bark had a small reduction in size and the other replication of bark did not show any reduction in particle size. Bark had initially smaller particle size before steam treatment, so fragmentation of particles was less likely happen for bark. For bark, steam treatment did not result in significant size reduction probably due to a less cellular and softer structure in the bark than in heartwood. Robinson et al. (2002) showed that Douglas-fir bark has naturally less polysaccharide concentration, cellulose (Glucan) and hemicellulose (Xylan and Mannan) contents. These components were influenced by the steam treatment before other components e.g., lignin (Robinson et al., 2002). So, less disintegration was observed for bark samples.

#### **4.3.3. Color**

Figure 4.1 shows pictures of treated and untreated samples. Treated samples were dark in color. D. Fir bark seems to be the darkest. Table 4.2 lists the color coordinate values  $L a b$  for untreated and treated samples. The value for coordinate  $a$  (-50 green to +50 red) varied for untreated samples from a minimum of 2.35 for Pine to a maximum of 15.40 for bark. The value for coordinate  $b$  (-50 blue to +50 yellow) varied for untreated samples from a minimum 17.1 for Pine to a maximum of 26.9 for bark. The white to black scale  $L$  (0 black to 100 white) did not vary much among untreated whitewood samples, 71.2 for Pine to 72.8 for D. Fir. The  $L$  value for bark was 47.8 representing a relatively darker color. The treated samples decreased in the  $a$  and  $b$

coordinates compared to the values for untreated samples, except for Pine samples. Most decrease was in  $L$  values, i.e. all samples became darker as is evident in Figure 4.1. The overall color change ( $\Delta E$ ) decreased for whitewood, ranging from 40.4 for Pine to 47.4 for Spruce. Bark had a decrease in overall color coordinate of 36.4.

Zhang and Cai (2006) explained that the changes of wood color during steam treatment were caused by a series of chemical reactions. Extractives react with the chemical constituents of wood cell wall under high temperature and humid conditions. During steam treatment furfural and some polysaccharides with low molecular weights are created from hemicelluloses degradation. Changes in lignin and extractives chemistry can also contribute to the color changes. Chromophoric groups (carboxylates and phenol) may be produced within the lignin or extractive molecules at high temperatures and humidity. As these components are dark in color (blue green), they lead to the darker color in wood appearance during steam treatment (Zhang and Cai, 2006). The decrease in  $a$  and  $b$  values can be explained by these chemical composition changes.

#### **4.3.4. Bulk, tapped and particle density**

Table 4.3 lists bulk, tapped and particle density of treated and untreated biomass. Bulk and tapped densities of whitewood samples increased after steam treatment. The loose bulk density of the untreated dry whitewood ranged from 0.09 (for Spruce) to 0.18 g/cm<sup>3</sup> (for D. Fir). The bulk density of untreated bark was 0.31 g/cm<sup>3</sup>, almost 1.5 times that of white D. Fir. The loose bulk density of steam treated Spruce increased the most to 0.13 g/cm<sup>3</sup> and that of D. Fir to 0.21 g/cm<sup>3</sup>. The loose bulk density of treated bark decreased from untreated 0.31 g/cm<sup>3</sup> to 0.28 g/cm<sup>3</sup>.

Tapped density represents a dense fill situation. The higher bulk and tapped densities of treated whitewood samples could be related to the higher ratio of fine particles for these samples after steam treatment (Figure 4.3). These fine particles fill the voids that would result in increased mass per unit volume. Particle density values for untreated samples ranged from 1.39 g/cm<sup>3</sup> to 1.41 g/cm<sup>3</sup>. Upon steam treatment, the particle density of whitewood decreased to 1.07 g/cm<sup>3</sup> (highest decrease for Spruce). The particle density of bark increased slightly from 1.40 g/cm<sup>3</sup> to 1.46 g/cm<sup>3</sup>.

Grous et al. (1986) reported an increase in pore volume (5 to 9 nm pore size) after steam treatment of Hybrid Poplar. Lam (2011) also observed an increase in pore volume in steam treated D. Fir and contributed this increase to the loss of volatiles. The strong smell during treatment of Spruce samples could also indicate more volatile loss for Spruce than other species that did not show as much loss in the particle density (mass). For bark, the percentage of fine particles did not increase after steam treatment (Figure 4.3). Robinson et al. (2002) evaluated the composition of D. Fir wood and bark samples before and after steam treatment. Their results showed a smaller mass loss for blends containing higher ratio of bark to whitewood. For bark samples, the pore size expansion was more effective on increasing the particle density compared to mass loss due to volatile loss. The porosity ( $\epsilon_0$ ) (Table 4.3) is an indicator of packing characteristic of the material, and not the internal pore size of samples. Table 4.3 shows that the packing porosity of whitewood samples decreased after steam treatment whereas that of bark samples increased. The more expanded bark particles created more void space between particulates in a bulk.

#### **4.3.5. *Ash content and calorific value***

Table 4.4 lists the percent dry basis ash content of the biomass before and after treatment. The ash content in the untreated white wood ranged from 0.07% in Pine to 0.22% in Spruce, and the ash content of the bark was 2.11%. For treated samples the ash content increased substantially, ranging from 0.28% in D. Fir to 0.94% in Spruce. The ash content of bark almost doubled from 2.11% to 4.13% after treatment. The standard deviation values for ash content of treated and untreated samples were relatively high and increased for treated samples. Lam et al. (2011) also reported the increase in the ash content after steam treatment. As these values are relative, they cannot directly show the increase in metal or inorganic content of samples; it could be an indicator of the relative loss of other components in the samples. Lam showed the loss of hemicellulose sugars after steam treatment of D. Fir (Lam, 2011).

Table 4.4 lists the higher heating value (HHV) for the treated and untreated biomass. Three species Spruce, Pine, and D. Fir had similar HHV of 18.61-18.81 MJ/kg. Untreated bark had a higher HHV at 19.13 MJ/kg. The HHV increased to 21.16 MJ/kg for Pine and to 23.58 MJ/kg for Spruce. In all cases, the standard deviation values for HHV

of each sample were small. Demirba (2001) found a linear correlation between HHV and lignin content. This can explain the increase in HHV of samples after steaming as Lam et al., (2011) and Kumar et al. (2010) found higher lignin contents for steam treated white wood samples.

#### **4.3.6. Carbon percentage**

Table 4.4 lists data on the elemental analysis of wood species before and after steam treatments. Carbon percentages increased from about 46.0% to 57.27% (the highest) for Spruce, and to 52.41% (the lowest) for D. Fir. Hydrogen and oxygen contents of treated biomass decreased. The amorphous structure of hemicellulose favors the -OH groups to be more reactive to steam. When exposed to steam, the hemicellulose polymer is hydrolyzed. This reaction removes the -OH groups thus lowering the oxygen and hydrogen content and increasing the carbon fraction. Yan et al. (2009) showed the carbon percentage of biomass treated with hot water increased from 50.3% to 56.1% for Pine particles. This increase was associated with considerable decrease in other elemental components such as oxygen, hydrogen, nitrogen and sulfur as is evident in Table 4.4. The color of carbon is naturally dark grey to black, except when in the hard and crystalline form of diamond. The darker color of treated samples (Figure 4.1) could also be an indicator of carbonization during steaming.

Table 4.5 lists correlation coefficients among untreated and treated biomass properties. Lightness (or whiteness) of untreated and treated biomass species had a correlation of 0.64 and 0.69 with increase in calorific value  $\Delta$ HHV and Carbon percentage ( $\Delta$ C). This is an indication that color may be one of the indicators of carbonization. Further research is needed to steam treat a specific species of biomass to various severities and to develop a statistical significance for correlating color and calorific value.

#### **4.3.7. Moisture adsorption**

Both treated and untreated samples were completely dried in the convection oven at 105°C for 24 hours prior to adsorption test (ASABE, 2008a). Table 4.6 lists equilibrium moisture contents of untreated and treated samples after 180 minutes of



exposure to 30°C and 90% (RH) in the humidity chamber. The equilibrium moisture content of untreated bark approached an average value of 0.139 (decimal, dry basis), followed by untreated Pine to an average value of 0.116. Untreated Spruce and D. Fir reached an equilibrium moisture content of 0.103. The equilibrium moisture of the treated samples decreased to 0.045 for Spruce and to 0.068 for Pine and bark. As discussed it in previous section, the lowered number of –OH functional groups decreased affinity of treated biomass to moisture. Reduced water adsorption is also the main reason for a decrease in equilibrium moisture content of the treated material. This decrease implies that the treated wood becomes hydrophobic. Moisture adsorption rate (constant  $k$ ) ranged from 0.021 min<sup>-1</sup> to 0.029 min<sup>-1</sup> for untreated samples. The adsorption rate decreased slightly to values ranging from 0.019 min<sup>-1</sup> to 0.028 min<sup>-1</sup> for the treated wood. Similar trend was also reported by Lam et al. (2011) for D. Fir. In our experiments, the decrease in the adsorption rate was the highest for Spruce.

The higher calorific values, higher hydrophobicity and also darker brownish color of steam treated material might be an indicator of a mild torrefaction (carbonization) during steam treatment. Although steam temperature at 220°C was lower than temperature for dry torrefaction (250-300°C), steam hastens the heating of the biomass (Sano et al., 2005). Table 4.7 compares the carbon percentage and higher heating value of untreated and treated Pine particles from this study with those obtained from (Phanphanich and Mani, 2011) for Pine and the heat values of this study for Spruce with those published by Li et al. (2012). They did not report carbon percentages (Li et al., 2012). Phanphanich and Mani (2011) and Li et al. (2012) treated biomass samples using hot nitrogen at elevated temperatures of up to 300°C for duration of 15 and 30 minutes. The carbon percentage and HHV of biomass prior to treatments were similar. The carbon percentage of the yellow Pine subjected to hot nitrogen at 250°C for 30 min reached 51.4% whereas the treated sample at 220°C with saturated steam for 5 minutes had a carbon percentage of 52.81%. The high calorific value of steam treated sample was similar to the torrefied sample at 275°C (21.66 vs. 21.82 MJ/kg). For Spruce treated by Li et al. (2012) for 15 minutes, the higher heating values at 300°C reached to 22.35 MJ/kg (Phanphanich and Mani, 2011; Li et al., 2012). The HHV and carbon percentage of treated wood showed that wet torrefaction could happen at lower temperatures and/or shorter residence time using saturated steam.

## 4.4. Pellet properties

### 4.4.1. *Energy to produce pellets*

Table 4.7 lists energy input for compacting particles to form a pellet in the cylindrical die. To compensate for variations in mass and volume of single pellets, specific energy is defined as the ratio of energy input (J) over pellet density ( $\text{g/cm}^3$ ) (Lam, 2011). The mean specific energy to compact the untreated particles ranged from a minimum of  $11.5 \text{ J.cm}^3/\text{g}$  for bark particles to  $30.2 \text{ J.cm}^3/\text{g}$  for Spruce and D. Fir particles. The corresponding specific compression energy increased for the treated samples for all species from  $24.2 \text{ J.cm}^3/\text{g}$  for bark to  $47.0 \text{ J.cm}^3/\text{g}$  for Spruce. The expulsion energy increased for the treated pellets compared to the pellets made from untreated particles. These results are consistent with the earlier work (Lam et al., 2011) where energy required pushing pellet out of the cylindrical die increased after steam treatment. The specific expulsion energy was lowest for untreated bark at  $4.5 \text{ J.cm}^3/\text{g}$  and was the highest for treated Spruce at  $31.4 \text{ J.cm}^3/\text{g}$ . This suggests that all treated pellets have a tendency to stick to the die and resisting to be pushed out of the cylindrical die. The treated Spruce pellets were the stickiest compared to other species. The unpaired student t-test was performed and T-statistics values were reported in Table 4.7 and Table 4.8 for all measurements. The T-statistics values showed that the treated and untreated values are independent and the differences are statistically significant ( $P=0.05$ ). Analysis of variance (ANOVA) test was performed in order to evaluate the effect of feedstock type on the values of measured characteristics. For all measured parameters reported in Table 4.7, the values of F-statistics were considerably higher than F-critical (obtained from ANOVA tables and was equal to 3.2). Based on the F-statistics values, we concluded that the values of parameters were significantly affected by feedstock type for  $P \leq 0.05$ .

Figure 4.4 plots the total energy input to make pellets from different softwood particles under 4000 N force. The bars are sums of both compression and expulsion energy for each species, per unit of mass. Both untreated and treated Spruce required more energy to form pellets. Treated Pine and Douglas fir required almost the same quantity of energy input. Bark required the least.

The required energy for heating particles from 25°C to 100°C is 93.75 kJ/kg calculated based on the specific heat of pellets of 1.25 kJ/(kg. K) (Guo et al., 2009). Adding this heat energy to mechanical energy input (at 4000 N compression) sums to roughly 150 kJ/kg for the untreated, and to 200 kJ/kg for the treated Spruce pellets (as the Spruce pellets consume the highest energy for formation). High capacity commercial pellet press mills are rated at about 55 (kW.h)/Mg (Power of 250 kW and pellet production capacity of around 4.5 Mg/h) or about 200 kJ/kg (Oberberger and Thek, 2010). The data in this research show that the existing commercial pellet mills have adequate power to produce steam treated pellets of any softwood species in this study. They would not need to be equipped with additional power to compact steam treated pellets.

#### **4.4.2. Mechanical strength of pellets**

Among untreated pellets, bark pellets had a much higher mechanical strength compared to untreated white wood pellets; untreated bark pellets could tolerate the maximum compressive force around 55 N before they broke. Untreated Douglas fir produced the hardest pellets among tested whitewoods, tolerating a maximum breaking force of about 32 N. These trends were not observed for pellets made of treated material. The maximum breaking force of steam treated bark pellets decreased considerably from 55 N to around 22 N. The maximum force (Table 4.8) to break treated whitewood samples was much larger than the maximum force to break untreated pellets; the treated Spruce pellets tolerated a force of 32 N compared to the maximum force of 16 N for untreated. This is the case for all pellets in spite of a lower density of the steam treated pellets. The density of pellets made from whitewood slightly decreased after steam treatment. Similarly, for bark the density of the pellets made from treated bark particles decreased.

The treated bark pellets had lower mechanical strength and density compared to untreated bark pellets. The lower density of steam treated bark is not well understood and may be attributed to the structure of bark that contains less cellulose and more extractives (Robinson et al., 2002). It was noted that the volatiles and extractives mass loss during steam treatment was evident as a strong odor was sensed during steam treatment. The increase in the breaking strength of whitewood pellets after treatment

was expected due to the higher volume of small particles after treatment. These fine materials could fill up the cavities between the larger particles and ultimately made the harder solid pellets. For bark samples, the amount of fine particles did not increase after the treatment and this size category did not contribute to an increase in the strength of treated bark pellets. Zandersons et al. (2004) stated that activation of lignin and changes in the cellulosic structure during steam treatment facilitated the formation of new bonds. Lignin and extractives have been reported to act as a binding agent that contributes to the strength of densified materials (Angle's et al., 2001; Granada et al., 2002). The melting temperature of lignin can be reduced from 140°C (van Dam et al., 2004) to about 100°C (commonly attained during commercial pelleting) in the presence of moisture (8%–15%) within biomass feedstocks (Lehtikangas, 2001). Donohoe et al. (2008) provided experimental evidence that treatment temperature above the range of lignin phase transition (around 120°C) causes lignin to coalesce into larger molten bodies that migrate within and out of the cell wall to redeposit on the surface of plant cell walls. Kaliyan and Morey (2010) stated that the reformed lignin provides solid bridges among particles after compression and cooling of pellets. So, it is speculated that stronger bonds in the cellular structure of the material after the treatment have led to the higher mechanical strength. However, further study needs to be done on the heterogeneous structure of bark material to explain the opposite effects of steam treatment on these samples.

To justify the higher pelletization energy of treated material compared to untreated samples, we applied lower densification forces and examined the strength of produced pellets (Table 4.8). The maximum breaking force of treated pellets made under 2000 N load was even higher than that of untreated pellets made at 6000 N force load (38.4 vs. 32 N). The compression energy for treated pellets at 2000 N was lower than that of untreated ones under 6000 N load (31.0 vs. 36.4 J.cm<sup>3</sup>/g). The values in Table 4.8 for compression of Douglas fir particles under 4000 N are not exactly the same as the values for Douglas fir in Table 4.9. The differences are in the ranges of the standard deviations. The expulsion energy was also comparable for treated pellets at lower loads (20.9 vs. 15.6 J.cm<sup>3</sup>/g) compared to untreated pellet at 6000 N. However, density of treated pellets made at lower forces (0.95 vs. 1.37 g/cm<sup>3</sup>) shows considerable decrease compared to density of untreated pellets made at 6000 N.

