PHYSICAL AND THERMAL CHARACTERIZATION OF GROUND WOOD CHIP
AND GROUND WOOD PELLET PARTICLES

by

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B.A.Sc., Shiraz University, 2008
M.A.Sc., Amirkabir University of Technology (Tehran Polytechnics), 2011

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF
THE REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

in
THE FACULTY OF GRADUATE AND POSTDOCTORAL STUDIES
(Chemical and Biological Engineering)

THE UNIVERSITY OF BRITISH COLUMBIA
(Vancouver)

March 2017

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Abstract

The goal of the present study is to characterize the ground chip and ground pellet particles with respect to their size, shape, density, flow properties, drying and pyrolysis mass loss. Commercial wood pellets and pulp-quality wood chips are used in this study. These commercial samples are ground in the laboratory using a range of grinder screen sizes. The grinder power input is measured. The ground particles are examined for their size and shape. The ground particles are thermally treated in a micro TGA equipment and in a lab-scale thin-layer drying/pyrolysis equipment. The grinding results show that grinding a whole pellet to the desirable particle sizes for pyrolysis (~1 mm) takes around 1/7 of energy required to grind a whole wood chip to the same mean particle size. Pellet particles are denser, more spherical and shorter than the needle-shape chip particles. The spheroid shape of ground pellet particles lowers the compressibility of bulk, lowers the cohesion among the particles and facilitates their flowability. Higher density and random fiber orientation of the pellet particles prolong the duration of their drying significantly compared to the drying time of thin and long wood chip particles. Further moisture diffusion modeling shows that the moisture diffusion rate inside the pellet particles is half of those inside the chip particles. Although chip and pellet particles show the same level of shrinkage in size of a single particle due to drying, ground pellet particles exhibit a larger reduction in their bed porosity than the bed porosity measured for ground chip particles. Both chip and pellet particles reach their fiber saturation point at a moisture content of around 0.50 (dry basis). The pyrolysis kinetic parameters are determined experimentally and a two-zone kinetic mechanism is modeled and validated using the experimental thin-layer pyrolysis data.
Preface

This PhD dissertation is divided into seven chapters and two appendices. The author, Hamid Rezaei, has done all the literature review, designing and constructing the apparatus, designing and conducting the experiments, data processing and analysis and preparation of manuscript and thesis under the main supervision of Professor Shahab Sokhansanj in the Chemical and Biological Engineering Department at the University of British Columbia (UBC). The co-supervisors are Professor C. Jim Lim and Professor Anthony Lau. The co-authors in the published papers are members of the Biomass and Bioenergy Research Group (BBRG). The co-authors contributed to the scientific content of the manuscripts. A version of each chapter of this dissertation is published in peer-reviewed journals and/or presented in conferences. The list of publications is presented as follows:

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<thead>
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<tbody>
<tr>
<td>A</td>
<td>Area of projected particle, $\text{mm}^2$</td>
</tr>
<tr>
<td>AR</td>
<td>Aspect ratio</td>
</tr>
<tr>
<td>AOR</td>
<td>Angle of repose, °</td>
</tr>
<tr>
<td>$b$</td>
<td>Geometrical factor</td>
</tr>
<tr>
<td>$C_{p,s}$</td>
<td>Particle specific heat capacity, $\text{J/kg.K}$</td>
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<td>Carr-compressibility index, %</td>
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<tr>
<td>D</td>
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<td>$d_{ci}$</td>
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<td>$E$</td>
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<tr>
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<tr>
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<td>Particle mass at temperature of 200 °C, kg</td>
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</table>
$m_{600}$  
Particle mass at temperature of 600 °C, kg

$m_b$  
Mass of bulk of particles, kg

$m_p$  
Mass of particle, kg

$M_0$  
Initial moisture content, kg water/kg dry material

$M$  
Instantaneous moisture content, kg water/kg dry material

$M_{cr}$  
Critical moisture content, kg water/kg dry material

$M_e$  
Final moisture content, kg water/kg dry material

MR  
Moisture ratio

$n$  
Order of pyrolysis mass loss

$n_p$  
Power of page drying model

$P$  
Perimeter of projected particle, mm

PSD  
Particle size distribution

$q$  
Heat of reaction, J/kg

$r_p$  
Rate of pyrolysis mass loss, kg/s

$r$  
Radial position, m

$R$  
Universal ideal gas constant, J/mol.K

$R_{conduction}$  
Conductive heat transfer resistance per unit area, m$^2$.K/W

$R_{convection}$  
Convective heat transfer resistance per unit area, m$^2$.K/W

RMSE  
Root mean square error

$S_p$  
Shrinkage coefficient of bulk volume
$S_p$  Shrinkage coefficient of average particle size

$S_s$  Surface area of a sphere having the same volume as the particle, mm$^2$

$S_v$  Actual surface area of particle, mm$^2$

SEM  Scanning electron microscope

SIP  Shrinkage intersection point

$t$  Time, s

$T$  Particle local temperature, K

$T_c$  Particle center temperature, K

$T_s$  Particle surface temperature, K

$T_h$  Heater temperature, K

$T_f$  Fluid temperature, K

TGA  Thermogravimetric analyzer

$V_b$  Volume of bulk of particles, cm$^3$

$V_{lb}$  Volume of loose bulk of particles, cm$^3$

$V_{tb}$  Volume of tapped bulk of particles, cm$^3$

$V_p$  Total volume of a particle, cm$^3$

$V_s$  Volume of solid part of a particle, cm$^3$

$V_{cp}$  Volume of closed pores of a particle, cm$^3$

$V_{op}$  Volume of open pores of a particle, cm$^3$
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{b,dry}$</td>
<td>Bulk volume of dry particles, cm$^3$</td>
</tr>
<tr>
<td>$V_{b,moist}$</td>
<td>Bulk volume of moist particles, cm$^3$</td>
</tr>
<tr>
<td>$W$</td>
<td>Particle width, mm</td>
</tr>
<tr>
<td>$x$</td>
<td>Distance, m</td>
</tr>
<tr>
<td>$x_i$</td>
<td>Mass fraction of particles retained in the $i^{th}$ sieve interval</td>
</tr>
<tr>
<td>$\chi$</td>
<td>Dimensionless conversion ratio</td>
</tr>
</tbody>
</table>

**Greek symbols**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>Thermal diffusivity</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Heating rate, °C/min</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Emissivity</td>
</tr>
<tr>
<td>$\varepsilon_b$</td>
<td>Bulk porosity, %</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Stefan-Boltzmann constant, W/m$^2$.K$^4$</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Circularity</td>
</tr>
<tr>
<td>$\psi$</td>
<td>Sphericity</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Particle density, g/cm$^3$</td>
</tr>
<tr>
<td>$\rho_b$</td>
<td>Bulk density, g/cm$^3$</td>
</tr>
<tr>
<td>$\rho_0$</td>
<td>Initial particle density, g/cm$^3$</td>
</tr>
<tr>
<td>$\rho_r$</td>
<td>Final biochar density, g/cm$^3$</td>
</tr>
<tr>
<td>$\rho_p$</td>
<td>Pycnometer density, g/cm$^3$</td>
</tr>
</tbody>
</table>
\[ \rho_{lb} \] Loose bulk density, g/cm\(^3\)

\[ \rho_{tb} \] Tapped bulk density, g/cm\(^3\)

\[ \rho_s \] Solid density, g/cm\(^3\)

\[ \tau \] Conversion time, min
Acknowledgements

Foremost, my sincere gratitude and appreciation goes to my PhD supervisors, Dr. Shahab Sokhansanj, Dr. C. Jim Lim and Dr. Anthony Lau for their excellent advice, time dedication and support. Their unconditional insight into my professional and personal development was a significant contribution to the achievements.

I also offer my gratitude to my committee members Dr. Xiaotao Bi and Dr. Maria Holuszko for their availability and continuous advice on my research. I am grateful to Mr. Staffan Melin and Mr. Les Marshal for their invaluable professional contributions to my research and facilitating our relationship with industrial sectors. I also owe a thank to all faculty and staff members of Chemical and Biological Engineering Department at the University of British Columbia specially Richard Ryoo, Dough Yuen, David Roberts, Ken Wong and Serge Milaire for their administrative and technical assistance.