## 4.5. Concluding remarks

In this chapter, Pine, Spruce, and Douglas fir whitewood and the Douglas fir bark were treated with pressurized steam at 220°C for 5 min. The objective was to determine the effect of steam treatment on the degree of carbonization (torrefaction) of softwood particles and also quality of produced pellets under different loads. The steam treatment resulted in a reduction in average particle size by as much as 25%. Pine particles showed the largest reduction in size while bark showed the least. The heating value of all samples increased as a result of steam treatment; the highest increase was 26% for Spruce, from 18.7 MJ/kg to 23.6 MJ/kg. The carbon percentage of the Spruce samples increased from 46.5% to 57.3%, whereas for treated Pine and Douglas fir the increase in carbon percentage was lower. The equilibrium moisture content of treated wood, placed in a chamber at 90% relative humidity and 30°C air, decreased from around 12% (before treatment) to about 6%. Bulk density of Spruce particles increased significantly from 0.09 g/cm<sup>3</sup> to 0.13 g/cm<sup>3</sup> after steam treatment. However, bulk density of D. Fir bark samples decreased from 0.31 g/cm<sup>3</sup> to 0.28 g/cm<sup>3</sup>. The higher calorific values, higher hydrophobicity, higher carbon percentage and dark brownish color of steam treated material indicated a mild degree of torrefaction (carbonization) when compared to torrefaction at temperatures of 300°C and higher. The results of the elemental analysis confirmed the carbonization of softwoods by steam treatment. In the densification process, Despite a slightly lower density, pellets made from treated particles had a higher mechanical strength (hardness) than the untreated pellets. The mechanical energy to compact steam treated material was higher than energy to make pellets from untreated wood. Douglas fir required the least energy input among debarked samples. Spruce was the stickiest pellet to be pushed out of the cylindrical die. Bark pellets consumed the lowest energy to be compacted and pushed out of the cylindrical die. To reduce this high amount of energy, steam treated material can be pelletized by applying one third of the force to arrive at even higher mechanical strength compared to pellets made of untreated particles. Applying one third of the force on treated material requires almost the same densification energy comparing to pelletization energy of untreated material under the higher force. However, the density of treated pellets is lower than the density of untreated pellets.

In the next chapter  $\text{SO}_2$ -catalyzed steam pretreatment is introduced as a way to obtain sufficient size reduction required for pelletization and enhance the mechanical strength of the resulting pellets. In this way, the energy required for steaming is expected to be offset by replacing the grinding step while a subsequent densification of the steam pretreated material is expected to provide pellets with higher mechanical strength.

**Table 4.1 Moisture content, geometric mean ( $d_{gm}$ ) and geometric standard deviation ( $S_{gm}$ ) of treated and untreated particles**

Species	Parameters	Moisture content (w.b.) (%)		Geometric mean & standard deviation parameters	particle size (mm)	
		Untreated	Treated		Untreated	Treated <sup>[a]</sup>
Pine	Mean	10.2	45.8	$d_{gm}$	0.503	0.370
	SD	0.1	3.1	$S_{gm}$	0.396	0.402
Spruce	Mean	9.9	40.6	$d_{gm}$	0.417	0.311
	SD	0.0	2.8	$S_{gm}$	0.328	0.362
Douglas fir	Mean	10.1	44.7	$d_{gm}$	0.408	0.321
	SD	0.0	2.1	$S_{gm}$	0.309	0.332
Bark	Mean	10.1	49.5	$d_{gm}$	0.231	0.199
	SD	0.2	3.9	$S_{gm}$	0.207	0.292

<sup>[a]</sup> The particle size analyses of “Treated” samples were done at 10% (w.b.) moisture content.

**Table 4.2 Color changes after steam treatment**

Species	Parameter		Untreated	Treated	$\Delta E^*$ (s.d.)
Pine	<i>L</i>	Avg	71.1	31.3	40.4 (0.02)
		s.d.	0.0	0.0	
	<i>a</i>	Avg	2.3	9.4	
		s.d.	0.0	0.0	
	<i>b</i>	Avg	17.1	17.4	
		s.d.	0.0	0.0	
Spruce	<i>L</i>	Avg	71.6	26.4	47.4 (0.06)
		s.d.	0.0	0.0	
	<i>a</i>	Avg	6.7	5.9	
		s.d.	0.0	0.0	
	<i>b</i>	Avg	24.7	10.2	
		s.d.	0.0	0.0	
D. Fir	<i>L</i>	Avg	72.8	28.8	45.3 (0.07)
		s.d.	0.0	0.1	
	<i>a</i>	Avg	9.0	8.3	
		s.d.	0.0	0.1	
	<i>b</i>	Avg	25.4	14.5	
		s.d.	0.0	0.1	
Bark	<i>L</i>	Avg	47.8	20.9	36.4 (0.03)
		s.d.	0.0	0.0	
	<i>a</i>	Avg	15.4	3.7	
		s.d.	0.0	0.0	
	<i>b</i>	Avg	26.9	5.4	
		s.d.	0.0	0.0	

\*n=3

s.d. Standard deviation



**Table 4.3 Bulk, tapped and particle solid densities of untreated and treated biomass**

Biomass	Param	Bulk density* (g/cm <sup>3</sup> )		Tapped density* (g/cm <sup>3</sup> )		Particle density* (g/cm <sup>3</sup> )		Porosity (%)	
		Untreated	Treated	Untreated	Treated	Untreated	Treated	Untreated	Treated
Pine	Avg	0.15	0.19	0.21	0.24	1.39	1.12	0.89	0.83
	s.d.	0.00	0.01	0.00	0.01	0.01	0.02	0.00	0.01
Spruce	Avg	0.09	0.13	0.13	0.17	1.39	1.07	0.94	0.88
	s.d.	0.00	0.00	0.00	0.00	0.02	0.01	0.01	0.02
D. Fir	Avg	0.18	0.21	0.24	0.27	1.41	1.18	0.88	0.82
	s.d.	0.00	0.01	0.00	0.00	0.02	0.02	0.01	0.01
Bark	Avg	0.31	0.28	0.40	0.34	1.40	1.46	0.78	0.81
	s.d.	0.01	0.01	0.01	0.01	0.00	0.06	0.01	0.01

\* n=3

s.d. Standard deviation

**Table 4.4 Ultimate\* and heat value\* analysis of untreated and steam treated ground biomass**

Biomass	Steam	Parameter	Ash (%)	HHV (MJ/kg)	C (%)	H (%)	N (%)	S (%)	O (%)
Pine	Untreated	Avg	0.071	18.80	46.65	6.73	0.15	1.04	45.42
		s.d.	0.100	0.10	0.21	0.05	0.01	0.02	0.35
	Treated	Avg	0.340	21.66	52.81	6.18	0.11	0.92	39.97
		s.d.	0.127	0.23	0.13	0.05	0.01	0.01	0.20
Spruce	Untreated	Avg	0.215	18.72	46.46	6.46	0.13	0.96	45.99
		s.d.	0.168	0.02	0.13	0.01	0.01	0.00	0.11
	Treated	Avg	0.938	23.58	57.27	5.78	0.12	0.85	35.97
		s.d.	0.040	0.19	0.01	0.03	0.00	0.01	0.03
D. Fir	Untreated	Avg	0.144	18.61	46.34	6.56	0.10	0.97	46.02
		s.d.	0.102	0.16	0.00	0.03	0.02	0.01	0.01
	Treated	Avg	0.279	21.16	52.41	5.94	0.08	0.91	40.65
		s.d.	0.066	0.42	0.04	0.00	0.01	0.01	0.02
Bark	Untreated	Avg	2.114	19.13	46.98	6.25	0.50	0.90	45.63
		s.d.	0.153	0.31	0.11	0.03	0.01	0.01	0.28
	Treated	Avg	4.128	22.48	54.52	5.80	0.48	0.87	38.32
		s.d.	2.222	0.16	0.07	0.02	0.01	0.00	0.10

\* n=3

s.d. Standard deviation

**Table 4.5 Equilibrium moisture content ( $M_e$ ) and moisture adsorption constant ( $k$ ) before and after treatment**

Biomass	Test	Equilibrium moisture content (dec.db)		Adsorption constant (min <sup>-1</sup> )	
		Untreated	Treated	Untreated	Treated
Pine	Run1	0.117	0.071	0.024	0.023
	Run2	0.115	0.064	0.028	0.028
Spruce	Run1	0.103	0.047	0.026	0.022
	Run2	0.104	0.043	0.029	0.019
D. Fir	Run1	0.103	0.067	0.022	0.026
	Run2	0.094	0.064	0.029	0.026
Bark	Run1	0.149	0.073	0.021	0.020
	Run2	0.129	0.065	0.029	0.025

**Table 4.6 Matrix of correlation coefficient among percent differences between untreated and treated biomass properties.**

	$\Delta L$	$\Delta E$	$\Delta HHV$	$\Delta C$
$\Delta L$	1.00	0.92	0.64	0.69
$\Delta E$	0.92	1.00	0.44	0.47
$\Delta HHV$	0.64	0.44	1.00	0.99
$\Delta C$	0.69	0.47	0.99	1.00

$\Delta L$ : difference in whiteness

$\Delta E$ : overall color difference

$\Delta HHV$ : difference in higher calorific value

$\Delta C$ : difference in carbon percentage

**Table 4.7 Comparing steam torrefaction with dry torrefactions on Pine and Spruce particles**

Sample	Species	Temp. (°C)	Residence time (min)	C (%)	HHV (MJ/kg)	Reference
Steam treatment	Pine	untreated 220	- 5	46.65 52.81	18.80 21.66	Present work
	Spruce	untreated 220	- 5	46.46 57.27	18.72 23.58	
Dry torrefaction	Pine	untreated	-	47.21	18.46	Phanphanich and Mani, 2011
		225	30	49.47	19.48	
		250	30	51.46	20.08	
		275	30	54.91	21.82	
		300	30	63.67	25.38	
Dry fluidized torrefaction	Spruce	untreated	-	-	18.93	Li et al., 2012
		280	15	-	20.82	
		290	15	-	21.80	
		300	15	-	22.35	

**Table 4.8 Energy input to make pellets and the required forces to crush pellets  
(pellets were made at 4000 N)**

Species	Parameters	Specific compression energy <sup>[a]</sup> (J.cm <sup>3</sup> / g)		Specific expulsion energy <sup>[a]</sup> (J.cm <sup>3</sup> / g)		Pellet density <sup>[a]</sup> (g/cm <sup>3</sup> )		Maximum breaking force <sup>[a]</sup> (N)	
		Untreated	Treated	Untreated	Treated	Untreated	Treated	Untreated	Treated
Pine	Mean	24.3	38.0	8.7	21.9	1.13	1.11	22.2	31.4
	SD	0.8	3.3	0.9	2.5	0.01	0.02	1.0	3.3
	T-statistics <sup>[b]</sup>	-	0.00	-	0.00	-	0.02	-	0.01
Spruce	Mean	30.2	47.0	17.6	31.4	1.06	0.94	16.3	32.5
	SD	2.6	2.8	1.1	5.4	0.01	0.04	1.7	2.6
	T-statistics <sup>[b]</sup>	-	0.00	-	0.00	-	0.00	-	0.00
D. Fir	Mean	30.2	37.8	13.8	26.5	1.10	1.06	32.3	38.9
	SD	1.8	3.9	1.6	1.7	0.01	0.05	1.2	9.9
	T-statistics <sup>[b]</sup>	-	0.00	-	0.00	-	0.05	-	0.03
Bark	Mean	11.5	24.2	4.5	6.7	1.26	1.10	55.3	21.7
	SD	2.0	4.9	0.1	1.1	0.01	0.01	3.8	2.3
	T-statistics <sup>[b]</sup>	-	0.00	-	0.01	-	0.00	-	0.00
	F-statistics <sup>[c]</sup>	159.0	89.1	207.9	50.1	530.1	22.5	130.6	4.1

<sup>[a]</sup> Number of repetitions=5;

<sup>[b]</sup> Mean of treated sample is significantly different than mean of untreated sample if  $P \leq 0.05$ ;

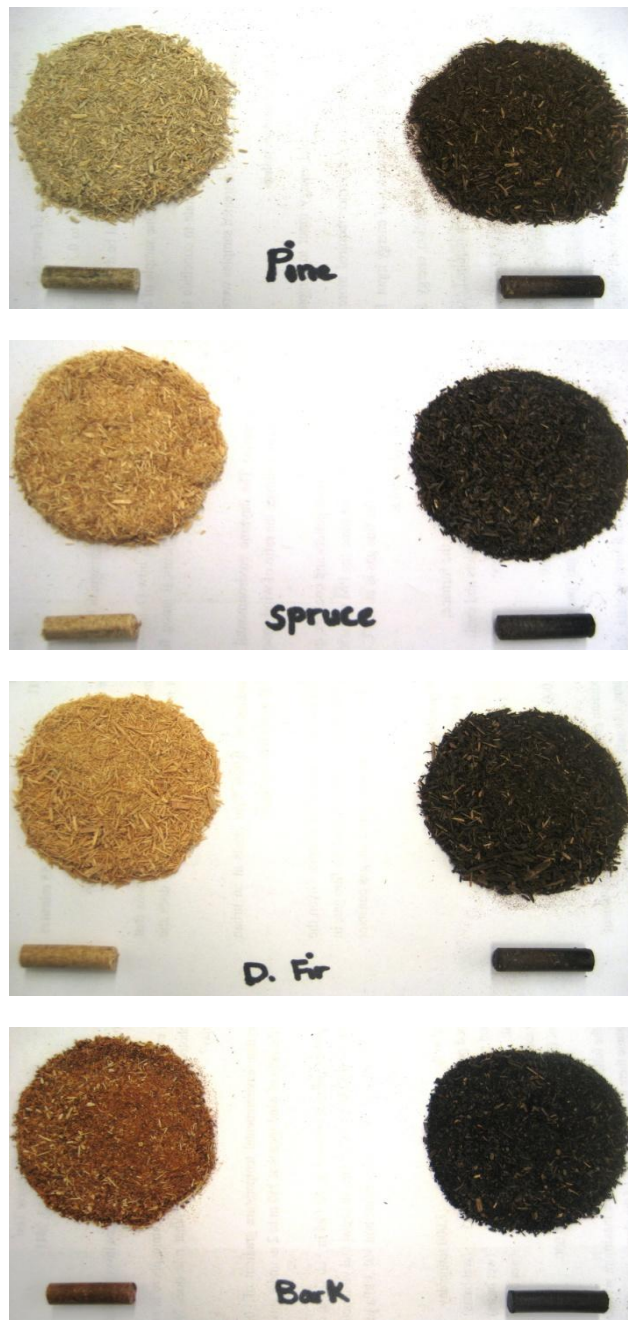
<sup>[c]</sup> The values of parameters were significantly affected by feedstock type for  $P \leq 0.05$ .

**Table 4.9 Characteristics of Douglas-fir pellets made from treated and untreated biomass at three levels of compression forces**

Force (N)	Parameters	Specific compression energy <sup>[a]</sup> (J.cm <sup>3</sup> / g)		Specific expulsion energy <sup>[a]</sup> (J.cm <sup>3</sup> / g)		Pellet density <sup>[a]</sup> (g/cm <sup>3</sup> )		Maximum breaking force <sup>[a]</sup> (N)	
		Untreated	Treated	Untreated	Treated	Untreated	Treated	Untreated	Treated
2000	Mean	20.9	31.0	7.9	20.9	1.04	0.95	15.6	38.4
	SD	0.2	1.3	0.5	4.5	0.02	0.04	1.9	7.1
	T-statistics <sup>[b]</sup>	-	0.00	-	0.01	-	0.02	-	0.00
4000	Mean	27.9	39.3	12.5	24.3	1.19	1.12	20.0	48.9
	SD	6.6	3.0	1.4	2.3	0.02	0.01	1.8	7.5
	T-statistics <sup>[b]</sup>	-	0.00	-	0.03	-	0.00	-	0.00
6000	Mean	36.4	42.5	15.6	30.5	1.37	1.30	32.0	58.6
	SD	4.1	4.5	1.7	2.1	0.01	0.03	3.0	6.1
	T-statistics <sup>[b]</sup>	-	0.00	-	0.00	-	0.00	-	0.00

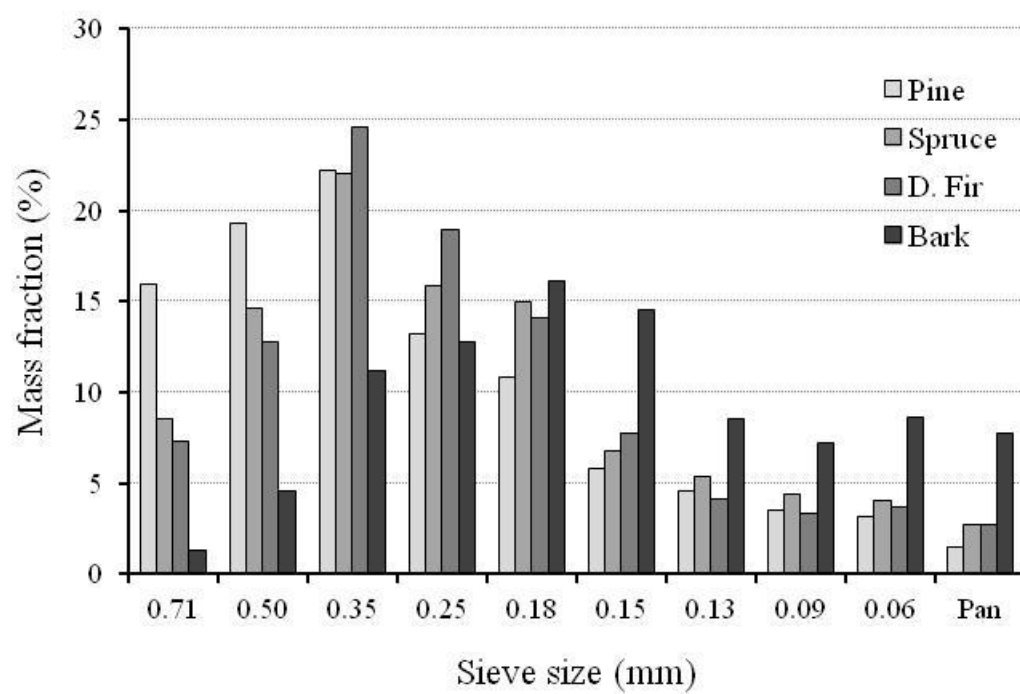
<sup>[a]</sup> Number of repetitions=5;

<sup>[b]</sup> Mean of treated sample is significantly different than mean of untreated sample if  $P < 0.05$ .

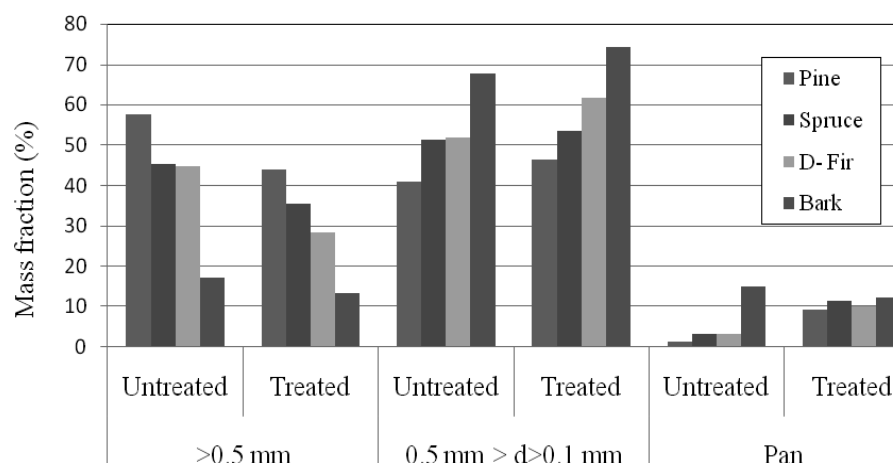


**Figure 4.1 Photos of untreated (left) and steam treated (right) samples**

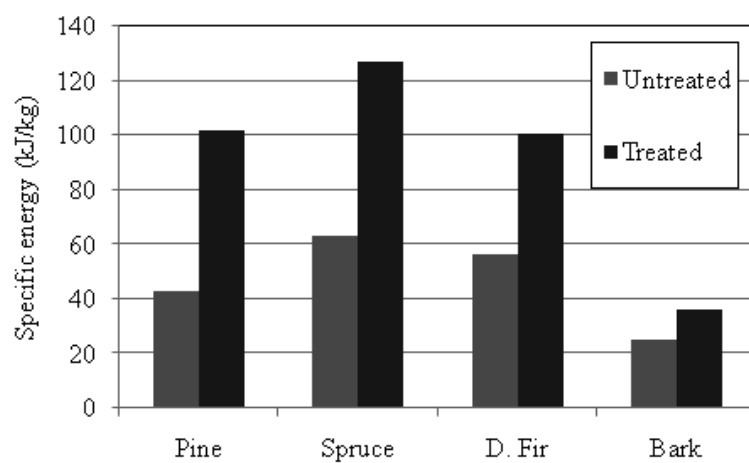




**Figure 4.2 Particle size distribution for untreated ground whitewood and bark**



**Figure 4.3 Distribution of three size groups of particles before and after steam treatment**



**Figure 4.4 Specific energy to compact and extrude pellets made from untreated and treated biomass.**

## **Chapter 5. SO<sub>2</sub>-catalyzed steam pretreatment for enhancing the strength and stability of softwood pellets**

### **5.1. Introduction**

Densification can partially resolve the logistical challenges encountered when large volumes of biomass are required for bioconversion processes to benefit from economies-of-scale. While already a preferred feedstock for combustion to produce heat and power from biomass, wood pellets can also, potentially, be used as a feedstock for bioconversion to produce fuel and chemicals via biochemical pathways. For all these applications, low mechanical strength and sensitivity to moisture of untreated pellets are still recurring issues hindering long term transportation and storage. Also, grinding the woodchips followed by a steam pretreatment and a subsequent densification operation demanded higher amounts of energy, thus limiting the economic attractiveness of the overall process (Lam, 2011). SO<sub>2</sub> catalyzed steam pretreatment has long been used as an effective pretreatment for the bioconversion of softwoods. The pretreatment efficiently solubilizes the hemicellulosic component while providing a water insoluble cellulose rich fraction amenable to enzymatic hydrolysis. Using SO<sub>2</sub> also improves the extent of lignin depolymerization and subsequent redistribution which is expected to facilitate binding between the particles during the pelletization process (Zandersons et al., 2004). Therefore, there is a potential to use SO<sub>2</sub> catalyzed steam treatment for producing high quality wood pellets as well as applying these produced pellets as a feedstock for bio-ethanol production. In the work described below, SO<sub>2</sub>-catalyzed steam pretreatment has been applied directly on the woodchips with the dual objectives of obtaining sufficient size reduction required for pelletization and enhance the mechanical strength of the resulting pellets. In this way, the energy required for steaming is expected to be offset by replacing the grinding step while a subsequent densification of the steam pretreated material is expected to provide pellets with higher mechanical strength.

## 5.2. Materials and methods

### 5.2.1. *Materials*

The biomass material tested in this research consisted of white softwood species, Douglas fir (*Pseudotsugamenziesii*). The freshly cut stem wood pieces grown in British Columbia Canada were brought to the lab and debarked manually, split, chipped and screened to an approximate size of 20x 20x 5 mm chips. The moisture content of the woodchip samples averaged 8% with a variation of  $\pm 1\%$  (wet mass basis) as received.

### 5.2.2. *Equipment and procedure*

Prior to steam pretreatment, the woodchips were impregnated by adding a specified amount (about 12 g) of  $\text{SO}_2$  (4% wt/wt of the substrate) to sealable plastic bags containing 300 g dry weight of chips (Bruno et al., 2009; Ewanick et al., 2007). Once the desired amount of  $\text{SO}_2$  entered the bag, the bag was immediately sealed and left for approximately 12 h before steam treatment. Steam pretreatment was conducted in a 2 L StakeTech (Stake Tech-Norvall, Ontario, Canada) steam gun (Forest Products Biotechnology/Bioenergy Group, UBC) at 200°C for 5 min. This treatment regime had previously been shown to be effective for Douglas fir woodchips (Lam et al., 2011; Kumar et al., 2010). A higher ratio of biomass to steam (1:1.5 w/w) was used to minimize moisture uptake by the solid in order to minimize post drying of the solids fraction. This higher solid-steam ratio is a deviation from previous studies (Ewanick et al., 2007; Kumar et al., 2010) where the objective has been to maximize sugar recovery. No washing of treated material was done in order to keep the moisture as low as possible. The optimum moisture content (MC) for pelletization was reported between 9-15% depending on different feedstock (Mani et al., 2006a; Relova et al., 2009). The treated material was directly oven dried at 40°C to reach to the target moisture content of about  $10 \pm 0.5\%$  for pelletization. Different analytical analyses (Chemical and elemental composition and ash content) and physical measurement (particle size distribution) were done on the ground biomass before and after pelletization. In the work reported here, we compared the quality of pellets made from  $\text{SO}_2$ -catalyzed steam treated Douglas fir chips with that of pellets made from untreated chips. The energy input to produce pellets

was measured and correlated to the physical and compositional characteristics of the pellets. Potential applications of SO<sub>2</sub>-catalyzed steam treated pellets were discussed.

### **5.3. Effect of SO<sub>2</sub>-catalyzed steam pretreatment**

#### **5.3.1. *Particle size distribution***

As was expected, SO<sub>2</sub>-catalyzed steam pretreatment drastically disrupted the rigid structure of woodchips (Figure 5.1a and b). The steam pretreated particles were slightly agglomerated after drying, but could be easily separated by hand, while size reduction was visually noticeable (Figure 5.1). After untangling the steam treated particles manually, from an approximate size of 20 x 20 x 5 mm for the original woodchips, the particle size was reduced to an overall size of about ~1.1 mm (Figure 5.2). Most of the particles were finer in size when compared to the size of the saw dust typically used for pelletization. Boussaid et al. (2000) reported similar degree of particle size reduction after steam treatment of woodchips in the presence of SO<sub>2</sub> catalyst. This degree of particle size reduction was found to be much greater than what was reported previously by Lam et al. (2011) after non-catalyzed steam treatment of Douglas fir chips.

It has been reported that smaller particles with a larger surface area per volume result in an increase particle to particle contact area, thus facilitating a closer packing, resulting in denser and more durable pellets (Mani et al., 2006b; Kaliyan and Morey, 2006). As larger particles, greater than 1 mm, generally act as predetermined breaking points in the pellet, an optimum particle size in the range of 0.5 to 0.7 mm has been recommended (Mani et al., 2006b). In contrast, Bergström et al. (2008) have suggested that, under high forces (more than 3000 N), raw material particle size distribution has a minor effect on physical and thermo-chemical characteristics of produced pellets formed from Scots Pine sawdust. These results were of practical importance as if oversized particles (more than 6 mm) were sieved off, the grinding process could be eliminated resulting in a cost reduction (Bergström et al., 2008). The work reported in this paper suggested that grinding may not be required for SO<sub>2</sub>-catalyzed steam pretreated material which might be directly pelletized at 4000 N force load to produce good quality pellets.

### **5.3.2. Chemical composition**

As was found in our previous work (Kumar et al. 2012), the carbohydrate and lignin content of untreated pellets did not differ considerably from those of woodchips (Table 5.1). Despite fairly similar chemical composition, a slight decrease in the hemicellulose sugars (Xylan and Mannan) and an increase in the glucose content were observed in pellets compared to woodchips. This was likely due to a loss of hemicellulose sugars from the heat and pressure used during densification as substantial heat is generated from friction between the feed particles and the wall of the die (Kaliyan and Morey, 2010). The compositional analysis of samples after steam pretreatment showed almost complete solubilization of hemicellulose sugars (Table 5.1) and, as a result, the cellulose and lignin content increased after pretreatment and pelletization (Table 5.1). Although pelletization slightly reduced the overall carbohydrate content of the biomass, more than 80% of the original carbohydrates were recovered even after steam pretreatment and pelletization. Almost all of the sugars survived the steam pretreatment were also recovered after pelletization (Table 5.1). As the steam treatment temperature at 200°C was much higher than that used for pelletization (about 70°C), the influence of pelletization on the hemicellulose degradation was negligible compared to the effect of SO<sub>2</sub>-catalyzed steam treatment (Table 5.1).

The sum of compounds in Table 5.1 was slightly lower or higher than 100%. While the >100% mass recovery could be justified as the result of polysaccharide hydration (cleavage of glycosidic bonds) during the treatment, the less than 100% recovery may be attributed to the presence or formation of water-soluble compounds (e.g., extractives and sugar degradation products) that were not quantified here.

### **5.3.3. Mechanical properties of the pellets**

The mechanical properties of pellets made of steam treated material improved as we expected based on our previous research and published literature (Shaw et al. 2009; Lam et al. 2011). Table 5.2 shows that the average pellet density increasing from 1.21 g/cm<sup>3</sup> for untreated pellets to 1.34 g/cm<sup>3</sup> for steam treated pellets. Although Lam et al., (2011) did not observed an increase in density in earlier work on steam treated Douglas fir, the addition of the SO<sub>2</sub> catalyst in the current work resulted in a reduction in particle

size leading to a stronger binding and higher density. The mechanical hardness of the treated pellets is typically represented by the maximum force required to break the pellets and this was almost doubled after pelletizing the SO<sub>2</sub>-catalyzed steam treated material compared to the untreated pellets (from 684.8 to 1341.6 N) (Table 5.2). This increase was substantially higher than what has been reported previously (Shaw et al., 2009; Lam et al., 2011). It was apparent that finer particles produced by the SO<sub>2</sub>-catalyzed steam pretreatment led to stronger binding during densification. In addition, the higher lignin and the soluble sugars content resulting from the SO<sub>2</sub> catalyzed steam pretreatment likely resulted in more efficient binding, thus improving the mechanical strength of the pellets (Lehtikangas, 2001). As mentioned earlier, lignin has been reported to act as a binding agent that contributes to the strength of densified materials (Angle's et al., 2001). It has been shown that SO<sub>2</sub> catalyzed steam pretreatment lowers the lignin's molecular weight, consequently decreasing the glass transition temperature compared to the lignin present in untreated wood (Zandersons et al., 2004). Therefore, the higher degree of lignin softening during the conditions of densification and the higher availability of lignin on the fiber surface probably resulted in stronger bonds between the particles. This led to the observed, higher mechanical strength of the pellets.

#### **5.3.4. *Energy input to make pellets***

The energy requirement for densification is largely governed by the two main energy inputs of, compressing the particles to form the pellets (compression energy) and, the energy required to push the formed pellets out of the cylindrical die (expulsion energy). When the force vs. displacement for making pellets from treated and untreated biomass was compared, the compression curves (Figure 5.3a and b) showed that, for up to 15 mm travel of the piston, the forces were low and increased gradually. Beyond 15 mm, the curves increased substantially over a short distance. The maximum force was reached at about 22 mm whereas for the treated material the maximum force was reached at about 18 mm. The increase in force beyond 15 mm was pronounced for the treated material whereas the increase in force was more gradual for the untreated material.

It was apparent from the plots of force vs. deformation for expulsion of pellets that the untreated and treated feedstocks were substantially different (Figure 5.3). The



length of the spacer used in the die was 12 mm meaning that it took 12 mm for the end of the pellet to reach the bottom of the die where the pellet emerged. As the pellet exited the die, the forces decreased until the entire pellet fell off the bottom of the die. The initial force required to initiate pushing the pellet out of the die increased gradually for the untreated pellet (Figure 5.3c) whereas the initial force to dislodge the pellet for the treated sample (Figure 5.3d) increased sharply. The maximum force in both cases exceeded 800 N. The force required to continue the movement decreases in case of the SO<sub>2</sub>-catalyzed steam treated pellet and reached the lowest recorded value in 12 mm of expulsion. In case of the untreated pellet, the kinetic friction increased up to 12 mm of expulsion and started to decrease when the pellet started to come out of the die. For an untreated pellet, it took about 18 mm to reach the lowest recorded force during expulsion (Figure 5.3c).