I acknowledge Biofuel Network of Canada for its financial support. This research is funded by BioFuelNet Canada, a network focusing on the development of advanced biofuels. BioFuelNet is a member of the Networks of Centers of Excellence of Canada program. Thanks are also extended to Fibreco Inc. for kindly providing required biomass feedstock for this research.

I also would like to thank all my colleagues in Biomass and Bioenergy Research Group (BBRG) especially Dr. Fahimeh Yazdanpanah, Dr. Mahmood Ebadian and Mr. Bahman Ghiasi for their valuable help and facilitating to conduct the experiments.

Special thanks are owed to my parents, who have supported me with their unlimited love. I owe my special thanks to my dear brothers, Hadi, Hamed and Hooman for their continuous and unconditional support not only during my academic progress, but the whole life.
To My Unique Mother, Sima

My Honorable Father, Mohammadjavad

&

My Loving Brothers, Hadi, Hamed and Hooman
Chapter 1: Introduction

1.1 Background

Crude oil and coal with high energy density and stable properties to store and transport used to be the preferred fuels for industrial and home applications [1]. Recent reduction in affordable fossil fuels and environmental concerns about the increased greenhouse gas (GHG) emissions from these fuels have motivated the public and private sectors to develop renewable energy sources. In recent years, the governments of Canada and the USA adopted regulations to phase out coal-fired power plants by 2030 and investigate other resources to reduce GHG emission. Biomass feedstocks are considered as the renewable resource with a near-zero CO$_2$ input-output balance [2-4]. Biomass is the only renewable energy source which may be used in all solid, liquid and gas phases [5]. But compared to fossil fuels, biomass is lower in energy (17-19 MJ/kg) and bulk density (60-100 kg/m$^3$) [6]; heterogeneous in physical, chemical and thermal properties; high in moisture [6], mineral [7] and oxygen contents [8]; highly hygroscopic [9] and difficult to handle [6]. Converting biomass to secondary liquid or gaseous fuels through thermal conversion processes is a way of increasing the energy density and transportability.

1.2 Literature Review

1.2.1 Pyrolysis

Pyrolysis is thermal conversion of biomass particles to secondary solid, liquid and/or gaseous fuels [10]. The liquid bio-oil obtained from pyrolysis of biomass shows promising properties to substitute the conventional fossil fuels (Table 1.1); although pyrolysis liquid has higher water content, lower heating value and higher oxygen content than petroleum fuel.
The breakdown of biomass particles takes place in a pyrolysis reactor by exposing them to an oxygen-free or deficit environment. As the temperature of the particle increases, different stages of thermal treatment occur. Drying happens first when a moist particle is heated up to temperatures of about 150 °C [12]. Biomass does not decompose during drying because temperatures up to 150 °C generally do not break down the solids [13]. At temperatures of 200-300 °C and in the absence of oxygen/air, various degrees of torrefaction happen and release volatile [14-17]. At temperatures of higher than 300 °C, more severe decomposition of biomass happens and structural changes such as change in chemical composition and porosity of particles occur in the solid matrix. Pyrolysis processes are generally categorized to “slow” and “fast” according to the time taken for processing the feed into pyrolysis products. Slow pyrolysis utilizes low temperatures of 300-400 °C over a residence time of 30 minutes to hours to maximize char formation. Fast pyrolysis is a rapid thermal
decomposition process to maximize the liquid fraction of products. It is discussed in the literature that the rate of heating biomass particle is a key parameter to achieve this goal [5, 18-20]. In industrial fast pyrolysis, biomass particles would be exposed suddenly to an environment of 400-600 °C for the biomass to heat up rapidly. The combined effects of particle size [18, 21-25], reactor temperature [26-30] and heating mechanisms (convection/radiation) [17] make a non-linear temperature profile inside the particle which affects the particles’ heating rate and consequently the rate of mass loss. The residence time of the volatile fraction in the pyrolysis reactor and its contact with solid particles should be less than 2-3 seconds to prevent the secondary reactions. Figure 1.1 displays a schematic diagram of an industrial fast pyrolysis process. In the following sections, a comprehensive literature review is presented to discuss the effects of various parameters related to feedstock and pre-treatments on efficiency of the pyrolysis process.

Figure 1.1 Schematic diagram of fast pyrolysis process, including drying, grinding, pyrolyzer, separation stages and condenser (the products are solid char, gaseous syngas and condensable bio-oil).
1.2.2 Feedstock Properties

1.2.2.1 Chemical Composition

A plant-based dry biomass has the main fractions of cellulose, hemicelluloses, lignin, extractives, and minerals. The composition of these fractions influences the distribution of pyrolysis products [31]. Table 1.2 lists the composition of a broad range of biomass species. Higher lignin content reduces the bio-oil yield at the expense of higher biochar yield in the pyrolysis process [21]. Feedstock composition also influences the energy density of the produced fuel. The extractives have the highest heating value in the wood. The higher heating values of biomass components are 17-18, 16-17, 25-26 and 33-38 GJ/tonne for cellulose, hemicellulose, lignin and extractives, respectively [32]. The fractions also have different reactivity rates and each decompose at their specific temperature range. Cellulose decomposes in 300-400 °C; hemicellulose decomposes in 200-300 °C and lignin decomposes continuously from 180 to 600 °C [15]. Table 1.3 lists pyrolysis liquid yield of various biomass species at tested temperatures and depicts the variability of produced bio-oil yield among the pyrolysis of different feedstocks. Apart from variability in conversion rate among species, the conversion rate increases with the reaction temperature.
### Table 1.2 Composition and ultimate analysis, ash content and calorific values of various biomass feedstocks.

<table>
<thead>
<tr>
<th>Biomass species</th>
<th>Composition (wt.%)</th>
<th>Ultimate analysis (wt.%)</th>
<th>Ash (wt.%)</th>
<th>HHV (MJ/kg)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cel.¹ Hem. Cel.² Lig.³</td>
<td>C H O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pine wood</td>
<td>42.10 27.71 25.06</td>
<td>45.92 5.27 48.24</td>
<td>0.35</td>
<td>18.98</td>
<td>[34]</td>
</tr>
<tr>
<td>Beech wood</td>
<td>41.73 37.10 18.92</td>
<td>46.70 5.70 47.60</td>
<td>1.04</td>
<td>-</td>
<td>[25]</td>
</tr>
<tr>
<td>Douglas fir</td>
<td>50.00 17.80 28.30</td>
<td>50.72 5.99 42.49</td>
<td>0.50</td>
<td>20.07</td>
<td>[36]</td>
</tr>
<tr>
<td>Spruce wood</td>
<td>41.10 20.93 28.02</td>
<td>48.91 6.02 44.64</td>
<td>0.30</td>
<td>19.26</td>
<td>[33]</td>
</tr>
<tr>
<td>Poplar aspen</td>
<td>49.90 22.42 18.10</td>
<td>- - -</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Poplar wood</td>
<td>42.20 16.66 25.66</td>
<td>48.45 5.85 43.69</td>
<td>1.43</td>
<td>19.71</td>
<td>[38]</td>
</tr>
<tr>
<td>Alder wood</td>
<td>32.30 23.50 24.80</td>
<td>48.27 6.02 45.11</td>
<td>0.30</td>
<td>18.96</td>
<td>[33]</td>
</tr>
<tr>
<td>Birch wood</td>
<td>35.70 25.10 19.30</td>
<td>49.05 6.28 44.17</td>
<td>0.30</td>
<td>18.40</td>
<td>[39]</td>
</tr>
<tr>
<td>Corn stover</td>
<td>36.40 22.61 16.63</td>
<td>- - -</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Corn cob</td>
<td>52.00 32.56 15.53</td>
<td>49.00 5.60 43.80</td>
<td>1.10</td>
<td>-</td>
<td>[21]</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>38.22 24.75 23.41</td>
<td>40.78 5.84 52.92</td>
<td>10.58</td>
<td>16.24</td>
<td>[41]</td>
</tr>
<tr>
<td>Rice straw</td>
<td>34.23 24.52 23.44</td>
<td>36.89 5.00 37.89</td>
<td>11.70</td>
<td>16.78</td>
<td>[42]</td>
</tr>
<tr>
<td>Rice straw</td>
<td>32.15 26.53 12.56</td>
<td>50.20 6.40 38.40</td>
<td>4.10</td>
<td>-</td>
<td>[21]</td>
</tr>
<tr>
<td>Tea waste</td>
<td>33.20 23.30 43.50</td>
<td>48.20 5.50 44.30</td>
<td>1.50</td>
<td>-</td>
<td>[21]</td>
</tr>
</tbody>
</table>