Surprisingly, the required compression energy decreased from 22.4 J.cm<sup>3</sup>/g for the untreated pellets to 17.9 J.cm<sup>3</sup>/g for the SO<sub>2</sub>-catalyzed steam pretreated pellets. The required expulsion energy was decreased from 6.6 J.cm<sup>3</sup>/g for the untreated pellets to 3.9 J.cm<sup>3</sup>/g for SO<sub>2</sub>-catalyzed steam pretreated pellets (Table 5.2). It appears that the fine and brittle SO<sub>2</sub>-catalyzed steam treated particles were easily crushed and subsequently compressed during densification to form the pellets. It was likely that the higher degree of lignin redistribution on the surface and the presence of soluble sugars facilitated better binding, requiring less amount of compression energy (Zandersons et al., 2004). In addition to the surface lignin and soluble sugars, a minor fraction of the lignin was probably sulfonated during SO<sub>2</sub>-catalyzed steam pretreatment, forming lignosulfonates which potentially acted as a lubricant during the process. A wide range of lubricant additives are known to contain sulfur (Gao et al., 2004) and it is possible that the presence of these 'lubricant like' components eased the expulsion of treated pellets and decreased the energy consumption.

### **5.3.5. *Moisture sorption properties of pellets***

As mentioned earlier, one of the main challenges with commercial wood pellets is their sensitivity to humidity. In the presence of even relatively low amounts of moisture wood pellets tend to fragment, resulting in the loss of structural integrity and shape and possible disintegration during transport and storage. Therefore, we next assessed the

stability of the untreated and SO<sub>2</sub>-catalyzed steam treated pellets under humid conditions (Figure 5.4). It was apparent that the moisture content of the pellets increased exponentially reaching an asymptote, at equilibrium conditions (Figure 5.4a). Interestingly, the steam treated pellets exhibited a higher affinity for moisture reaching an ~20% moisture content by weight, which was two times higher compared to that of untreated pellets. However, despite the increase in moisture absorption capacity, the steam pretreated pellets were stable and could hold their integrity after 1 day in a humidity chamber (with a relative humidity of 90%) whereas the untreated pellets lost their integrity after 4 hours (Figure 5.5a and b). When the pellets were immersed in water, the untreated pellets disintegrated immediately after immersion while the treated pellets remained intact even after a week (Figure 5.5c and d). It was apparent that, while the hydrophilic components such as soluble sugars increased the water adsorption capacity of the steam treated pellets, the hydrophobic components, particularly the redistributed lignin, provided a coating which lowered the rate of adsorption and maintained the strong binding and integrity of the pellet. Figure 5.1c and d show the SEM images of untreated and treated Douglas fir particles with 5k magnification. From these images, the changes due to the treatment on the particles surface became clear. Similar to Angle's et al. (2001), we also observed the re-condensed lignin droplets on fiber surface after the SO<sub>2</sub>-catalyzed steam pretreatment (Figure 5.1c and d).

In previous work, Lam et al. (2011) showed that the equilibrium moisture content ( $M_e$ ) of untreated pellets decreased from about 10.2% (d.b.) to a minimum of 5.9% (d.b.) for non-catalyzed steam treated pellets. In contrast we found considerably higher ( $M_e$ ) values for treated pellets (20.6% d.b.) when compared to untreated pellets (9.2% d.b.) while the steam pretreated pellets took a longer time to reach equilibrium. In both studies the sorption constant rates decreased. However, the adsorption rate ( $k$ ) reduction was much higher in the current work, from 0.01 min<sup>-1</sup> for untreated pellets to 0.001 min<sup>-1</sup> for SO<sub>2</sub>-catalyzed steam treated pellets (Figure 5.4b). It appears that the soluble sugars present in the steam pretreated pellets are highly hydrophilic, which would readily adsorb water under humid conditions. This likely resulted in a higher moisture adsorption by the steam pretreated pellets. In addition, it is possible that the SO<sub>2</sub>-catalyzed steam pretreatment "opened up" the lignocellulosic matrix more severely and exposed more of the cellulose micro-fibrils such that water could more easily penetrate and be retained by

the cellulose. The SEM images in Figure 5.1d show the rougher surface of the particles after the treatment. Several researchers have also shown that sulfur can involve in a hydrogen bond formation similar to oxygen (Francuski et al. 2011; Gregoret et al., 1991). The formation of these additional sites for water adsorption might explain the higher equilibrium moisture content of the treated samples.

## **5.4. Discussion on practical application of this research**

Higher mechanical strength and stability of SO<sub>2</sub>-catalyzed steam treated pellets in a humid environment make these pellets desirable for shipping and handling to any biomass-based facility. In our previous study, Kumar et al. (2012) showed that SO<sub>2</sub>-catalyzed steam treated pellets were comparable with SO<sub>2</sub>-catalyzed steam treated softwood chips in terms of sugar recovery (Table 5.1) and enzymatic hydrolysis yield at the same conditions. This conclusion has practical importance as the current study showed the much higher stability of these pellets as well. More than 60% of the pellets prepared from steam pretreated softwood were carbohydrates, which indicated that the material could be potentially used for bioconversion applications. Previously, we have shown that an additional steam pretreatment was not required for obtaining the soluble sugar recovery and a reasonable enzymatic hydrolysis of the cellulose fraction (Kumar et al., 2012). However, due to the higher mechanical strength of the steam pretreated pellets, a mild mixing should be employed to loosen the treated pellets in water within a reasonable time leading to an efficient fractionation and recovery of the soluble sugars before the enzymatic hydrolysis step. This is while the energy saving on the grinding, shipping and handling steps of highly stable treated pellets is more than enough to compensate the energy required for the mild mixing step in the bioconversion process.

In order to determine the suitability of the pellets prepared from steam pretreated softwood for combustion and co-firing applications, the higher heating values and elemental composition were compared to those of the original pellets (Table 5.3). It was apparent that the higher heating value of the SO<sub>2</sub>-catalyzed steam treated pellets (treated at 200 °C for 5min) and original pellets were similar ~at 19 MJ/kg and they were generally lower than what has been observed with torrefied pellets (Tumuluru et al., 2011). The good recovery of carbohydrate even after a steam pretreatment and

pelletization implied that hydrolysis reactions were more predominant during the pretreatment step (Ramos, 2003). This reaction is less likely to change the heating value of the material whereas, during torrefaction, pyrolysis reactions predominate (Tumuluru et al., 2011). The lower O/C and H/C ratios from the elemental analysis (Table 5.3) also resembled mild torrefaction conditions. One possible explanation for unchanged heating values, but higher carbon ratios could be the presence of higher sulfur in the treated product (Table 5.3). The combustion energy of sulfur is much lower than carbon and as a result, can decrease the overall calorific heating value. Despite a slightly higher ash content observed in the steam pretreated pellets, the values were low enough to not raise any issues for any combustion applications.

## **5.5. Concluding remarks**

In this chapter, sulfur dioxide catalyzed steam treatment of woodchips resulted in a substantial reduction in particle size, enabled direct pelletization without any further size reduction step. Subsequent pelletization of this treated material resulted in denser pellets with considerably higher mechanical strength, while minimizing the energy required for densification. The treated pellets remained intact even under high humid conditions, made them more suitable for long term storage and shipping. While high calorific values and low ash content make the treated pellets desirable feedstocks for thermo-chemical conversion, the good recovery of original carbohydrates from treated pellets make them viable feedstocks for any biochemical-based conversion.

**Table 5.1 Chemical composition of untreated and steam treated Douglas-fir chips and pellets (% dry weight) (numbers in the brackets represents standard deviations for n=3)**

Samples	Arabinan	Galactan	Glucan	Xylan	Mannan	Lignin
Untreated woodchips	1.2 (0.0)	2.2 (0.0)	47.3 (0.4)	4.9 (0.1)	11.7 (0.1)	29.8 (0.8)
Untreated pellet	1.3 (0.1)	2.8 (0.1)	48.0 (1.5)	3.7 (0.2)	7.3 (0.3)	30.5 (0.3)
Treated woodchips	0.7 (0.0)	2.0 (0.0)	48.1 (0.7)	2.2 (0.1)	9.7 (0.4)	35.0 (0.2)
Treated pellet	0.6 (0.1)	2.1 (0.1)	49.3 (2.2)	2.2 (0.2)	9.5 (0.6)	33.2 (0.3)

**Table 5.2 Mechanical properties of steam treated and untreated pellets (numbers in the brackets represents standard deviations for n=10)**

Douglas-fir sample	Pellet density (g/cm <sup>3</sup> )	Max. breaking force (N)	Compression energy (J.cm <sup>3</sup> /g)	Expulsion energy (J.cm <sup>3</sup> /g)
Untreated pellets	1.21 (0.01)	684.8 (94.4)	22.4 (1.7)	6.6 (3.3)
Treated pellets	1.34 (0.01)	1341.6 (168.8)	17.9 (2.7)	3.9 (2.1)

**Table 5.3 Elemental analysis of samples (numbers in the brackets are standard deviations for n=3)**

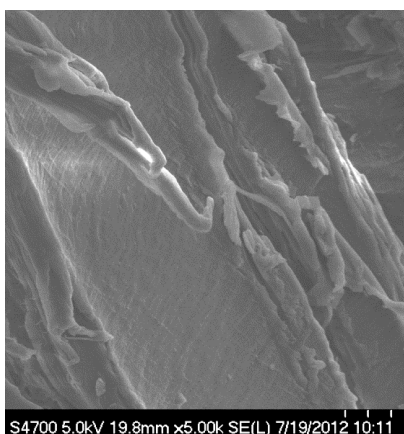
Douglas-fir sample	Higher heating value (MJ/kg)	Ash (%)	C (%)	H (%)	N (%)	S (%)	O (%)
Untreated pellet	18.6 (0.1)	0.1 (0.0)	46.3 (0.0)	6.5 (0.1)	0.1 (0.0)	0.5 (0.0)	46.6 (0.1)
Treated pellet	18.6 (0.0)	0.6 (0.1)	51.7 (0.2)	5.8 (0.1)	0.1 (0.01)	1.1 (0.1)	41.3 (0.2)



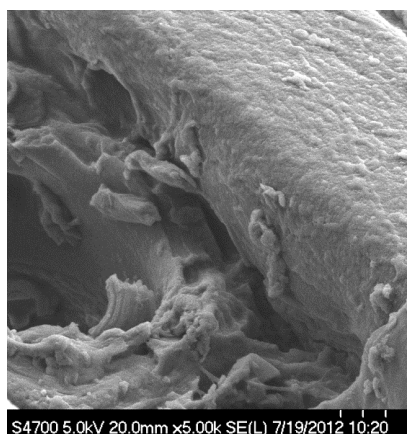
(a)



(b)



(c)



(d)



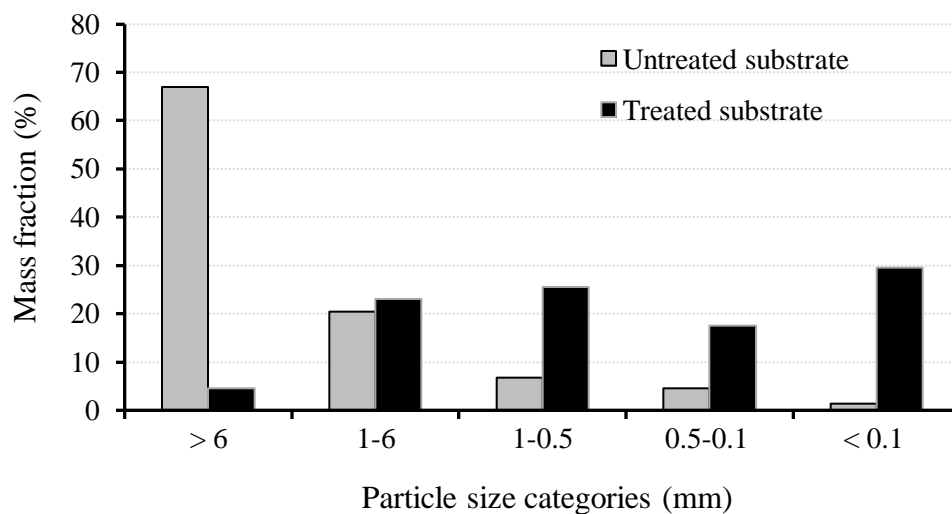
(e)



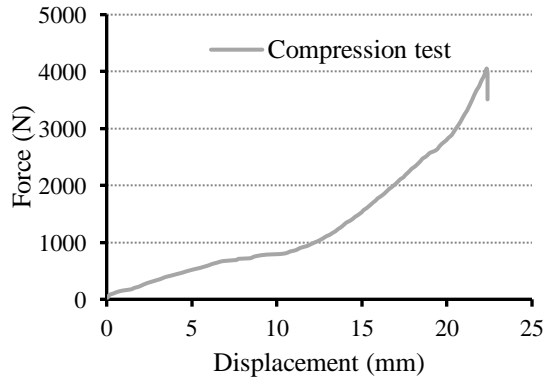
(f)

**Figure 5.1** Appearance of raw material and pellets made in this study: (a) original Douglas fir woodchips, (b) SO<sub>2</sub>-catalyzed steam treated and dried woodchips, (c) SEM image of untreated Douglas fir particles with x5K magnification, (d) SEM image of SO<sub>2</sub>-steam treated Douglas fir particles with 5K magnification, (e) pellets made from untreated particles, (f) pellets made from SO<sub>2</sub>-steam treated particles.

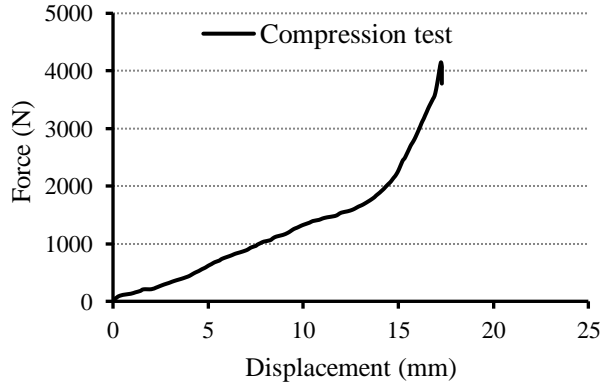




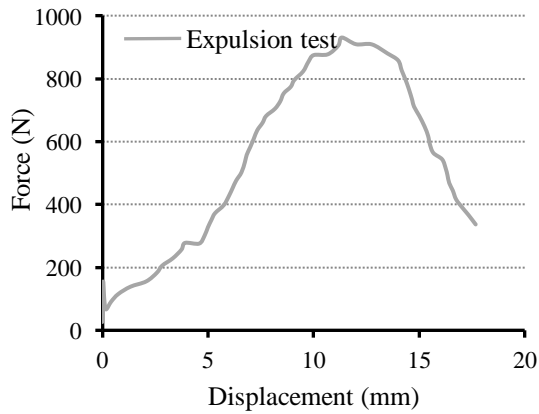
**Figure 5.2 Particle size distribution for untreated (gray) and  $\text{SO}_2$ -catalyzed steam treated substrates (dark) before pelletization.**



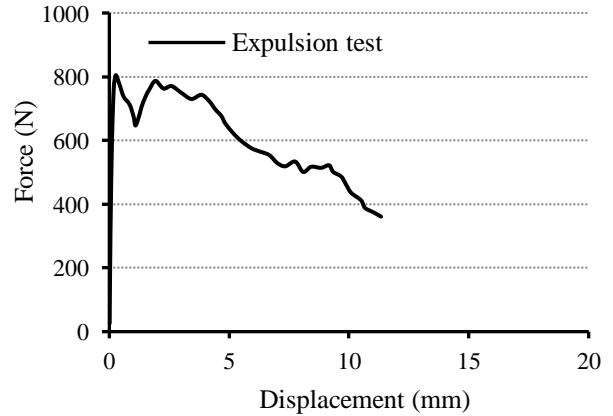
(a)



(b)

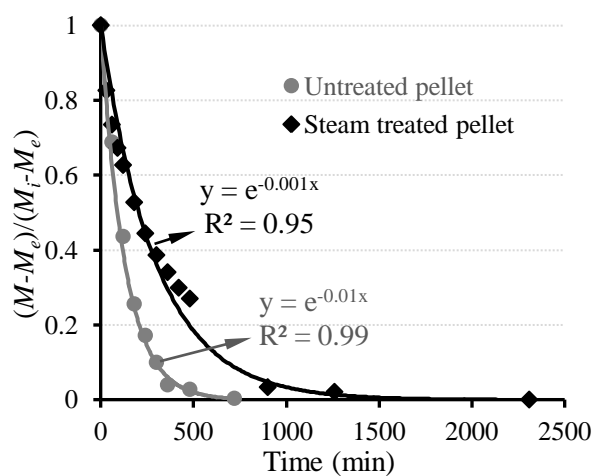
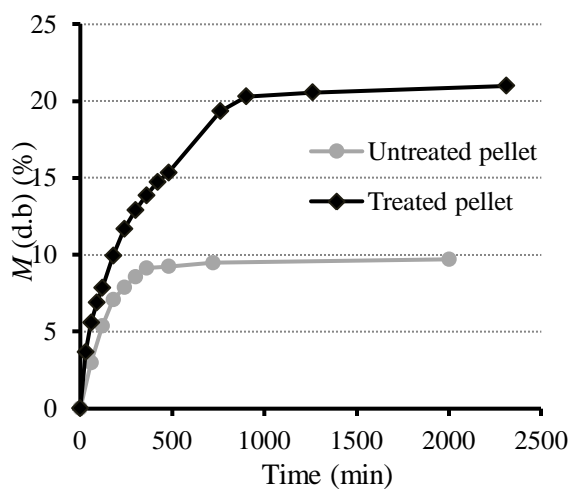


(c)



(d)

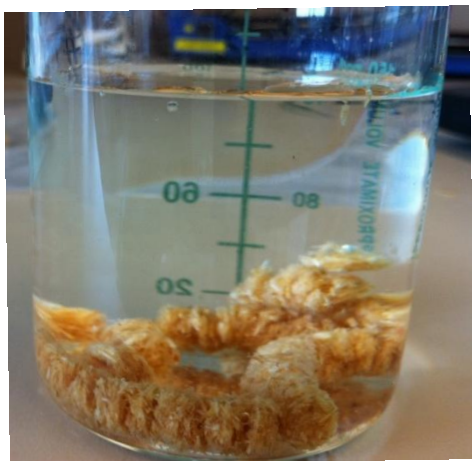
**Figure 5.3 MTI generated plots of force vs. displacement. The top plots are compression curves for (a) untreated and (b)  $\text{SO}_2$ -catalyzed steam treated particles; the lower plots are the expulsion curves of pellets out of die for (c) untreated and (d)  $\text{SO}_2$ -catalyzed steam treated pellets. The areas under these curves are computed to yield energy input for compression and energy input for pellet expulsion.**



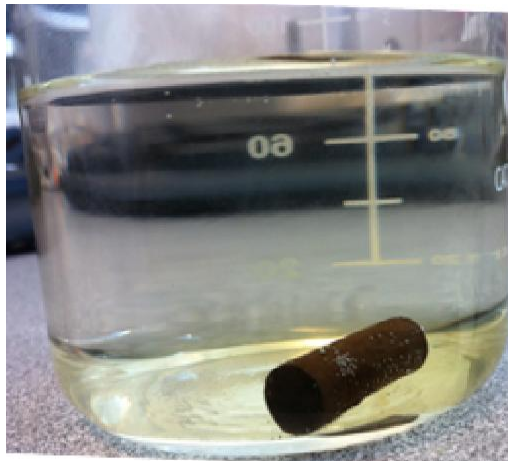
(a)

(b)

**Figure 5.4 (a) Pellet moisture content vs. time when placed in the humid chamber (30°C – 90%). Treated pellets reached to higher equilibrium moisture content than the untreated sample. (b) Moisture adsorption rate constant. Treated pellets reached equilibrium moisture content in longer time.**



(a)



(b)



(c)



(d)

**Figure 5.5 Moisture sorption tests: (a) untreated pellet right after immersing in water, (b) treated pellet after one week immersing in water, (c) appearance of an untreated pellet reached to equilibrium moisture content in humid chamber (30°C – 90% RH) after 4 h, (d) unchanged appearance of a treated pellet reached to equilibrium moisture content after 24 h**

## **Chapter 6. Superheated steam drying and treatment of cellulosic biomass to improve the quality of pellets**

### **6.1. Introduction**

Similar to what we have found in the previous chapters, several studies showed the increased moisture content of produced solid fraction up to two times after a hydrothermal pretreatment (Saddler et al., 1983; Brownell et al., 1986; Lam et al., 2011; Reza et al., 2012). This can lead to doubled energy consumption for drying. On the other hand, forest residues as a future feedstock for densification process are wet, mostly with an initial moisture content of 50% or greater (wet basis). So, the void volume of wood can be filled by condensate before steam temperature is reached in a steam pretreatment. Further heat transfer is controlled by the slower process of surface condensation and conduction into the cooler particle interiors. This leads to uneven cooking of wood, higher steam consumption in wood treatment and the high moisture content of treated wood (Brownell et al., 1986). As drying of raw material is the most energy consuming stage in a pellet plant (Mani et al., 2006a), adding a hydrothermal pretreatment prior to densification, in order to improve the quality of produced pellets, may make the economy of the whole system questionable (Lam, 2011). In this chapter, we have integrated drying and hydrothermal pretreatment steps in a pressurized reactor with the dual objectives of obtaining dry and pretreated feedstock and ultimately producing high quality pellets. Steam was generated from the moisture inside the material and no external steam was applied for the hydrothermal treatment. The thermodynamics of the system and the effect of temperature were investigated. The effect of this treatment on the physical properties of material such as particle size distribution, bulk density and moisture adsorption capacity was studied. Elemental analysis was done and the composition was correlated with the calorific heating value of

produced material. The mechanical strength and quality of produced pellets were investigated to assess the effectiveness of this hydrothermal pretreatment prior to pelletization.

## **6.2. Materials and methods**

### **6.2.1. *Materials***

The biomass material tested in this research consisted of white softwood species, Douglas fir (*Pseudotsugamenziesii*). The freshly cut stem wood pieces, provided by Malcolm Knapp Research Forest in Maple Ridge, BC, were brought to the lab and debarked manually. The pieces were naturally dried by spreading them on a stack of wire mesh trays in the laboratory environment from about 50% moisture content to about 20% (moisture contents are expressed in wet mass basis (w.b.) or as stated otherwise). This natural drying was necessary for any further grinding in this research. After grinding of wood pieces by a hammer mill (Model 10HMBL, Glen Mills Inc., Clifton, NJ) equipped with the a screen size of 1.6 mm, the moisture content of ground sample was adjusted back to about 50% (MC) by spraying distilled water on the sample inside a glass jar. The glass jar was sealed completely and kept in a refrigerator for about a month while it was shaken each day for well mixing and penetration of moisture inside particles before any further treatment. The amount of material conditioned was about 800 g.

### **6.2.2. *Equipment and procedure***

Drying and hydrothermal treatment was conducted in a 1 L pressure vessel (Model 316L SS Double-Ended DOT-Compliant Sample Cylinder, Swagelok) at the same time. The outlet of the vessel was equipped with a 12.7 mm diameter ball valve, controlled by an electrical actuator for rapid discharging of the treated biomass into ambient pressure. The inside temperature and pressure of the reactor were measured by 1.6 mm diameter K-type thermocouples (Omega, Stamford, USA) and digital pressure transducers (Omega, Stamford, USA), respectively. The thermocouple was connected to a temperature controller to regulate power input to the heater wrapped

around the reactor. Data were acquired by the LabView 8.2 software (National Instruments, Austin, Texas, USA).

In each experiment, specific amount of wet biomass (around 50 g or 17 g) with about 50% moisture content (w.b.) was loaded to the reactor (not preheated before). Based on the amount of loadings and initial moisture content, we could calculate the amount and specific volume ( $\text{cm}^3/\text{g}$ ) of present water in a closed fixed volume of the vessel, considering the occupied volume by biomass itself. The top inlet was completely sealed after loading. The heater around the pressure vessel heated up the content of the reactor till the inside temperature reached the set temperature ( $180^\circ\text{C}$  -  $280^\circ\text{C}$ ). Once the temperature was reached, the biomass was kept at the set temperature for 5 min and then the content of the reactor was discharged suddenly into a cloth mesh bag (Spectra Nylon mesh,  $20\mu\text{m}$  opening, USA) at the ambient temperature and pressure. The cloth mesh opening size was chosen in a way that it allowed the passage of steam molecules but not the solid particles. The moisture content of collected materials was measured immediately after collection (ASABE, 2008a). The mass loss was calculated based on the dry mass recovered vs. the initial dry mass for each loading. The treated materials were kept in sealed plastic containers at  $6^\circ\text{C}$  for further analysis.

For smaller loadings of biomass (17 g of biomass or about 8.5 g water), the specific volume of water/steam is larger (Figure 6.1b) and as a result, by heating up the system, the moisture vaporizes through constant volume line (A to B) and disappears as the last drop of liquid vaporizes. Any further heating produces superheated steam (steam with lower pressure than saturation pressure at a given temperature) whose pressure deviates from the saturation line (Figure 6.2). Figure 6.2 shows the experimental data of pressure vs. temperature in our system. To be ensured of the system, two different amount of pure water (according to the amount present with the biomass, 8.5 g and 25 g) was tested in a same manner as when we have the wet material in the system. Figure 6.2 also shows the theoretical line extracted from the steam table in thermodynamic textbooks. As we expected, the line of the 8.5 g water deviated from the saturation line at around  $165^\circ\text{C}$  and formed the superheated steam by further heating. When we had 17 g of wet biomass (corresponded to 8.5 g of water) same deviation was observed at about  $165^\circ\text{C}$ . We concluded that the thermodynamic behavior of our system can be predicted from that of the pure water. Therefore, the final

state of steam (saturated or superheated) at the set temperature was assumed from the thermodynamic diagrams of pure water.

For larger loadings (50 g of wet biomass) the specific volume of water/steam is smaller (but still higher than the specific volume of water at the critical point,  $V_g^{C_r}$ ) (Figure 6.1b) and, as a result, by further heating of the system, some fraction of the moisture still remained in the liquid phase. Figure 6.2 shows the saturation line in the case of larger loadings of biomass. The lower saturation pressures in the case of wet biomass could be related to the fact that some part of moisture in wood existed as bound water in the cell walls (Johansson et al., 1997). In the work reported here, we have evaluated the drying and treatment effects of the hydrothermal process on the physical and compositional characteristics of the treated and untreated ground samples and also produced pellets. We also compared the quality of pellets made from superheated steam treated Douglas fir grounds with that of pellets made from saturated steam treated and untreated materials. The energy input to produce pellets was measured and compared for different treatment conditions.

### 6.3. Drying effect and material loss

No external steam was applied in any of the treatment runs and steam was generated from the moisture inside the particles. Also, by application of cloth mesh bags, the almost complete separation of solid products from the gaseous fraction was achieved. So, as expected the moisture content of material was reduced from the initial value of around 50% (w.b.) to final moisture content of 41.0% to 2.1% (w.b.) depending on the set treatment temperature (Table 6.1). It was expected that in case of superheated steam treatment the final moisture content was reduced to the bound water content of wood. The bound water portion of wood is lower at higher temperatures (Fyhr and Rasmuson, 1996; Johansson et al., 1997). Table 6.1 shows this reduction in the final moisture contents at higher temperatures in the case of superheated steam treatments. For saturated steam treatment at each process temperature, the final moisture content can be calculated and well-predicted from the specific volume of saturated liquid and specific volume of saturated vapor at that temperature, by solving the following equations together,



$$\begin{cases} m^l \cdot v_g^l + m^v \cdot v_g^v = V^T \\ m^l + m^v \approx W \cdot MC \end{cases} \quad 6-1$$

$m^l$  is the amount of moisture remained in the particles in the liquid phase,  $v_g^l$  is the specific volume of saturated liquid at the treatment temperature,  $m^v$  is the amount of moisture vaporized into the steam phase,  $v_g^v$  is the specific volume of saturated vapor at the treatment temperature and  $V^T$  is the total volume of pressure vessel after deduction of the volume occupied by wet biomass.  $W$  is the total mass fed to the reactor (g) and  $MC$  is the moisture content of loaded feedstock (w.b.). Table 6.1 shows the calculated final moisture content values at each temperature. For treatments at 280°C, even for large loadings the system reached the superheated state and so the final moisture content of the treated material was very low, 4.1% (w.b.). However, at 200°C, even at small loadings of biomass, the system remained in the saturation zone (Figure 6.1b) and the final moisture content could be calculated (Table 6.1).

The percentages of mass loss increased with increasing the treatment temperature for both saturated steam treated material and superheated one (Table 6.1). At all temperatures, the material loss was higher when the samples treated and the steam reached the saturation condition. One explanation is that, during saturation steam treatments, the pressure of the reactor is much higher (Figure 6.2) and as a result the moisture inside the material was kept in the liquid form at higher temperatures. The hot compressed liquid water on the fibers caused hydrolysis reactions which usually need less activation energy compared to pyrolytic decomposition reactions which is more common during dry steam treatments (Libra et al., 2011). Therefore, the principal biomass components are less stable under wet conditions, which lead to lower decomposition temperatures.

## **6.4. Measurements on ground biomass**

### **6.4.1. *Particle size distribution***

Figure 6.3 shows the geometric mean diameter of raw material and also saturated and superheated steam treated samples. The geometric standard deviations were demonstrated on each bar. Superheated steam treatment did not reduce mean particle size of treated samples considerably up to 250°C. In contrast, particle size of saturated steam treated samples showed higher reductions at even low treatment temperatures, 200°C. From Figure 6.2, it was clear that during the saturation steam treatments, the final pressure of the system was higher than when the system reached the superheated steam state. The higher pressure caused the moisture inside the material to remain in the liquid phase up to the higher temperatures and brought about more degradation and disruption of wood constituents. Similarly, at higher treatment temperatures, even in the case of superheated steam treatments, due to the higher final steam pressure and also the pressure build up from the gases products, less bound water remained in the particles and more degradation took place.

### **6.4.2. *Calorific heating value and elemental analysis***

The values of calorific content of pelletized biomass were reported in Table 6.2 for untreated and steam treated (saturated and superheated) samples. Increasing the treatment temperature resulted in higher calorific heating values in both treatments. However, this increase was much considerable when the particles treatment reached the saturated steam state (from initial value of 18.84 MJ/kg to 22.44 MJ/kg at 280°C treatment). This improvement in the energy content of steam saturated treated pellets, again, was much higher than values found for dry torrefaction at the same temperature of about 280°C (Table 4.7). In case of superheated steam treatments, even at high temperatures, the increase in calorific heating values was lower but still comparable to those of dry torrefied pellets (Table 4.7). Table 6.2 also shows the carbon, hydrogen and oxygen contents of ground samples. Elemental analysis data were also following the same trend as higher treatment temperatures resulted in more increase in carbon percentages (less oxygen contents), especially in the case of saturated steam treated samples. In Chapter 5, it was shown that the heating value of carbon element is higher

than other elements. So, the increase in carbon percentage could lead to higher final heating value of products. It seems that superheated steam treatment is more like a thermal treatment as water evaporates at lower temperatures and pressures before having a chance to cause considerable chemical changes of the biomass.

Table 6.2 also demonstrated ash contents of untreated and treated samples. Similarly, saturated and superheated steam treated materials had highest ash contents at treatment temperatures of 220°C. Lam et al. (2011) found the same trend in their work. One explanation for this observation could be related to the fact that at 220°C other components of the wood, especially hemicellulose, underwent almost complete degradation, but not yet produced degradation by-products such as furfural or pseudo-lignin (Lam, 2011). The loss of hemicellulose of wood would have resulted in higher apparent percentage of ash. At temperatures higher than 220°C, the production of these by-products could counteract the loss of hemicellulose and result in less ash percentages. In most treatment conditions, the values of ash for superheated steam treatments were considerably lower than those of saturated treated samples. Hasibuan and Wan Daud (2009) concluded that the solubility of ash species (especially, Silica particles) in superheated steam is higher than in hot water (saturated water). The results of current study also showed that when steam reached superheated conditions, the ash content reduced at all treatment temperatures.

## **6.5. Characterization of pelletized samples**

### **6.5.1. *Pellet density and mechanical strength***

Table 6.3 represents the density and mechanical strength of densified material, before and after treatments. The mechanical stability of pellets has been evaluated by the maximum force needed for their breakage. The density of pellets made of material treated with superheated steam was lower than the density of untreated and also saturated steam treated pellets. At superheated conditions, material became bone dried and mostly thermally treated (vs. hydrothermally treated). This could be a reason for the lower densities for the produced pellets. However, at saturated steam conditions, the presence of liquid water at temperatures higher than 170°C facilitated the hydrothermal

treatment and led to the lignin redistribution on the fiber surface. Data on the maximum breaking force of saturated steam treated pellets also confirmed the better binding of particles at this treatment conditions. Again, the maximum strength and density were observed at a treatment temperature of 220°C (for both saturated and superheated steam conditions). From the particle size reduction effect of saturated steam treatment (Figure 6.3), we expected a considerable increase in pellet density and strength of produced pellets, especially at 220°C. The smaller particles can filled up the void spaces between particles and increase the packing of these treated materials.