¹ Cellulose; ² Hemicellulose; ³ Lignin

### Table 1.3 Bio-oil yield in fast pyrolysis of various biomass feedstocks.

<table>
<thead>
<tr>
<th>Biomass Type</th>
<th>Temperature (°C)</th>
<th>Bio-oil yield (wt.%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pine wood</td>
<td>450</td>
<td>55.0</td>
<td>[44]</td>
</tr>
<tr>
<td>Waste furniture sawdust</td>
<td>450</td>
<td>65.0</td>
<td>[45]</td>
</tr>
<tr>
<td>Wood sawdust</td>
<td>650</td>
<td>74.0</td>
<td>[46]</td>
</tr>
<tr>
<td>Corn cob</td>
<td>550</td>
<td>56.8</td>
<td>[47]</td>
</tr>
<tr>
<td>Municipal, livestock and wood waste</td>
<td>500</td>
<td>39.7</td>
<td>[48]</td>
</tr>
<tr>
<td>Pine wood</td>
<td>450</td>
<td>50</td>
<td>[49]</td>
</tr>
<tr>
<td>Rice husks</td>
<td>450</td>
<td>60</td>
<td>[50]</td>
</tr>
<tr>
<td>Corn cobs and corn stover</td>
<td>650</td>
<td>61.6</td>
<td>[51]</td>
</tr>
<tr>
<td>Sugar cane waste</td>
<td>470</td>
<td>56.5</td>
<td>[52]</td>
</tr>
</tbody>
</table>
Table 1.2 lists the ultimate tests for combustion showing biomass is primarily made of carbon, hydrogen and oxygen. High oxygen content of biomass (~40-50%) is a bottleneck of produced bio-oil through fast pyrolysis. Unstable and corrosive properties of bio-oil (due to the high oxygen content) make it not qualified enough for transportation and storage [23].

Minerals are present in all biomass species, in a much lower amount than carbon, hydrogen and oxygen elements. Agricultural biomass has much more mineral contents than woody biomass. Mineral species that are present in the biomass result in a higher ash production after the thermal conversion processes. The biochar typically contains up to 90% of the biomass minerals [53]. Biomass-fired boilers experience serious fouling and corrosion problems due to the elements such as potassium, chlorine, sulfur, silicon, calcium and magnesium [54]. Ash shifts the size distribution of the char to smaller sizes that makes their recovery from the gas stream challenging. Incomplete separation of char and volatiles causes continuous secondary reactions in the liquid phase [23, 55, 56] that accelerates the aging phenomenon and contribute to its instability [57, 58]. Aging phenomena is defined as a slow increase in viscosity bio-oil resulting from secondary reactions [23]. Minerals have catalytic effect on the rate of secondary reactions [59]. Table 1.2 lists the elemental composition, ash content and higher heating value (HHV) present in a range of biomass species.

1.2.2.2 Physical Properties

Woody biomass may be used as pyrolysis feedstock in the form of either wood chips or wood pellets [2, 3, 60]. Wood pellets have higher bulk density and more homogenous physical properties than wood chips [61, 62]. Due to the heat and mass transfer limitations, it is recommended to reduce the size of feedstock to particles smaller than 2 mm prior to feeding a pyrolyzer or
combustion chamber (power boiler) [18, 21-25]. Ground wood particles flow in the pipe lines leading to the conversion unit. Size distribution, shape and density of the biomass particles affect their flow properties and kinetics of drying and thermal decomposition [25, 61, 63-65].

1.2.2.2.1 Particle Size

Grinding reduces the dimensions of a particle and that increases the particle’s specific surface area (ratio of the particle’s surface area to its mass). The same relationship holds for a bulk of particles where the surface area of the solids increases in a given volume of bulk particles. Therefore, the rate of heat and mass transfer between the particles and surrounding gas increases with a reduction in the size of the particle. On the other hand, grinding to smaller particles requires more energy input. The challenge is to find the optimum size of particles where the total energy input be at its minimum level.

Figure 1.2 shows the published data on percent yields of three fractions solids, liquids, and gases from pyrolysis for a range of particle sizes. Only the apricot stone pyrolyzed at 800 °C showed a yield that was sensitive to particles size. An increase in particle size increased the char yield at the expense of less liquid yield [18, 21-25, 38, 63, 66]. Basu et al. [38] showed that the core of larger particles take longer to heat up than the core of smaller particles. For needle-shape particles, the effect of particle length was insignificant. A few researchers did not observe any effect of particle size on yield of fractions at a pyrolysis temperature of 500 °C. For example, Şensöz et al. [67, 68] did not observe any meaningful influence of particle size on the pyrolysis products of rapeseed (Brassica napus L.) in the range of 0.22-0.85 mm [67] and of debarked pine in the range of 2-5 mm [68]. Encinar et al. [69] reported that liquid yield was independent of
biomass particle size during pyrolysis of 0.4-2.0 mm grape residue and olive residue particles pyrolyzed at 500 °C.

Most of the published data recommend that particles in the range of 1-2 mm are appropriate for fast pyrolysis [19, 24, 66, 70-73]. However, the effect of particle size on the pyrolysis process needs more work. The range of particle sizes tested in various studies are seldom comparable and a study on a wider range of particle size seems necessary. The published literature also do not address the challenges associated with commercial grinding and feeding the bulky light weight biomass in the reactor.

Figure 1.2 Effect of biomass particle size on yields of solid, liquid and gas products [66, 67, 69].
1.2.2.2  Particle Shape

The American Society of Agricultural and Biological Engineers (ASABE) specifies mechanical sieving (S424.1, 2007) as a standard method to determine the particle size distribution of biomass particles. Particles pass through the sieves based on their width. The length of particles does not influence the reported mean and distribution of particle size. Similarly mechanical sieving may not differentiate among irregular-shaped biomass particles [74]. Conducting the mechanical sieving for several samples is laborious [75, 76].

Machine vision is a practical alternative to mechanical sieving that determines the actual dimensions and shape of single particles [77]. Machine vision is not subjective and is repeatable over the same image [78, 79]. The shortcoming of image analysis is two-dimensional analysis that omits the thickness of the particles [76, 78]. Tannous et al. [74] stated that taking a photograph and measuring the thickness of a single Douglas fir particle was not practical and reliable. Tannous et al. assumed that the thickness of a particle is 30% of its width.

Literature established a series of shape factors to describe and evaluate the shape, form and structure of the particles. Shape factors provide quantitative information about the particle shape. Riley [80] stated the difficulty of 3D picturing of particles and introduced the projected shape factor that is based on width, length, and the diameter of an inscribed circle or of a circumscribed circle. In a comprehensive review of shape factors, Trottier et al. [81] defined shape factors using two or three dimensions of an individual particle and categorized the shape factors using four parameters: (1) dimensional ratios, (2) sphericity that indicates the deviation of a particle from a sphere or circle, (3) roundness and circularity that show angularity and sharpness of corners, and (4) roughness that shows surface structure. Figure 1.3 illustrates the concept of various shape factors associated with a single wood particle.
1.2.2.2.3 Particle Density

A whole wood chip is produced from chipping a tree. A wood chip may have a width of 30-50 mm, length of 50-100 mm and a thickness of 5-10 mm. Pellets are produced from compacting saw dust. A whole wood pellet typically measures 6.4 mm in diameter (using pellet die with opening diameters of 0.25 inches) and anywhere from 3 to 30 mm in length. Figure 1.4 shows the picture of a wood chip and white wood pellet before grinding. Table 1.4 lists the typical dimensions and density of wood chip and wood pellet. Particle density influences the rate of heat and mass transfer inside the biomass particles. Studies on biomass density in the literature attribute biomass density to the type of tested biomass. Pelletized biomass is denser, has higher bulk density and has more homogenous physical properties than an un-processed wood chip [61, 62]. Wood pellet provides a convenient form of biomass for its handling, storage and feeding to pyrolysis reactors [60, 82]. Pellet is a promising feedstock option that is compatible with existing facilities in the
combustion plants [83, 84]. Although wood pellets are used mainly for oxidative combustion applications in boilers and pellet stoves at present, wood pellets may also become a potential feedstock for the pyrolysis operation to produce bio-oil. Fast heating of a pellet is challenging and a non-uniform temperature inside the pellet decreases the particles’ heating rate and yields in more biochar.