### **6.5.2. Mechanical energy input for pelletization**

Table 6.3 shows the specific energy required to compress the material in a piston-die pelletizer and also the energy consumed for pushing the formed pellet out of the die. The compression energy reduced when the feedstock was treated by saturated steam (from 21.83 J.cm<sup>3</sup>/g to the lowest value of 17.93 J.cm<sup>3</sup>/g at 220°C). In the case of superheated steam treated pellets, the required compression energy was higher than that of untreated pellets (from 21.83 J.cm<sup>3</sup>/g to the lowest value of 27.96 J.cm<sup>3</sup>/g at 220°C). Again the smaller particles produced due to the steam treatments at 220°C could help binding and lowering the compression energy. The expulsion energy increased for all treated materials, whether treated by saturated steam or superheated steam. This higher expulsion energy corresponds to our previous results and also those of Lam et al. (2011). The sum of compression and expulsion energy is considered as total required mechanical energy input for pelletization. The values extracted from Table 6.3 show a higher total energy of pelletization for treated pellets compared to untreated pellets, except for pelletization of saturated steam treated material at 220°C. The total energy input at this condition is slightly lower than untreated one (28.5 J.cm<sup>3</sup>/g vs. 29.4 J.cm<sup>3</sup>/g) while the produced pellets are harder and denser.

### **6.5.3. Stickiness of treated samples**

Figure 6.4 pictures the force vs. displacement curves during expulsion of pellets (made of saturated steam treated material at different treatment temperatures) from the cylindrical die. The first peak is a representative of the force required to initiate movement of a formed pellet, inside the press channel. As Figure 6.4 shows, the

initiation force for material treated at 220°C is the highest while the consequent force to continue this movement is the lowest. Similarly for the treated material under superheated steam treatment conditions, Figure 6.5 shows these graphs at various process temperatures. Again, the initial force required for material treated at 220°C was the highest. We interpreted these peaks as a factor of stickiness of treated material during pelletization. The particles treated at 220°C were much stickier. This could explain the higher density and more stable pellets made of treated samples at 220°C.

#### **6.5.4. *Moisture adsorption of pellets***

Figure 6.6 depicts the moisture uptake rate of completely dried pellets during exposure to 90% relative humidity at 30°C. All graphs ultimately reached a constant value which was considered as an equilibrium moisture content (EMC) of the pellet. Both treatments resulted in hydrophobic pellet products. Increasing treatment temperature led to a lower EMC for both saturated and superheated steam treated pellets. However, saturated steam treated pellets generally adsorbed less moisture from the environment compared to pellets treated with superheated steam at the same temperature. On the other hand, superheated steam treated samples reached the final constant values of moisture content faster; i.e., the adsorption rate constant of  $k$  is larger in case of superheated steam treated pellets.

### **6.6. Concluding remarks**

Previous chapters showed the increased moisture content of produced solid fraction up to two times after treatment, this could lead to doubled energy consumption for drying. In this chapter, wet Douglas fir wood particles were dried and hydrothermally treated, simultaneously, before pelletization. Raw material with  $50 \pm 2.5\%$  MC was fed to a batch reactor and heated up to a specific temperature (200-280°C) then kept at the set temperature for 5 min. Steam was generated from the moisture inside the material and no external steam was applied for the hydrothermal treatment. Douglas fir particles dried from the initial MC to 41.0% to 2.1% MC (w.b.) for treatments at 180-280°C, respectively, depending on the final state of produced steam. The reactor's pressure vs. temperature curves have conformity with thermodynamic curves of pure water. So, the

MC of treated/dried material can be predicted from the saturated values of steam table for water. The calorific heating value and carbon percentage of treated/dried samples increase considerably with increasing the treatment temperature. This increase is highly comparable to that of dry torrefaction at high temperatures. Density and mechanical strength of pellets made of treated/dried material are the highest at 220°C pretreatment temperature and starts to decrease beyond this treatment condition. Superheated steam treatment/drying makes the pellets hydrophobic, but to a less degree compared to saturated steam treated pellets.

**Table 6.1 Drying effect of the hydrothermal treatment (numbers in the brackets represents standard deviations for n=3)**

Samples	Initial moisture content (w.b.) (%)	Final moisture content (w.b.) (%)	Calculated final moisture content (w.b.) (%)	Mass loss (%)
Sat-Treated at 180°C	47.8 (0.0)	41.0 (0.1)	42.7	2.5 (0.5)
Super-Treated at 200°C	49.6 (0.0)	13.5 (0.1)	11.5	7.6 (0.5)
Sat-Treated at 200°C	49.5 (0.1)	40.2 (0.2)	41.7	12.1 (0.8)
Super-Treated at 220°C	49.8 (0.0)	3.4 (0.1)	-	15.9 (0.4)
Sat-Treated at 220°C	49.5 (0.1)	34.6 (0.1)	36.5	18.5 (0.8)
Super-Treated at 250°C	48.3 (0.2)	2.3 (0.0)	-	23.3 (1.0)
Sat-Treated at 250°C	49.5 (0.0)	25.6 (0.1)	21.7	27.0 (0.9)
Super-Treated at 280°C	49.1 (0.1)	2.1 (0.1)	-	24.3 (1.0)
Sat-Treated at 280°C	49.5 (0.1)	4.2 (0.1)	-	30.3 (1.1)

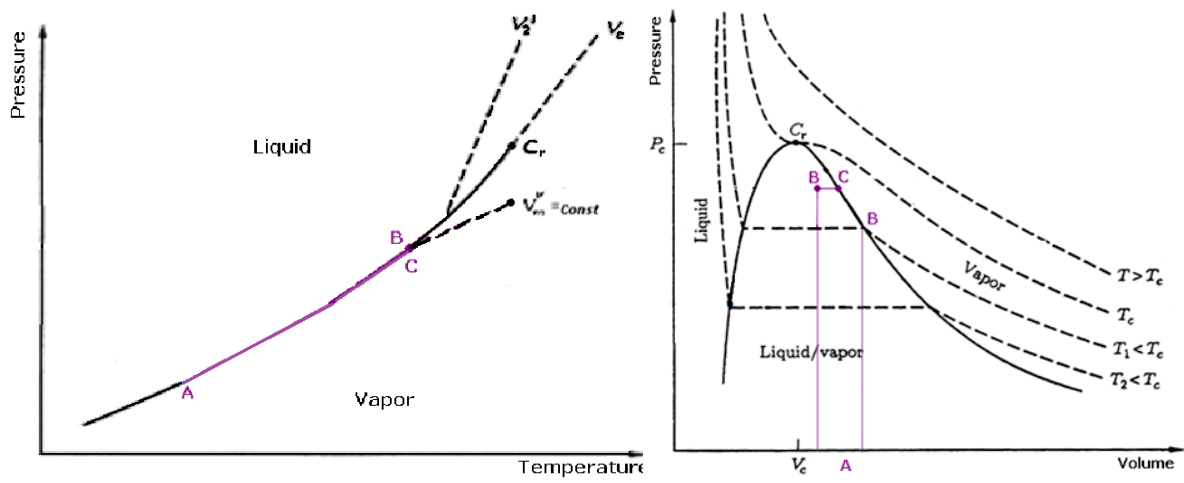
**Table 6.2 Thermo-chemical properties of samples (numbers in the brackets represents standard deviations for n=3)**

Samples	Ash content (%)	HHV (MJ/kg)	C (%)	H (%)	O (%)
Untreated	0.44 (0.03)	18.84 (0.09)	46.7 (0.2)	6.4 (0.1)	46.4 (0.1)
Sat-Treated at 180°C	0.40 (0.02)	19.14 (0.12)	51.1 (0.1)	6.4 (0.1)	42.0 (0.3)
Super-Treated at 200°C	0.22 (0.05)	19.02 (0.08)	50.5 (0.1)	6.2 (0.0)	42.7 (0.1)
Sat-Treated at 200°C	0.38 (0.04)	19.64 (0.09)	53.4 (0.0)	6.1 (0.0)	40.1 (0.1)
Super-Treated at 220°C	0.37 (0.06)	18.98 (0.07)	51.0 (0.1)	5.9 (0.0)	42.6 (0.1)
Sat-Treated at 220°C	0.69 (0.10)	20.62 (0.08)	54.4 (0.0)	5.9 (0.1)	39.3 (0.0)
Super-Treated at 250°C	0.42 (0.01)	19.41 (0.11)	54.5 (0.1)	5.6 (0.1)	39.9 (0.2)
Sat-Treated at 250°C	0.33 (0.09)	20.92 (0.10)	56.0 (0.1)	5.7 (0.0)	37.9 (0.1)
Super-Treated at 280°C	0.17 (0.08)	20.19 (0.08)	54.9 (0.1)	6.0 (0.1)	38.9 (0.0)
Sat-Treated at 280°C	0.28 (0.07)	22.44 (0.12)	56.7 (0.1)	6.4 (0.0)	36.6 (0.1)



**Table 6.3 Mechanical properties of produced pellets and energy inputs for densification (numbers in the brackets represents standard deviations for n=10)**

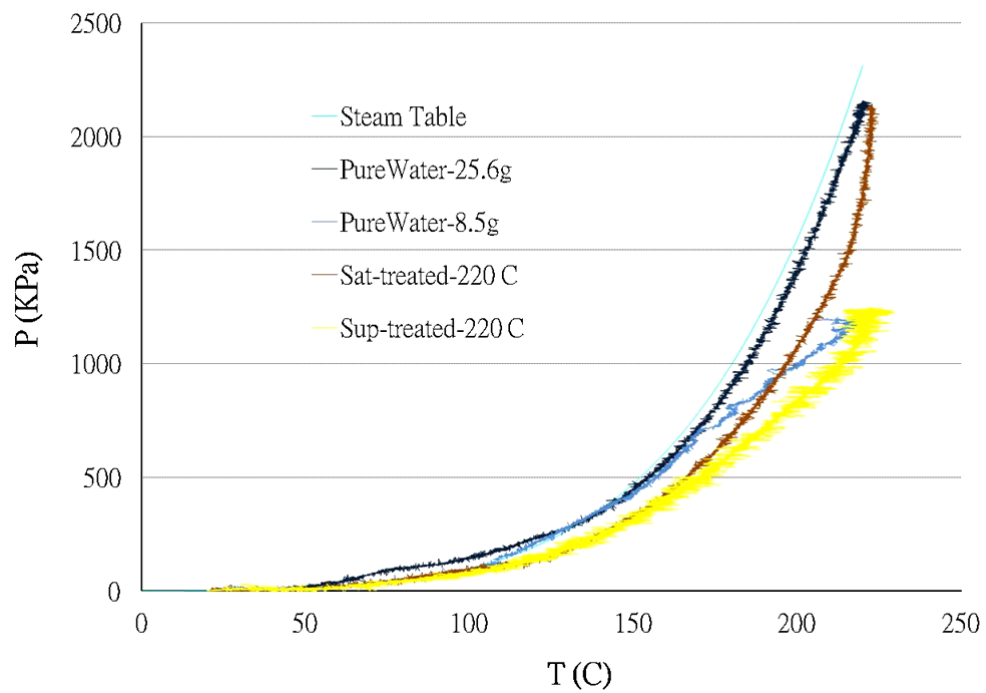
Samples	Pellet density (g/cm <sup>3</sup> )	Compression energy (J.cm <sup>3</sup> /g)	Expulsion energy (J.cm <sup>3</sup> /g)	Max. breaking force (N)
Untreated	1.19 (0.02)	21.83 (1.59)	7.57 (2.68)	888 (27)
Sat-Treated at 180°C	1.15 (0.02)	21.68 (2.19)	17.49 (5.84)	1204 (276)
Super-Treated at 200°C	1.10 (0.03)	31.87 (3.20)	30.79 (3.24)	798 (128)
Sat-Treated at 200°C	1.19 (0.04)	20.74 (1.00)	20.30 (2.85)	1220 (303)
Super-Treated at 220°C	1.17 (0.02)	27.96 (1.37)	25.50 (5.90)	1322 (174)
Sat-Treated at 220°C	1.28 (0.01)	17.93 (1.24)	10.57 (0.89)	1745 (134)
Super-Treated at 250°C	1.10 (0.05)	28.16 (3.79)	29.64 (7.71)	914 (106)
Sat-Treated at 250°C	1.24 (0.04)	19.45 (1.06)	19.72 (2.46)	1128 (53)
Super-Treated at 280°C	0.95 (0.02)	35.82 (0.87)	34.02 (2.92)	457 (95)
Sat-Treated at 280°C	1.16 (0.01)	23.15 (2.24)	21.75 (3.11)	1114 (89)



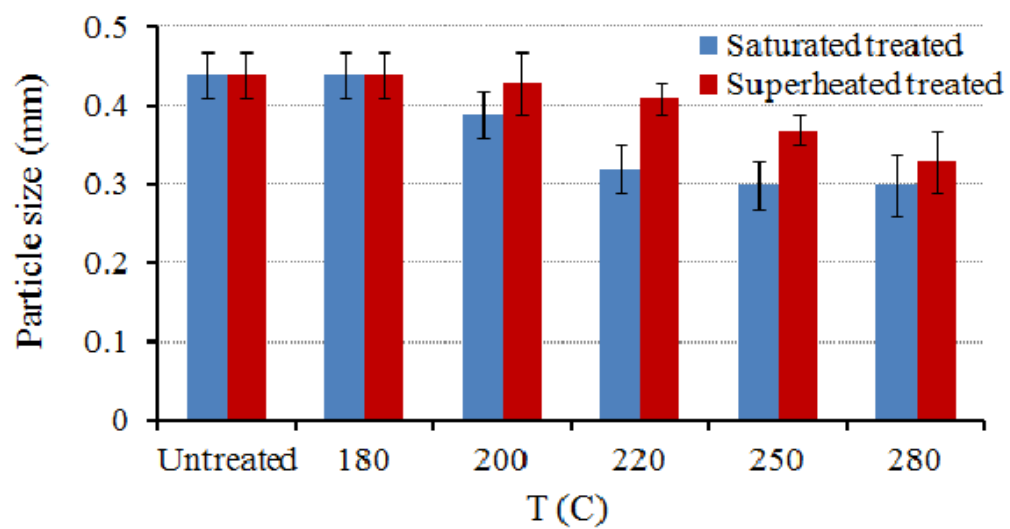
(a)

(b)

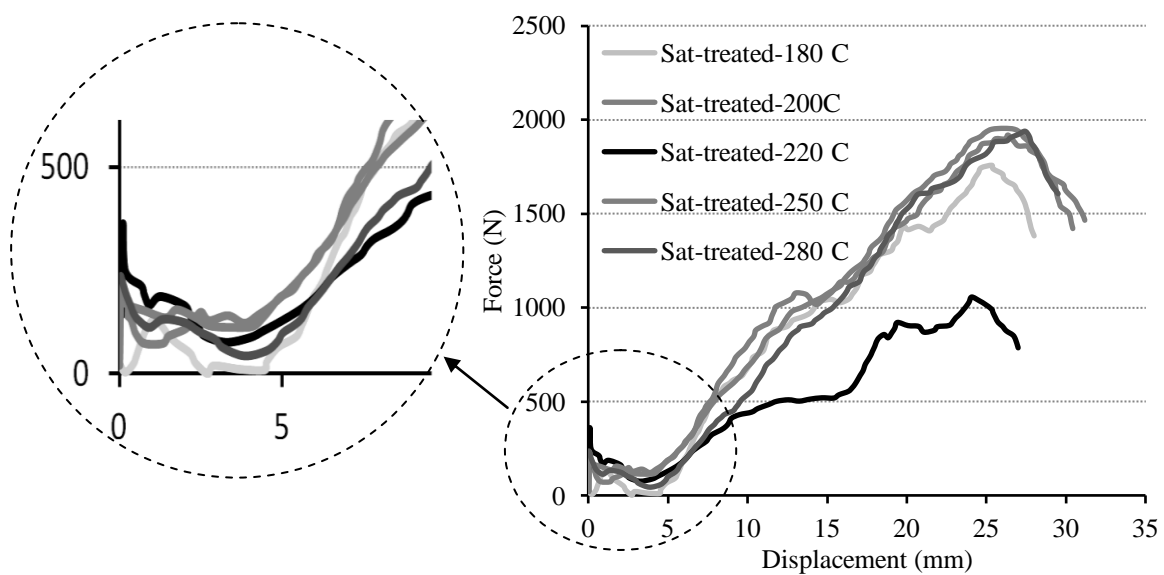
**Figure 6.1 Thermodynamic curves for pure water, (a) liquid/vapor phase equilibrium boundaries, (b) saturation region**



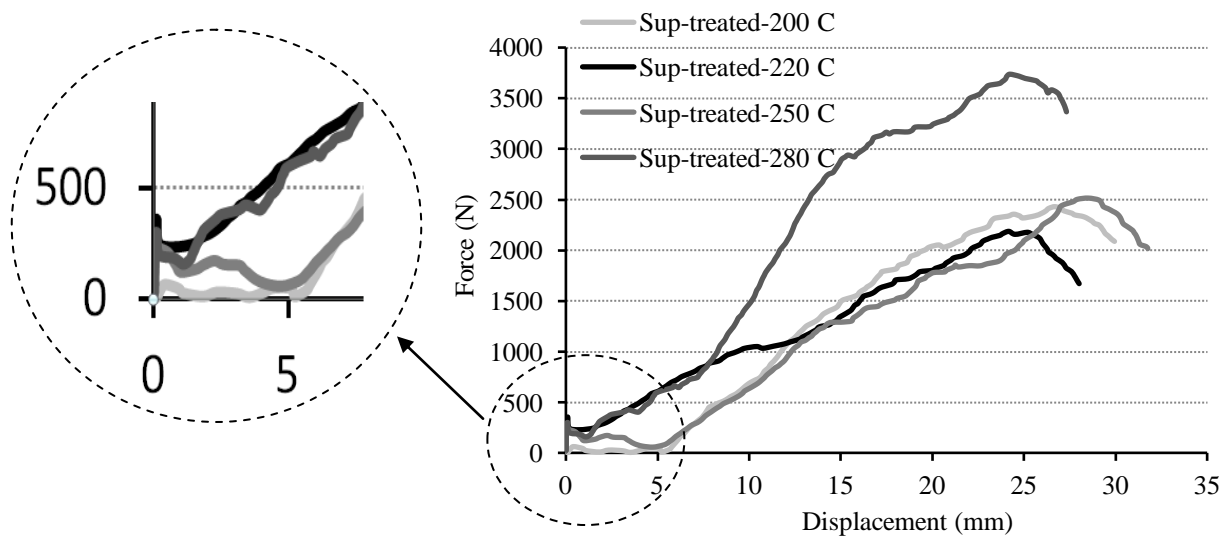
**Figure 6.2** *Equilibrium pressure vs. temperature curves for the experimental reactor*



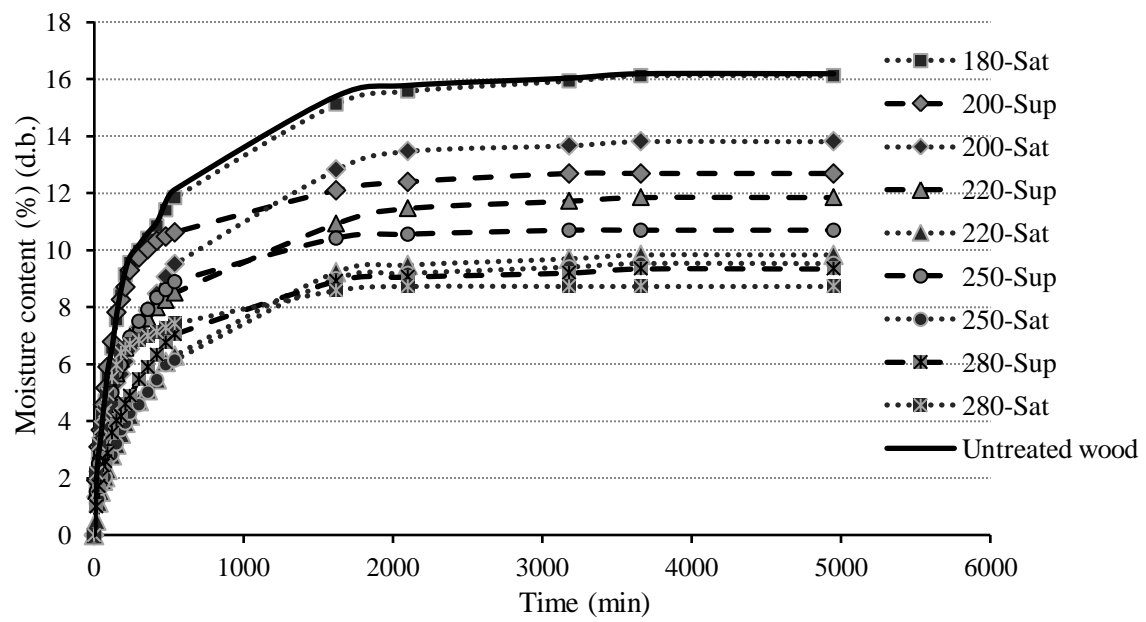
**Figure 6.3** Size reduction effect of hydrothermal treatments at different treatment temperatures



**Figure 6.4** *Expulsion curves for saturated steam treated samples at different treatment temperatures*



**Figure 6.5** *Expulsion curves for superheated steam treated samples at different treatment temperatures*



**Figure 6.6 Moisture uptake rates of pellets made of samples treated at different conditions**

## **Chapter 7. Analysis of mass and energy balances**

### **7.1. Introduction**

Although steam pretreatment is an energy intensive process, the benefits gained from enhancing the quality of biomass may offset extra energy input and associated costs. There are published literatures on techno-economic and energetic analyses of steam pretreated woody biomass for enzymatic hydrolysis and fermentation for bioethanol production (Shevchenko et al., 2001; Zimbardi et al., 2002; Mabee et al., 2007). Lam (2011) conducted an analysis of mass and energy balance for the production of commercial pellets from steam treated and untreated feedstock. He concluded that with steam pretreatment included the total direct energy input increased substantially. In this research, mass and energy balances are included to evaluate the potential improvements over the saturated steam treatment Lam (2011) suggested.

### **7.2. Development of analysis method**

Figure 7.1 shows a typical pelleting plant consisting of major unit operations. The major cost factor unit operations are: drying, pellet mills, and size reduction (Mani et al., 2006b). In this chapter, the mass and energy balances for these major operations plus a new hydrothermal pretreatment (Figure 1.3) are developed. The calculations conducted based on the laboratory data obtained in Chapters 4 to 6. In some cases, the commercial data, taken from a 45,000-tonne conventional pellet plant operation in Princeton, BC, Canada, have been used for estimations (Mani, 2005).

The pellet plant at Princeton had an annual production of 45000 tonnes. The plant processed 10.35 t/h of feedstock at 50% (wet basis) moisture content to 6 t/h of



pellets at 10% (wet basis) moisture content. The plant operated 24 h a day, 310 days per year that corresponds to an annual utilization of 85%. Although the raw feedstock to this plant was saw dust and shavings from an adjacent saw mill, we also include debarked woodchips at 50% moisture content in calculations. We envision that a steam explosion plant would also process woodchips as the supply of saw dust dwindles. The debarked woodchips are sized to 20 mm by 20 mm by 2 mm (length, width, thickness).

### 7.2.1. Drying

The wet biomass is dried from initial moisture content till the desirable final moisture was reached in a conventional dryer (THELCO laboratory PRECISION oven, Thermo Electron Corporation), operating at temperatures about 80°C. In this calculation, we assume there are no extractives or volatile losses during the drying process and only the moisture is exhausted from the system.

Determination of amount of water evaporated ( $m_e$ ):

$$m_{i,bd} = m_i \times x_{i,bd} \quad 7-1$$

$$mc_i = \frac{1 - x_{i,bd}}{x_{i,bd}} \quad 7-2$$

$$mc_f = \frac{1 - x_{f,bd}}{x_{f,bd}} \quad 7-3$$

$$m_f = m_{i,bd} \times (1 + mc_f) \quad 7-4$$

$$m_e = m_i - m_f \quad 7-5$$

where  $m_{i,bd}$  and  $m_{f,bd}$  are the initial and final bone dried biomass mass (kg),  $x_{i,bd}$  is the solid fraction of the biomass (wet basis),  $mc_i$  is the initial feed moisture content

(d.b.) (dimensionless),  $x_{f,bd}$  is the solid fraction of the biomass (wet basis),  $mc_f$  is the final product moisture content (d.b.) (dimensionless).

Energy input to drying operation:

Total heat required for 1 kg of bone dried feedstock ( $\Delta H_d$ ):

$$\Delta H_{d1} = C_{p,solid}(T_{d,out} - T_{d,in}) \quad 7-6$$

$$\Delta H_{d2} = mc_i \times C_{p,water}(T_{vapor} - T_{d,in}) \quad 7-7$$

$$\Delta H_{d3} = (mc_i - mc_f)\Delta H_{Latent} \quad 7-8$$

$$\Delta H_{d4} = (mc_i - mc_f)C_{p,vapor}(T_{d,out} - T_{vapor}) \quad 7-9$$

$$\Delta H_{d5} = mc_f \times C_{p,water}(T_{d,out} - T_{vapor}) \quad 7-10$$

$$\Delta H_d = \sum_{i=1}^5 \Delta H_{di} \quad 7-11$$

where  $\Delta H_{d1}$  is the heat required to increase the initial biomass feed from  $T_{d,in}$  to  $T_{d,out}$  (kJ/kg),  $C_{p,solid}$  is the heat capacity of the wood sawdust = 2.81 kJ/(kg.°C),  $T_{d,in}$  is the drying unit inlet temperature of the feed,  $T_{d,out}$  is the drying unit outlet temperature of the dried product,  $\Delta H_{d2}$  is the heat required to increase the moisture content of the initial biomass feed from  $T_{d,in}$  to  $T_{vapor}$  (kJ/kg),  $C_{p,water}$  is the heat capacity of the water = 4.18 kJ/(kg.°C),  $T_{vapor}$  is the temperature of the water vapor,  $\Delta H_{d3}$  is the heat required for the removal of the moisture content of the biomass as the water evaporates from  $mc_i$  to  $mc_f$  (kJ/kg), latent  $\Delta H_{Latent}$  is the latent heat of the water vapor = 2260 (kJ/kg),  $C_{p,vapor}$  is the heat capacity of the water vapor = 2.01 kJ/(kg.°C),  $\Delta H_{d4}$  is the heat required for increasing the temperature of the moisture content removed from the biomass from

$T_{vapor}$  to  $T_{d,out}$  (kJ/kg),  $\Delta H_{d5}$  is the heat required to increase the temperature of the moisture content inside the wood from  $T_{vapor}$  to  $T_{out}$  (kJ/kg).

Total energy input to drying operation ( $E_{d,total}$ ):

$$E_{d,total} = \frac{\Delta H_d m_{i,bd}(1 + \eta_{hl})}{m_p \eta_{dryer}} \quad 7-12$$

where  $E_{d,total}$  is the total heat required for drying of the initial biomass (kJ/kg),  $\eta_{hl}$  is the dryer heat loss assumed in this study 20%,  $\eta_{dryer}$  is the dryer efficiency =80% (That is 20% heat loss through the drying step, assumed in this research), and  $m_p$  is the total mass of pellet produced in the plant.

### 7.2.2. Size reduction

The dried woodchips are conveyed to the hammer mill and ground through a 1.6 mm screen. There is an assumption of 1% moisture loss during the grinding process and exhaust as vapor. The size reduced particles are conveyed to the densification process. The net energy required for size reduction can be estimated from Kick's law by knowing the initial and final size of the feedstock (Naimi, 2008; Hosseini et al., 2010):

$$\Delta E = K_k \ln \frac{L_f}{L_p} \quad 7-13$$

where  $\Delta E$  is the energy consumption for size reduction (kJ/kg),  $K_k$  is the Kick's constant (kJ/kg).  $L_f$  and  $L_p$  are the initial and final sizes of the feedstock (mm), respectively. The Kick's constant used here is 100 kJ/kg reported by Esteban and Carrasco (2006).

So, the energy input for size reduction,  $E_{sr}$ , per tonne of produced pellet (MJ/t) is:

$$E_{sr} = \frac{\Delta E (0.99) m_f}{\eta_e m_p} \quad 7-14$$

where  $\eta_e$  is the conversion efficiency of the electricity = 45%, and constant of 0.99 accounts for the 1% mass loss (water and fine particles loss) during size reduction.

### 7.2.3. *Densification*

The recovered finely ground sawdust is compressed into about 6 mm diameter, 20-30 mm long pellets in a press mill. The energy input for pelletization of untreated Douglas fir wood powder was estimated from the compression and expulsion data using a single die with a heating element at 70-100°C. The compression and expulsion energy were determined by the area under the force-displacement curves. The total energy for pelletization (kJ) is defined as the sum of the compression energy (kJ) and the expulsion energy (kJ) in this case. The energy per mass (kJ/kg) and energy per pellet density J/(g/cm<sup>3</sup>) of the pelletization unit operation were reported in Chapters 4 to 6. We assumed 20% mass loss during densification due to moisture evaporation and solid loss.

The mechanical energy input for pellet production,  $E_p$ , per tonne of produced pellet (MJ/t) is:

$$E_p = \frac{(E_{com} + E_{exp})(0.8)(0.99 m_f)}{\eta_e m_p} \quad 7-15$$

where  $\eta_e$  is the conversion efficiency of electricity to mechanical forces= 45%, and constants of 0.8 and 0.99 account for the 20% and 1% mass losses during pelletization and size reduction operations, respectively.

### 7.2.4. *Hydrothermal treatment*

The energy input for hydrothermal pretreatment is calculated based on steam temperatures, pressure and time measured from our experimental unit available at the

UBC Clean Energy Research Center (CERC). The enthalpies of saturated vapour ( $h_g$ ) and enthalpies of latent heat of vaporization ( $h_{fg}$ ) at the reaction temperature are used to calculate the energy input for steam generation in the boiler. The maintenance heat is calculated by estimating power input to maintain the steam reactor chamber at the treatment temperature.

Energy required for saturated steam generation in the boiler:

$$E_1 = \frac{m_w \times h_g}{\eta_b} \quad 7-16$$

where  $E_1$  is the energy required to generate saturated steam in the boiler (kJ),  $m_w$  is the total amount of water evaporated in the boiler,  $h_g$  is the enthalpy of saturated vapor (kJ/kg) and  $\eta_b$  is the efficiency of boiler at 75%.

Since the reactor is assumed to be thermally insulated perfectly, here we assume the energy required to sustain the reaction temperature of the steam is equal to the heat loss of the steam to the solid particle of biomass. Energy required to sustain the reaction temperature of the steam treatment chamber ( $E_2$ ) is:

$$E_2 = \frac{h_c A (T_g - T_s) t}{\eta_e} \quad 7-17$$

where  $E_2$  is the energy required to sustain the reactor temperature (kJ),  $h_c$  is the heat transfer coefficient across the reactor wall (kW/m<sup>2</sup>.K) = 100,  $A$  is the area (m<sup>2</sup>) of the reactor chamber exposed to the heating tapes,  $T_g$  is the temperature of the steam (K),  $T_s$  is the temperature of environment (K), and  $t$  is the reaction time of the steam treatment (s), and  $\eta_e$  is the conversion efficiency of the electricity generation = 45%.

Energy input to hydrothermal treatment unit:

$$E_{HT} = \frac{(E_1 + E_2)}{m_p (1 - s)} \quad 7-18$$

where  $E_{HT}$  is the energy input to hydrothermal treatment unit per unit mass of produced pellet (kJ/kg),  $E_1$  is the energy required to generate steam in the boiler (kJ),  $E_2$  is the energy required to sustain the treatment reactor temperature (kJ),  $m_p$  is the mass of produced treated pellets, and  $s$  is the solid yield of the samples (%).

### 7.3. Energy inputs comparison

The energy consumptions are evaluated and compared based on the reported mass losses and energy balances developed in the previous sections and Chapters 4 to 6, for the major unit operations in a plant. Table 7.1 lists the energy inputs for the individual operations and treatments performed at 220°C, based on one kg of pellets produced. In cases of external steam treatment and SO<sub>2</sub>-catalyzed steam treatment, the gain in the moisture content of treated material caused higher drying energy inputs compared to that of untreated samples. In case of treatments using the internal moisture for steam generation, the drying energy was much lower; however, the treatment itself took much longer time (50 vs. 5 min in case of external steam treatment) and caused considerable treatment energy inputs compared to that of external steam treatment. SO<sub>2</sub>-catalyzed steam treatment eliminated the need for size reduction and saved the grinding energy. Also, the pelletization energy required to densify the SO<sub>2</sub>-catalyzed steam treated material was lower than energy inputs for other treatments.