![Figure 1.4 Picture of pine wood chip (left) and white wood pellet (right).](image)

**Table 1.4 Dimensions and density of wood chip and wood pellet [72].**

<table>
<thead>
<tr>
<th>Property</th>
<th>Wood chip</th>
<th>Wood pellet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimensions</td>
<td>Width 30-50 mm</td>
<td>Diameter 6.4 mm</td>
</tr>
<tr>
<td></td>
<td>Length 50-100 mm</td>
<td>Length 3 to 30 mm</td>
</tr>
<tr>
<td></td>
<td>Thickness 5-10 mm</td>
<td></td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>0.4-0.6</td>
<td>1.2-1.4</td>
</tr>
<tr>
<td>Bulk density (g/cm³)</td>
<td>0.2-0.3</td>
<td>0.6-0.7</td>
</tr>
</tbody>
</table>
Literature recommends to reduce the size of biomass particles to smaller than 2 mm for a more efficient thermal conversion [18, 21-25]. Pauilauskas et al. [85] investigated the pyrolysis of a softwood pellet and observed a small rate of heat diffusion inside the pellet and releasing volatiles out of the pellet. The center of a pellet took about 5-10 minutes to reach the pyrolysis temperature. Erlich et al. [82] measured char yield and shrinkage of whole pellets and shredded chips made from bagasse and a softwood (species not known) in a pyrolysis reactor. The size of particles ranged from 6 mm (near diameter of a whole pellet) to 40 mm (length of a woodchip). Higher density pellets of bagasse resulted in higher char yield and smaller shrinkage during pyrolysis. They did not test the pyrolysis of ground pellets. Jeguirim et al. [86] compared the kinetics of thermal degradation of ground coffee and whole pellets made from pure spent coffee. The experiments were done in a thermogravimetric analyzer (TGA) with a slow heating rate of 5 °C/min up to the temperature of 900 °C. The results showed that the rate of degradation for slow pyrolysis were the same for ground and pelletized coffee.

1.2.3 Flow Properties

Physical properties such as particle size, particle shape, density and surface roughness affect the flow properties of particles [74, 87-91]. Predicting the pressure drop across a bed of particles [92], hoppers, screws, pneumatic transportation in pipe lines and feeding systems in thermochemical conversion processes are the industrial examples that show the importance of flowability of the biomass particles. Biomass particles are cohesive and stick together in a flowing stream and cause a variety of flow issues. Bridging of biomass particles in the feeding system of a gasifier is a common industrial problem [93, 94].
The analysis methods applied to characterizing the flowability of minerals can be applied to characterizing biomass particles as well [65, 74, 89, 90, 95-101]. Comparing the loose and tapped bulk densities gives a quick estimation of bulk compressibility [65, 97]. A larger difference before and after the tapping process implies the higher tendency of the particles make a compact bulk. Particle size, particle shape, particle density, the way that particles are arranged in the bulk and friction among the particles influence the bulk density [65, 97, 102]. The dimensionless numbers of “Hausner ratio (HR)” and “Carr-compressibility index (CCI)” quantify the bulk compressibility [74]. Although these numbers have a similar concept that compare the bulk density before and after tapping, both are used in the literature to evaluate the relative flowability of materials. Hausner ratio is the ratio of bulk density after tapping to bulk density before tapping [74, 80].

\[
HR = \frac{\rho_{tb}}{\rho_{lb}}
\]  
(1.1)

where \( \rho_{lb} \) (g/cm\(^3\)) and \( \rho_{tb} \) (g/cm\(^3\)) are loose and tapped bulk density, respectively, of ground biomass particles. The Carr-compressibility index is expressed as follows [74, 80].

\[
CCI = (1 - \frac{\rho_{lb}}{\rho_{tb}}) \times 100
\]  
(1.2)

In a comprehensive fluidization review, Geldart et al. [103] showed that the particles with HR less than 1.25 are free-flowing and easy to fluidize; particles with HR greater than 1.4 are cohesive and difficult to fluidize; and particles with HR values of 1.25-1.4 have partial properties of both groups. The CCI values between 5-15, 12-16, 18-21, and 23-28% indicated excellent, good, fair, and poor flowability, respectively. Tannous et al. [74] showed that HR and CCI values of ground Douglas-fir particles decreased with increasing particle size. By increasing the particle size in the Sauter diameter range of 74-781 µm, HR and CCI values decreased from 1.85 to 1.32 and
from 45.84 to 24.06, respectively. Besides, smaller particles packed more with tapping and had poor flow properties compared with the larger particles. Wu et al. [87] showed that the bulk density of wood pellets is about 2-3 times that of wood chips, but they did not compare the bulk density of ground chip and ground pellet particles. Lam et al. [65] found out that the longer particles of both wheat straw and switchgrass were compressed more than short particles during the tapping process.

Angle of repose (AOR) is another index to evaluate the flowability of particles. AOR is the angle of piled particles with respect to the horizontal surface. AOR indicates the failure properties of free flowing bulk under gravity [91]. AOR depends on the particle size, particle shape, cohesiveness and stickiness of particles. An increase in particle size is accompanied by a decrease in the cohesiveness [74, 95]. It is suggested that an AOR below 30° shows good flowability, 30-45° some cohesiveness, 45-55° true cohesiveness and above 55° very high cohesiveness [95]. In some other studies [96, 99, 104], AOR of 40° was identified as the criteria for free flowability. Wu et al. [87] analyzed the angle of repose for wood chips (lengths of 20, 40 and 100 mm) and wood pellets (diameters of 6, 8 and 12 mm), and showed that wood pellets with AOR values of 35-38° were more flowable than wood chips with AOR values of 44-46°. They did not measure the AOR of ground chip and ground pellet particles. Although AOR is an inexpensive and quick method to compare the flow properties of particulate materials, it is sensitive to the measurement procedure [105] and scale of the experiment [95]. It is important to follow the same experimental procedure to have the comparable results.
1.2.4 Drying

Biomass particles are dried for a more-efficient thermal combustion in power plants [2, 4, 106] and in pyrolysis reactors to produce bio-oil [14, 20, 23, 70, 107]. A fresh biomass have a high moisture content of up to 80% [32]. High moisture content reduces the heating value of the fuel, shifts the ignition point to higher temperatures [6], and inhibits the rise of temperature inside particles [26, 27]. In many industrial plants, wood pellets are stored in the open spaces and pellets usually are rewetted by rain prior to being ground to the powder (up to 0.30-0.40 dry basis).

Reduced particle and reactor temperatures lower the liquid yield at the expense of a larger fraction of biochar and non-condensable gases [25-27, 63, 108]. Water has a catalytic effect on volatile cracking. Di Blasi [109] showed that moisture content conducts the pyrolysis reaction to a low activation energy path that promotes the formation of char, non-condensable gases and more water. Biomass should be dried down to less than 10% moisture content to improve the quality of produced fuel [18].

In the power plants, the particles flow pneumatically using the re-circulated hot gases. Some of the initial moisture content of the biomass evaporates while passing through pipelines towards the combustion chamber. The rest of the moisture is evaporated during the initial phase of pyrolytic reactions in the combustion chamber [14, 20, 23, 70, 107]. For direct heat generation, wood particles are combusted in an atmospheric air. For pyrolysis applications, the reaction takes place in either oxygen-free or oxygen-deficit environments. In the latter case, pure nitrogen replaces the air.

Size of particles [110], initial moisture content [111], drying temperature [110, 112, 113], relative humidity of drying gas [114, 115] and particle heating rate [116, 117] influence the rate of moisture loss. Another biomass property that influences the rate of heat and mass transfer is the
density of a single particle [4, 13, 74, 111, 113, 116, 118, 119]. Ground pellet particles are denser than un-processed wood chip particles and may show a different heat and mass transfer rate.

Dehydration of fresh wood causes a reduction in the dimension of wood in a direction normal to the microfibril orientation, whereas the longitudinal shrinkage is usually negligible [120, 121]. Mazzanti et al. [122] showed that the longitudinal shrinkage for poplar wood is negligible. Tyler et al. [123] showed that the radial shrinkage of beech wood is about 70 times of longitudinal shrinkage.

1.2.5 Pyrolysis Modeling

Thermal treatment of a single particle should be investigated as a simultaneous kinetic, heat and mass transfer phenomena in both solid and gas phases. The rate-controlling mechanisms such as heat and mass transfer processes strongly depends on the particle size. As the particle size increases, the heat and mass transfer get slower and become rate controlling instead of the chemical kinetic. Most of the published laboratory scale data recommend the 1-2 mm particles to be used in the fast pyrolysis process [19, 24, 66, 70-73]. The commercial pyrolysis processes may use the particles as large as 3-6 mm [124-126] to reduce the cost of size reduction. In the case of large particles, mass transfer resistances inside the particle may influence the volatile yield of pyrolysis due to the possible secondary and tertiary reactions. In the range of up to 2 mm particles, the mass transfer does not control the rate of pyrolysis [127-131]. Literature reported that the heat transfer and reaction kinetics are the most rate-controlling mechanisms in the pyrolysis of a single biomass particle [128, 129, 132-134]. Babu and Chaurasia [130] did a comprehensive study of pyrolysis reactions to compare mathematical models with experimental data. They reported that only the most simplified model that ignores the particle shrinkage and mass transfer limitation inside the
particle is adequate to predict mass losses over a wider range of pyrolysis temperatures. Janse et al. [131] supported the importance of heat transfer compared to mass transfer inside the particle. Their work on particles in the size range of 0.2-1.0 mm shows that an extensive investigation of internal mass transport in fast pyrolysis modeling of single biomass particles is not necessary, whereas an accurate and stable heat transfer model coupled with a reaction kinetic scheme is adequate.

Pyle and Zaror [128] categorized the heat transfer models to be applied in different ranges of particle size. They used dimensionless Biot (\(Bi\)) and Pyrolysis (\(Py\)) numbers to define the valid region of simplified lumped and intrinsic kinetic models. They stated that a heat conduction model coupled with the mass loss kinetic gives a good description of primary pyrolysis reactions. As particle size increased in the range of 0.25-13 mm, the reaction time increased. Simmons and Gentry [134] used analytical solution of a simplified one-dimensional heat transfer model to determine the particle size ranges free of heat transfer limitations. They showed that slower heating of particles at the low reactor temperature (~300 °C) increases the critical particle size. Yang et al. [135] stated that isothermal reaction assumption is not valid for particles larger than 0.25 mm, and in practice the heating rate of the particle is limited by its low thermal conductivity [109].

The majority of the pyrolysis modeling studies used the experimental data of Pyle and Zaror [128] and Koufopanos et al. [136]. Babu and Chaurasia [130] showed that an one-dimensional heat transfer model coupled with the mass loss kinetic relation predicted the experimental data of Koufopanos et al. [136] well. Babu and Chaurasia [128] modeled the pyrolysis of 0.25-13 mm biomass particles in the temperatures up to 730 °C. Larger particles prolonged the conversion time. But, the increase depended upon pyrolysis temperature. Larger particles raised the yield of char and decreased the yield of volatiles for the primary reaction. Grioui et al. [137] modeled thermal
treatment of thick pine wood (~2 cm) using a conduction heat transfer model coupled with the mass loss kinetic. The results agreed well with experimental data of Pyle and Zaror [128]. Lu et al. [4] modeled the devolatilization process in a heated nitrogen environment up to the temperature of 1350 °C. Their experimental and modeling results showed that the spherical particles react slower than the cylindrical and slab particles. Volatile yield decreased with an increase in the particle size. Haseli et al. [138] numerically investigated the pyrolysis of a single biomass particle in the size range of 0.25-1.0 mm. Their model included a one-dimensional heat conduction, flow of gas within the pores of a single particle and exothermic formation of char. Their results showed that an increase in diameter caused a linear increase in both reaction time and char density.

1.3 An Industrial Example - Ontario Power Generation (OPG)

Wood pellets can replace coal in large power production systems [83]. The Atikokan and Thunder Bay power generation stations in Canada are examples of this replacement [84]. Wood pellet is a promising option that is compatible with existing facilities in combustion plants. For a more efficient combustion, wood pellets are pulverized to particles smaller than 2 mm. Figure 1.5 shows the particle size distribution of pulverized pellet particles in an industrial coal pulverizer which was modified to be compatible with wood pellet (Atikokan Power Station, Ontario Power Generation).

The pulverized particles flow pneumatically in the pipelines feeding the combustion chamber. To transport the particles in the pipe lines and to save energy, the hot exhaust gas of the reactor (600-800 °C) is re-circulated. To prevent pre-combustion of the wood particles, the hot gas is diluted with air to reduce its temperature to around 100 °C. The particles exposed to hot gas flow and dry simultaneously in the pulverizer and/or pipelines. A necessary set of engineering data
is required to design this part of the operation; such as solid handling characteristics, drying characteristics, equilibrium moisture contents, and shrinkage of particles. There is information about the drying of various biomass species in the literature, but there is limited information on the comparative drying rates of ground chip and ground pellet particles in the literature.

![Particle size distribution of industrial pulverized pellet particles](image)

Figure 1.5 Particle size distribution of industrial pulverized pellet particles (pulverized by a coal pulverizer at Ontario Power Generation, OPG).

1.4 Identifying Knowledge Gap

Pyrolysis of biomass happens in an oxygen-free or deficit environment to produce solid, liquid and/or gaseous fuels. The liquid bio-oil obtained from the pyrolysis of biomass shows promising properties to substitute the conventional fossil fuels; pyrolysis liquid needs to be upgraded in terms of water content, heating value, solid content and oxygen content. Physical properties such as size, shape, density and moisture content of biomass feedstock influence the operational and conversion efficiencies. The combined effects of particle properties and treatment
temperature influence the temperature distribution inside the particle which consequently affects the conversion efficiency.

The size and density of a particle are among properties that influence the devolatilization rate during pyrolysis. The rate of heat and mass transfer increases as a particle gets smaller. On the other hand, grinding to a smaller particle takes more energy. Furthermore, particle size influences the efficiency of particles’ handling and feeding to the conversion chamber. Smaller particles have an increased contact surface in a flowing stream of particles which makes a more cohesive bulk. In addition to the particle size, particle shape/geometry influences the bulk flowability. Under a no-load condition, the more-round particles flow easier. Published literature mostly addresses the effects that biomass species, particle size and moisture content have on the flowability. The effect of shape of ground particles on flowability is not well-documented in the literature due to the difficulty of characterizing or quantifying particle shape.

Another physical property that influences the rate of heat and mass transfer is particle density. Studies on biomass density in the literature attribute biomass density to the type of tested biomass. Pellet is a densified form of ground chip particles (and/or saw dust) that has more-uniform physical properties than un-processed ground wood chip particles. Wood pellets are becoming a potential feedstock for the pyrolysis operation to produce bio-oil. For pyrolysis applications, the pellet should be ground to the size range of 1-2 mm. Pelletization is expected to change the size distribution, shape and density of ground chip particles. There is limited information on the physical and thermal characterization of ground wood pellet particles. The evolution of properties of particles during pelletization is not addressed in the literature. The objective of this thesis is to conduct a detailed analysis of ground wood pellets with respect to their size, geometry, and flow properties and relate these properties to handling of pellets in combustion applications.
1.5 Research Objectives

Size, shape and density of wood particles influence their flowability and the rate of heat and mass transfer. For industrial applications, wood pellets are ground to the small particles, in the size range of 1-2 mm, prior to feeding them to a conversion reactor. Reviewing the literature shows that the ground pellet particles are not investigated in terms of their physical and thermal properties that influences their flowability, drying and pyrolysis. The overall objective of the current research is to characterize the ground chip and ground pellet particles with respect to their size, shape, density, flow properties, rate of drying and further pyrolysis. The specific tasks of this research are as follows:

Characterize ground chip and ground pellet particles of pine wood with respect to their size, shape, density and flow properties.