### 7.4. Concluding remarks

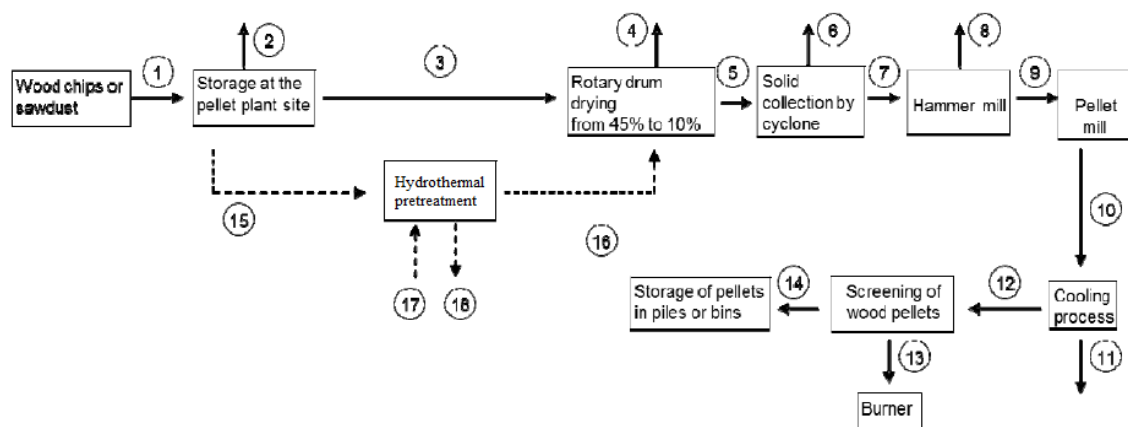
In this chapter, the energy and mass balances were developed. The energy inputs in case of different hydrothermal treatments were calculated and compared to the energy input for untreated material. The energy ratios reported based on the untreated case. From various hydrothermal treatments explored in this research, SO<sub>2</sub>-catalyzed steam pretreatment has the lower energy ratio; confirming that by applying the SO<sub>2</sub>-

catalyst in the process of steam treatment of softwood particles, much more stable and harder pellets are produced while the energy consumption is lowered compared to what Lam (2011) found (also repeated in this research) for the external steam treatment.

**Table 7.1 Direct energy Input per unit kilogram of produced pellets at 10 % m.c. (w.b.) to the biomass pelletization process with the laboratory data of different hydrothermal treatments**

Operations	Energy inputs (MJ/kg)				
	External saturated steam treated	SO <sub>2</sub> -catalyzed saturated steam treated	Internal saturated steam treated	Internal superheated steam treated	Untreated
Drying	4.52	4.57	1.61	0.0	3.01
Size reduction	0.82	0.0	1.13	1.29	1.31
Pelletization	0.27	0.20	0.24	0.29	0.24
Hydrothermal treatment	4.30	3.95	6.63	7.65	0.0
Total energy input	9.91	8.72	9.61	9.23	4.56
Energy ratio	2.17	1.91	2.11	2.02	1.0





**Figure 7.1 Unit operations and process flow in a pellet production plant (Lam, 2011)**

## **Chapter 8. Conclusions and future work**

### **8.1. Overall conclusions**

Three softwood species Pine, Spruce, and Douglas-fir and a sample of Douglas fir bark are ground and treated with pressurized saturated steam at 220°C for 5 min. The key physical characteristics of treated and untreated biomass are measured and compared. Also, the effects steam treatment has on the particle size, energy input to form pellets, pellet density, and the strength of pellets are quantified. Using external saturated steam in a hydrothermal treatment reduces the geometrical mean diameter of particles, leading to as high as 25% size reduction. Bark particles do not show the same degree of size reduction as the white wood fractions do. The treatment increases the calorific value of biomass. The highest increase of 26% in heating value is observed for Spruce. The carbon percentage of all treated samples increases significantly due to the loss of oxygen and hydrogen in hydroxyl (–OH) functional groups. This increase is comparable to that of dry torrefaction at high temperatures. This result proves the hypothesis that steam treatment as a mild wet torrefaction can be as effective as severe dry torrefaction.

Steam treatment reduces mechanical strength of bark pellets, but it increases the maximum breaking force of whitewood treated pellets. Among the three species tested, the mechanical strength of Spruce pellets has the largest increase after steam treatment. Mechanical energy input to make pellets from treated material is higher compared to untreated pellets for all species and bark samples. Bark does not require the same high amount of mechanical energy compared to whitewood, before or after treatment. To reduce the consumption of this high amount of energy, steam treated material can be pelletized by applying one third of the force to arrive at an even higher mechanical strength compared to pellets made of untreated particles. Applying one third of the force on treated material requires almost the same densification energy compared

to pelletization energy of untreated material under the higher compression force. However, the density of treated pellets is lower than the density of untreated pellets.

Knowing the benefits of steam pretreatment on the quality of produced pellets and its necessity in bioconversion process to produce bioethanol from lignocellulosic woody biomass, there appears to be a potential to combine steam treatment for the production of high quality wood pellets and application of these pellets for bioethanol production. Sulfur dioxide catalyzed steam treatment is applied directly on Douglas fir woodchips, results in a substantial reduction in particle size and enables direct pelletization without any further size reduction step. Subsequent pelletization of this treated material results in denser pellets with considerably higher mechanical strength, while minimizing the energy required for densification. The treated pellets remain intact even under high humid conditions, made them more suitable for long term storage and shipping. While high calorific values and low ash content make the treated pellets desirable feedstocks for thermo-chemical conversion, the good recovery of original carbohydrates from treated pellets makes them viable feedstocks for any biochemical-based conversion.

The increased moisture content of produced solid fraction, up to two times after hydrothermal treatments presented in earlier chapters, leads us to integrate drying and hydrothermal pretreatment steps in a pressurized reactor. Steam is generated from the moisture inside the material and no external steam is applied for the hydrothermal treatment. The reactor pressure vs. temperature curves have conformity with thermodynamic curves of pure water. Depending on the initial loading of wet biomass into a fixed volume reactor, the final state of produced steam (superheated or saturated) and final moisture content of treated/dried material can be predicted from the saturation values of steam table. Douglas fir particles are dried from initial  $50 \pm 2.5\%$  moisture content to  $41.0\%$ - $2.1\%$  MC (w.b.) for treatments at  $180$ - $280^\circ\text{C}$ , respectively, depending on final state of produced steam. The calorific heating value and carbon percentage of treated/dried samples increase considerably with increasing the treatment temperatures. This increase is highly comparable to that of dry torrefaction at high temperatures. Density and mechanical strength of pellets made of treated/dried material are the highest at  $220^\circ\text{C}$  pretreatment temperature and start to decrease beyond this pretreatment condition. Due to the lower maximum pressure achieved in the treatment

reactor, superheated steam treated samples become bone dried and thermally (instead of hydrothermally) treated, so consume more compression and expulsion energy during pelletization and are less hydrophobic compared to saturated steam treated materials.

## **8.2. Recommendations for future studies**

The current study investigated the effect of different hydrothermal treatments on improving the wood pellet quality for handling and storage. Different bioenergy applications were considered for the produced treated pellets. Much work yet to be done in this area. The following works are recommended for future investigations derived from this study:

1. The main focus of this study was on the produced solid fraction of hydrothermal treatment. However, the vapour/gas fraction is also worth investigation from compositional point of view and also its application.
2. Study of different loadings of SO<sub>2</sub> impregnation in a steam pretreatment to improve quality of produced pellets.
3. Study the hydrothermal pretreatment of SO<sub>2</sub> impregnated wet woodchips without applying the external steam.
4. Hydrothermal pretreatment and drying of wet woodchips using the pressurized external superheated steam.
5. Include the importance of understanding the fundamental of material properties for pelletization.

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## Appendix A

The author conducted the following brief study on superheated steam drying at the University of Manitoba's Biosystems Engineering under the direction of Professor Stefan Cenkowski. Superheated steam has been used for drying in different industries, but its effects on the composition of woody biomass for biofuel production have not been considered. This work investigates the changes in lignin, extractives, ash contents and critical physical properties of Pine, Douglas fir wood and bark samples after steam treatment. In this study, samples were exposed to superheated steam at 160 °C for 15 min and a steam velocity of 1.5 m/s under the atmospheric condition.

### EXPERIMENTS

The biomass chips and grinds were subjected to the superheated steam in an open system under atmospheric pressure. The superheated steam system consists of a steam generator, a super heater, conveying pipelines, regulating valves, a drying chamber, a condensation system, instrumentation, temperature controllers and a data acquisition system. This unit is available at the University of Manitoba (Figure A. 1). The author conducted these tests at the University of Manitoba.

Poplar Pine, Douglas fir wood and also Douglas fir bark were steam dried in this study. Wood logs were debarked in University of British Columbia for high putridity of samples and then their size reduced to 1 to 2 mm by knife mill. Moisture content of ground material was determined by ASABE Standard S358.3 and the samples kept in sealed plastic bags. Steam drying was performed in University of Manitoba, Winnipeg, for 15 min, with steam velocity of  $1.5 \pm 0.05$  m/s and steam temperature of  $160 \pm 2.0^\circ\text{C}$  for each sample. Processing times were determined from previous experiments on thermal treatment of woody materials in an oven (Esteves et al., 2008) and considering the Equilibrium Moisture Content (EMC) in atmospheric steam drying (Tang et al., 2001). In these set of experiments, processing time of 15 min was chosen according to processing temperature 160°C. Steam velocities were calculated using the mass flow rate, read from the steam condensation from condenser, and the specific volume, obtained from superheated steam tables for processing temperature at atmospheric pressure, and also the cross-sectional area of sample tray. The sample tray was a cylinder with 20 micro meter mesh on the bottom and top of sample to prevent the material to fly away. During steam drying, sample tray was hanging from a balance for simultaneous weight recording. In addition to this, the initial and final weights of the samples were measured manually. The detailed description of steam drying unit has been published by Pronyk et al. (2008).

Several measurements before and after superheated steam treatment were considered to investigate the effects of superheated steam pretreatment on different characteristics of raw materials for pelletization. These measurements, which are important for further densification, are moisture content, bulk density, calorimetric heating value, colorimeter (for some samples), ash, extractives and lignin contents.

### Results and discussion

Figure A. 2 shows the drying kinetics for Pine wood. Similar graphs are developed for other samples. The bumpy line between the data points is due to the shakes of sample holder during

steaming. Because of this shaky environment, initial and final weights are also measured manually (Table A. 1).

Table A. 1 shows the results of physical and chemical analyses done on wood and bark samples, before and after steaming. Both sample weight and moisture content reduced for all samples after treatment; however more reduction in sample weight (6.78%, 10.41% and 13.21% for Pine, Douglas fir wood and bark, respectively) rather than moisture content (3.89%, 8.37% and 8.63% for Pine, Douglas fir wood and bark, respectively) was observed. This could indicate some other changes taking place during drying; for example, acetone extractable content reduced considerably for all samples; this is supported by previous studies on formation of organic compounds such as carboxylic acids, methanol, aldehydes and anhydro-glucoses, all originated from extractive resins, compounds in the exhaust stream (Bjork and Rasmuson, 1996). Also, ash contents of woody material are lower while that of bark sample shows slightly increase after treatment.

Acid Soluble Lignin (ASL) percentages did not change significantly in most measurements; however, Acid Insoluble Lignin (AIL) contents showed increase after steaming for all samples (up to 7.3% increase). This effect is highly desirable for further densification because of binding ability of lignin during pelletization. Most treated material had also higher calorimetric heating values; this could be result of both lower moisture content, since less heat is used for vaporization and higher insoluble lignin content, since there is a highly significant linear correlation between klason lignin and higher heating value (White, 1987).

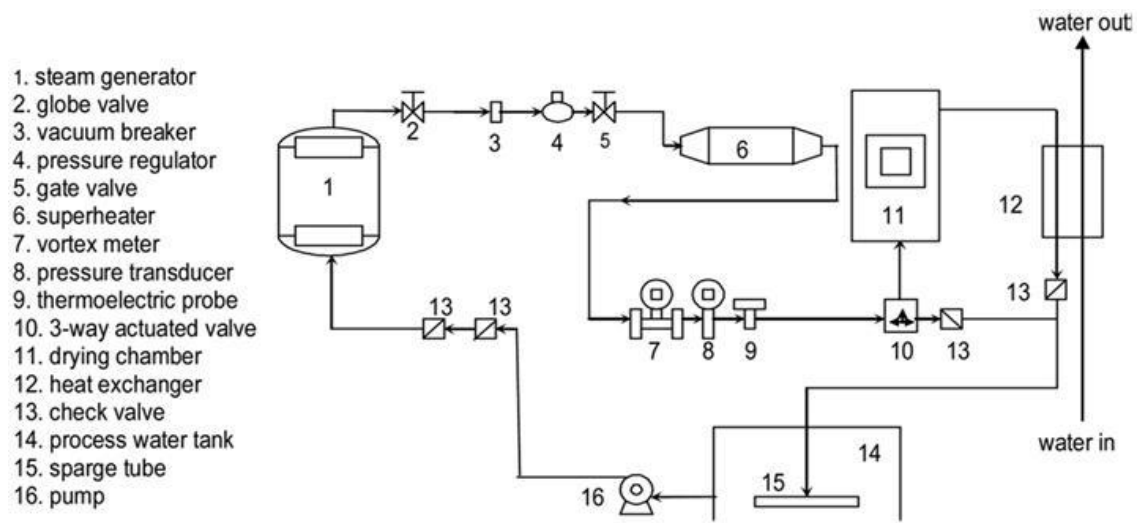
Another critical physical property for a solid biofuel is the tapped density. Tapped density is the maximum mass of loose material that can be filled in unite of volume after tapping (Lam et al., 2008). The steam treated materials have lower tapped density and it is beneficial for transportation of pellets made of these materials when using trucks.

### **Concluding remarks**

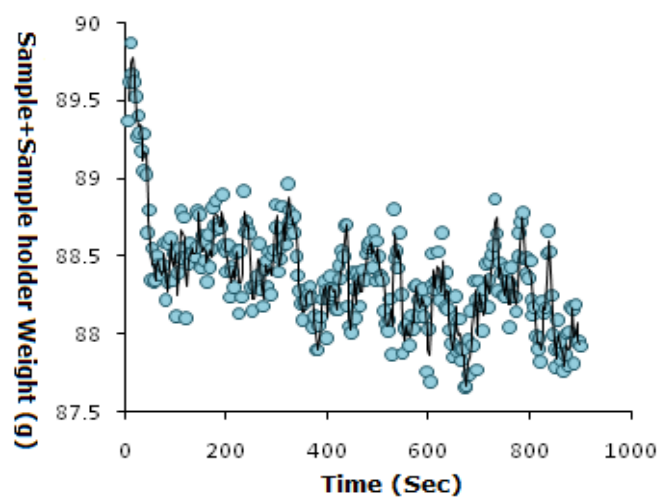
The objective of this research was to investigate the suitability of steam drying as a pretreatment prior to densification for solid biofuel production. Some critical characteristics of material were considered and measured before and after treatment. The trend of compositional changes seems favorable for producing more durable and harder pellets.

**Table A. 1 Physical and chemical characteristics of samples before and after steam drying**

Sample Name	Pine Wood		Douglas Fir Wood		Douglas Fir Bark	
	untreated	SD	untreated	SD	untreated	SD
<b>Physical Measurements</b>						
<b>Sample Weight (g)</b>	10.03	9.35	12.58	11.27	6.21	5.39
<b>Moisture Content (%)</b>	5.33	1.43	11.24	2.87	10.74	2.11
<b>Tapped Density (kg/m<sup>3</sup>)</b>	373	322	204	159	204	175
<b>Heating Value (MJ/kg)</b>	19.53	19.28	18.78	19.03	20.19	20.99
	19.49	19.29	18.84	18.81	20.15	21.14
<b>Chemical Measurements</b>						
<b>Ash Content (db) (%)</b>	0.53	0.41	0.68	0.32	2.57	2.78
<b>Acetone Extracted (db) (%)</b>	2.65	1.92	1.61	0.96	14.58	11.51
<b>Acid Soluble Lignin (db) (%)</b>	0.62	0.59	0.58	0.51	1.33	1.45
	0.6	0.56	0.56	0.52	1.48	1.59
<b>Acid Insoluble Lignin (db) (%)</b>	25.51	32.87	27.01	29.72	57.49	58.73
	30.67	36.01	30.13	29.76	56.89	56.27



**Figure A. 1 Schematic diagram of superheated steam drying; open system**



**Figure A. 2 Steam drying kinetics for Pine sample**