Investigate the effects particle size, density, temperature and initial moisture content have on mass loss during drying and subsequent pyrolysis.

Develop mathematical models to represent physical properties of a ground particle and the rate of biomass devolatilization using differential models.

In this study, Chapter 2 presents the micro- and macro-scale characterization of physical and flow properties of ground wood particles. Chapter 3 is based on the experimental work conducted in a thermogravimetric analyzer (TGA). Chapter 4 describes a thin-layer TGA apparatus that was designed, constructed and calibrated by the author of this thesis, Hamid Rezaei, for conducting the experiments of this PhD project. Chapter 5 presents the results on the thin-layer drying of ground chip and ground pellet particles, modeling the drying process using the drying rate constant and
moisture diffusion coefficient, effect of carrying gas and shrinkage in single particle and bulk volume of particles. Chapter 6 presents a detailed pyrolysis modeling of a single wood particle. Chapter 7 lists the overall conclusions and recommendations for further studies. Appendixes A and B present supplementary information in support of Chapters 2 and 6, respectively.
Chapter 2: Size, Shape and Flow Characterization of Ground Chip and Ground Pellet Particles

Size, shape and density of biomass particles influence their flow properties. Pelletizing wood particles increases the particle density and reduces the variability of physical properties among biomass particles. In this chapter, pine chips prepared for pulping and commercially produced pine pellets were dried down to 4-5% (dry basis) and ground in a hammer mill using grinder screens of 3.2, 6.3, 12.7 and 25.4 mm perforations. The physical properties of ground chip and ground pellet particles were determined in terms of their particle size distribution, actual dimensions, particle shape, density and flow properties. The specific tasks of the current chapter are presented as follows:

Characterize ground chip and ground pellet particles in terms of their specific grinding energy, size distribution and density.

Conduct image analysis on single ground chip and ground pellet particles to measure their actual dimensions and determine their shape.

Determine the flow properties of ground chip and ground pellet particles.

Develop empirical correlations to relate the specific grinding energy, dimensions and flow properties of ground chip and ground pellet particles to the grinder screen size.
2.1 Material and Methods

2.1.1 Sample Preparation

Pine wood chips (30x30x5 mm) and commercially produced pine wood pellets (diameter of 6 mm and lengths of 12-24 mm) were supplied by Fiberco Inc. (North Vancouver, BC, Canada). The moisture content of the received chips was in the range of 30-40% (wet basis). Upon their delivery to the lab at UBC, the chips were dried in a THELCO laboratory PRECISION oven (Thermo Electron Corporation, Model 6550) at 80 °C down to 4-5% moisture content. After cooling, the dried chips were crushed in a hammer mill (Glen mills Inc., USA; Model 10HMBL) installed with four grinder screen sizes having circular perforations of 3.2, 6.3, 12.7 and 25.4 mm (Figure 2.1). Moisture content of commercial pellets was 5% and thus were not dried. Similar to wood chips, wood pellets were ground using the same hammer mill, but with three grinder screen sizes (3.2, 6.3 and 12.7 mm perforations). The 25.4 mm grinder screen size was found to be too large for pellet grinding. Figure 2.2 and Figure 2.3 also show the chip and pellet particles that were ground using four different grinder screens.

![Grinder screens](image)

*Figure 2.1 Grinder screens with circular perforations of 3.2, 6.3, 12.7 and 25.4 mm used in the laboratory scale hammer mill.*
2.1.2 Specific Grinding Energy

Pine chips and pine pellets (5 kg each) were fed to the hammer mill using a vibratory feeder. The vibratory feeder provided a steady-state flow of material into the grinder. The rotating speed of the conveying belt in the feeder was set to feed the material during a 2-minute time interval, resulting in a feeding rate of 2.5 kg/min. The electrical line of the grinder was connected to a
current meter. A data-logging system recorded the current (ampere) by the time and converted to energy consumption (J/s). The consumed energy was averaged over the steady-state period and divided by the feeding rate (kg/s) to obtain and the specific grinding energy, $E_g$ (kJ/kg).

2.1.3 Particle Size Distribution

2.1.3.1 Mechanical Sieving

The procedure outlined in ANSI/ASAE Standard S319.4 was followed to conduct the sieving particle size distribution analysis. To determine the particle size distribution of each mixed ground sample, a tap sieve shaker (Ro-Tap RX 94) installed with various mesh sieves of 0.25, 0.5, 1.0, 1.4, 2.0, 2.8 and 6.3 mm was used. The meshes were arranged from the smallest to the largest mesh size. The shaker subjected the samples to oscillation and tapping for 10 minutes. The mass retained on each sieve was weighed. The mass-averaged diameter of particles was calculated using equation (2.1) [74].

$$d_{sv} = \frac{1}{\sum x_i/d_i}$$

(2.1)

where $x_i$ is the mass fraction of particles retained in the $i^{th}$ interval of mean diameter ($d_i$) between two sequent sieves.

2.1.3.2 Laser Diffraction

To determine the particle size distribution using a size analyzer machine, a Malvern Mastersizer equipment (Malvern Instrument, Series 2000) equipped with a dry measurement module (Scirrocco series) was used. The equipment used laser diffraction technique for size measurements in the range of 0.02–2000 µm. Therefore, only the particles ground with grinder...
screen of $d_{gs}=3.2$ mm were analyzed using the mastersizer. A tablespoon (a few grams) of particles was analyzed three times.

2.1.4 Pycnometer Density

The solid density of a particle refers to the mass of the particle divided by the volume of the particle’s skeleton ($\rho_s = m_p / V_s$). In a gas pycnometer, helium or nitrogen gas can penetrate the mesopores (2-50 nm), but their access to the micropores (<2 nm) and closed pores are limited. Therefore, the pycnometer density is a value in between particle density and solid density. Pycnometer density is the particle’s mass divided by the total volume of solids and closed pores, $\rho_p = m_p / (V_s + V_{cp})$ [74]. In this study, pycnometer density was measured using a nitrogen gas pycnometer, (Quantachrome Instruments, Boyton Beach, FL, USA; Model MVP-D160-E). The unit has two chambers. The first chamber is the reference cell with a volume of 11.67 cm$^3$. The second chamber is the sample cell with a volume of 29.42 cm$^3$. The pressure of the reference cell was adjusted to around 117 kPa. The pressurized nitrogen diffused into the bed and the pores of particles in the sample cell. The total volume of the skeleton and closed pores was calculated using the pressure difference measurement and ideal gas law. All density measurements were repeated five times to achieve the reproducibility of results.

2.1.5 Bulk Density and Porosity

Loose bulk density refers to the mass of bulk of the sample divided by its aerated volume ( $\rho_{lb} = m_b / V_{lb}$ ). Constant mass of 200 g of each ground sample was smoothly poured into a graduated cylinder. The volume of loose sample was recorded ($V_{lb}$). The vessel was dropped under
its own mass from a height of 10 cm at different times. The volume of tapped particles was recorded in each 10-tap interval ($V_{tb}$). The tapping process continued till no variation in bulk volume was observed. The tapped bulk density was obtained via dividing the mass of the sample by the volume of tapped sample ($\rho_{tb} = m_b / V_{tb}$). The Hausner ratio (HR) and Carr-compressibility index (CCI) were calculated using equations (2.2) and (2.3) [74, 80].

$$HR = \frac{\rho_{lb}}{\rho_{tb}}$$ (2.2)

$$CCI = (1 - \frac{\rho_{lb}}{\rho_{tb}}) \times 100$$ (2.3)

where $\rho_{lb}$ (g/cm$^3$) and $\rho_{tb}$ (g/cm$^3$) are loose and tapped bulk density, respectively, of ground biomass particles. Bulk porosity was calculated using equation (2.4) [92, 139].

$$\varepsilon_b = 1 - \frac{\rho_b}{\rho_p}$$ (2.4)

where $\varepsilon_b$, $\rho_b$ and $\rho_p$ are bulk porosity, bulk density (g/cm$^3$) and particle density (g/cm$^3$), respectively.

### 2.1.6 Angle of Repose

In this study, the Geldart apparatus was used to conduct the angle of repose analysis of ground biomass particles. Figure 2.4 shows the schematic side view of the Geldart apparatus. The full procedure of measuring the angle of repose using the Geldart apparatus is given in the literature [95, 96]. In turn, a 50-g representative sample each of ground chip and ground pellet particles was weighed out. The ground materials were poured gently on a vibrating sheet that was installed with a 45° inclination. Due to the vibration, the particles were directed to a funnel, and dropped by gravity force onto a plate. A semi-cone pile was formed. Dashed line in Figure 2.4. represents the
pile of biomass particles. Because of the scattered shape of the pile edge, reading the height and radius of the pile was challenging. Therefore, the side view of the formed pile was pictured and the angle-measurement tool in the ImageJ software was used to measure the angle of repose.

![Figure 2.4 Schematic of the Geldart apparatus to measure angle of repose [95, 96].](image)

### 2.1.7 Image Processing

A representative 500 g of mixed ground materials were spread on a flat tray to a uniform depth. The samples were divided into 16 sub-parts. Using a spoon, a group of particles was picked randomly from the sample to be pictured. All ground pellet samples (ground using 3.2, 6.3 and 12.7 mm screens) and chip samples (ground using 3.2 and 6.3 mm screens) were observed and pictures were taken by a high-resolution microscope. The maximum vision range of microscope was limited to 13-15 mm. Therefore, the chip particles that were ground using 12.7 and 25.4 mm screens were pictured as a group of separated particles by a high-resolution scanner connected to
a computer. Pictures were analyzed using an image processing software (ImageJ ver. 1.49h, National Institutes of Health, USA). ImageJ is a simple and open source software to conduct the image analysis. It is a Java-based image processing software, developed by the US National Institute of Health (NIH).

Figure 2.5 shows the full algorithm of image processing. ImageJ software was calibrated using a known-dimension kit to convert the pixel length to the millimeter. Image processing requires the binary images. In binary pictures, “0” is assigned to the background’s pixels and “1” is assigned to the pixels inside the particle’s border. Colored images are converted to the grey-scale images by a “RGB Stack” command. The grey-scale pictures were converted into the binary images by proper thresholding. Igathinathane et al. [77] explained that using the same thresholding procedure may increase the halo effect around the particles and underestimate the particle’s dimensions. Thus, a specific thresholding procedure was examined and implemented for each particle picture. The actual dimensions of the ground particles were measured using the ellipse fitting technique in ImageJ software. The ellipse fitting plug-in fits the best ellipse on the particle’s picture. ImageJ gives the major axis and minor axis of the ellipse that are representative of particle length (L) and particle width (W), respectively (Figure 2.6).
Figure 2.5 Procedure flowchart of particle image analysis using ImageJ software.

**Taking pictures by:**
- Microscope: Ground chips (3.2 & 6.3 mm) & Ground pellet (3.2, 6.3 and 12.7 mm)
- Scanner: Ground chips (12.7 and 25.4 mm)

**ImageJ pre-processing:**
- Colored picture to grey scale stack picture
  (Image > Type > RGB Stack)
- Grey scale picture to binary (black and white) picture
  (Image > Adjust > Threshold)

**ImageJ commands:**
- Set measurements: area, perimeter, shape descriptor, fit ellipse
- Analyze > Tools > ROI manager
- Selecting the particle > Add > Measure
Figure 2.6 Determining width (W), length (L), inscribed circle (d_{ci}) and circumscribed (d_{cc}) circle for single chip and pellet particles.

2.1.8 Shape Factors

Using the outputs of image analysis, aspect ratio (AR), $W/d_{gs}$ and $L/d_{gs}$, sphericity, circularity and roundness are calculated. $d_{gs}$ (mm) is the grinder screen opening size. The most common shape factor is the aspect ratio (AR), which is defined as the ratio of its width (W) over its length (L), equation (2.5) [74]. AR value ranges between zero and one.

$$AR = \frac{W}{L}$$ (2.5)

Equivalent diameter is the diameter of a sphere that has the same volume-to-surface area ratio as the particle of interest. Owing to difficulty in measuring the surface area and volume of irregular-shape particles, a two-dimensional equivalent spherical diameter ($d_{eq}$) is suggested by Biagini et al. [3] in equation (2.6).
\[ d_{eq} = (L \times W^2)^{1/3} \]  

Sphericity (\( \psi \)) of a particle indicates how closely the particle’s shape looks like a sphere. Sphericity is defined as surface area of a sphere having the same volume of the particle (\( S_v \)) divided by the actual surface area of the particle (\( S_s \)) [81, 140]. A quicker method is proposed based on the two dimensional measurements of inscribed circle diameter (\( d_{ci} \)) and circumscribed circle diameter (\( d_{cc} \)) [80]. Inscribed circle is the largest circle that fits inside the particle’s boundary. Circumscribed circle is smallest circle that encloses the particle’s boundary. This technique determines the sphericity, as expressed in equation (2.7) [74].

\[ \psi = \sqrt{d_{ci} / d_{cc}} \]  

Circularity (\( \phi \)) is another shape factor that indicates angularity or sharpness of corners in a two-dimensional analysis [74, 78, 81], as expressed in equation (2.8).

\[ \phi = \frac{4\pi A}{P^2} \]  

where \( A \) (mm) and \( P \) (mm) are the projection area and perimeter of the particle, respectively. ImageJ counts the number of pixels inside the particle’s boundary to determine area (A) and counts the number of pixels of particle’s boundary to determine perimeter (P). Circularity is 1 for a sphere and 0.785 for a square. Similar to circularity, roundness is an indicator of angularity of a particle profile and shows the presence of sharp corners. The calculation of roundness based on individual curvature in the particle profile that is time consuming and laborious. However, a correlation, as expressed in equation (2.9), [74, 78] may be used to determine roundness.

\[ \text{Roundness} = \frac{4A}{\pi L^2} \]
Similar to circularity, roundness has the largest value of “1” for a circular object. It is important to mention that comparing the same shape factor obtained from different studies could be confusing, since different concepts are assigned to the same shape factor. For example, Biagini et al. [3] defined roundness as (1/circularity) of what has been defined in this study. It is important to know what concept is addressed for each shape factor.

2.1.9 Development of Empirical Correlations

Empirical correlations were developed to relate the specific grinding energy ($E_g$, kJ/kg), Hausner ratio (HR) and Carr-compressibility index (CCI, %) to the grinder screen size ($d_{gs}$, mm). Based on literature review [65, 74, 95], a power-law relation was used to fit the experimental data. The model parameters were determined using the Levenberg-Marquardt non-linear regression method. Coefficient of determination ($R^2$), chi-square ($\chi^2$) and root mean square error (RMSE) evaluated the fitting goodness of the proposed correlations. The values of $\chi^2$ and RMSE were calculated as follows [116, 141].

$$\chi^2 = \frac{\sum_{i=1}^{N} (\text{Pred}_i - \text{Exp}_i)^2}{N - n} \quad (2.10)$$

$$\text{RMSE} = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (\text{Pred}_i - \text{Exp}_i)^2} \quad (2.11)$$

where $\text{Pred}_i$ and $\text{Exp}_i$ are predicted and experimental values of either $E_g$, HR or CCI. N is the number of experimental data and n is the number of parameters in the model.
2.2 Results and Discussion

2.2.1 Grinding Energy

The specific grinding energy of chips declined drastically from 124 kJ/kg for the 3.2 mm grinder screen to 28 kJ/kg for the 25.4 mm grinder screen (Figure 2.7). By comparison, the specific grinding energy of pellets declined slightly from 16 kJ/kg for the 3.2 mm grinder screen to 12 kJ/kg for the 12.7 grinder screen. Generally, much more energy is consumed to grind chips than pellets. For example, for a similar grinder screen of 3.2 mm that produced the similar particle size distribution, grinding chips used about 7 times more energy than pellets. Since pellets are made from the previously-ground particles, they were easier to be ground. The empirical correlations and the statistical parameters relate the specific grinding energy \( E_g \) to the grinder screen size are displayed in Figure 2.7 and Table 2.1.

\[
\begin{align*}
E_{g,\text{chip}} &= 268.26 \times d_{gs}^{-0.65} \\
E_{g,\text{pellet}} &= 22.14 \times d_{gs}^{-0.24}
\end{align*}
\]

Figure 2.7 Specific energy required to grind the chips and pellets \((d_{gs}=3.2, 6.3, 12.7 \text{ and } 25.4 \text{ mm})\).
Table 2.1 Developed empirical correlations to predict specific grinding energy consumption, dimensions and flow properties of ground chip and ground pellet particles as a function of grinder screen size (d_{gs}, mm).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Correlation</th>
<th>$R^2$</th>
<th>$\chi^2$</th>
<th>RMSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground chip particles</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Specific grinding energy consumption ($E_g$, kJ/kg)</td>
<td>$E_g = 268.26d_{gs}^{-0.65}$</td>
<td>0.99</td>
<td>7.16</td>
<td>0.46</td>
</tr>
<tr>
<td>Width (W)</td>
<td>$W = 0.18d_{gs} + 0.61$</td>
<td>0.98</td>
<td>0.03</td>
<td>0.08</td>
</tr>
<tr>
<td>Length (L)</td>
<td>$L = 0.92d_{gs} + 2.53$</td>
<td>0.99</td>
<td>0.77</td>
<td>0.12</td>
</tr>
<tr>
<td>Mass-averaged diameter ($d_{sv}$)</td>
<td>$d_{sv} = 0.08d_{gs} + 0.42$</td>
<td>0.95</td>
<td>0.02</td>
<td>0.05</td>
</tr>
<tr>
<td>Equivalent spherical diameter ($d_{eq}$)</td>
<td>$d_{eq} = 0.30d_{gs} + 1.00$</td>
<td>0.98</td>
<td>0.11</td>
<td>0.10</td>
</tr>
<tr>
<td>Hausner ratio (HR)</td>
<td>$HR = 1.84d_{gs}^{-0.14}$</td>
<td>0.99</td>
<td>2.73E-4</td>
<td>0.01</td>
</tr>
<tr>
<td>Carr-compressibility index (CCI, %)</td>
<td>$CCI = 57.43d_{gs}^{-0.37}$</td>
<td>0.96</td>
<td>3.39</td>
<td>0.84</td>
</tr>
<tr>
<td>Ground pellet particles</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Specific grinding energy consumption ($E_g$, kJ/kg)</td>
<td>$E_g = 22.14d_{gs}^{-0.24}$</td>
<td>0.99</td>
<td>1.45</td>
<td>0.67</td>
</tr>
<tr>
<td>Width (W)</td>
<td>$W = 0.09d_{gs} + 1.23$</td>
<td>0.99</td>
<td>1.81E-4</td>
<td>0.01</td>
</tr>
<tr>
<td>Length (L)</td>
<td>$L = 0.12d_{gs} + 2.22$</td>
<td>0.95</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>Mass-averaged diameter ($d_{sv}$)</td>
<td>$d_{sv} = 0.01d_{gs} + 0.46$</td>
<td>0.97</td>
<td>1.31E-4</td>
<td>0.01</td>
</tr>
<tr>
<td>Equivalent spherical diameter ($d_{eq}$)</td>
<td>$d_{eq} = 0.10d_{gs} + 1.49$</td>
<td>0.99</td>
<td>7.28E-4</td>
<td>0.02</td>
</tr>
<tr>
<td>Hausner ratio (HR)</td>
<td>$HR = 1.33d_{gs}^{-0.04}$</td>
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<td>7.49E-5</td>
<td>0.01</td>
</tr>
<tr>
<td>Carr-compressibility index (CCI, %)</td>
<td>$CCI = 26.01d_{gs}^{-0.19}$</td>
<td>0.97</td>
<td>2.17</td>
<td>0.41</td>
</tr>
</tbody>
</table>

There is an important explanation that should be mentioned. Pellet requires additional energy to be processed and produced (drying, grinding and compaction). That is why pellet is more expensive than chip. The overall energy required to produce ground pellet particles is greater than ground chip particles. But, the current study considers the differences from the view point of a
pyrolysis operator who is a consumer of either chip or pellet commodities. The results of the current chapter, including grinding energy, identify what advantages the pyrolysis operator obtains by paying more for an upgraded and high-quality feedstock (pellet). All the presented results are required to have a more reliable economic analysis and justify the pellet’s price.

2.2.2 Particle Size Distribution

Figure 2.8 shows the particle size distribution (PSD) of ground chip and ground pellet particles obtained from mechanical sieving. Chip particles had a wide spread PSD, but the PSD of pellet particles had a narrower spread. PSD of chip particles changed significantly with changing grinder screen, but PSD of pellet particles showed less variability with grinder screen. It comes from the fact that internal particles of pellets were ground using a 3-5 mm grinder screen before the pelleting process [74, 142]. The mass-averaged particle sizes (\(d_{av}\)) also show the less variability among the pellet particles. Chip particles had the \(d_{av}\) of 0.58, 0.87, 1.59 and 2.29 mm for grinder screens of 3.2, 6.3, 12.7 and 25.4 mm, respectively. Of pellet particles were 0.50, 0.56 and 0.64 mm for grinder screens of 3.2, 6.3 and 12.7 mm, respectively.

Literature recommends the optimum particle size of less than 2 mm for pyrolysis/combustion processes [18, 21-25]. The PSD shows that more than 88% of pellet particles, no matter what grinding level was applied, were always smaller than 2 mm. Nevertheless, grinding wood chips using only grinder screen of 3.2 mm gives an appropriate PSD for thermal conversion applications. The 3.2 mm grinder screen produced the chip and pellet particles with similar PSD. Most of the particles were retained on the 0.25 and 0.5 mm sieves.
Figure 2.8 Particle size distribution (PSD) of ground chip and pellet particles obtained by mechanical sieving.

2.2.3 Particle Dimension and Shape

Image processing of single particles showed that the actual dimensions and shape of ground chip and ground pellet particles were not similar (Figure 2.9). Chip particles had rectangular shape and a small AR of 0.21-0.22, whereas the pellet particles were more circular and had an AR of 0.62-0.64. It means that for a similar particle width, the pellet particles were 3 times shorter than chip particles. Chip particles had a uniform width alongside their length, but the pellet particles were completely irregular in shape. Table 2.2 lists the details of image processing results for all chip and pellet samples.

Ground chip and ground pellet particles were also different in terms of their dimensions. Inspection of their $W/d_{gs}$ and $L/d_{gs}$ shape factors reveals that both width and length of the pellet particles were smaller than the grinder screen opening size ($d_{gs}$), whereas the lengths of chip particles were always greater than the grinder screen opening size. This is another reason to show
that why the pellet particles passed through the grinder screens’ open area easier. Figure 2.10 demonstrates that width and length of both chip and pellet particles increased linearly with the grinder screen opening size ($d_{gs}$). Empirical linear correlations also have been developed to relate the average width and length of ground particles to the grinder screen size (Table 2.1).

Even though the mechanical sieving process separates the particles based on their width, Figure 2.10 shows that the mass-averaged diameter ($d_{sv}$) obtained from mechanical sieving was always less than the actual width of particles. Apparently, mechanical sieving underestimated the actual dimensions of the particles, since $d_{sv}$ was about 50% of the width of the chip particles and 33% of the width of the pellet particles.
Figure 2.9 Microscopic pictures of ground chip and ground pellet particles.

Figure 2.10 Variation of average width (W), average length (L), mass-averaged diameter ($d_{sv}$) and equivalent spherical diameter ($d_{eq}$) with grinder screen size ($d_{gs}$) for ground chip and ground pellet particles.
Table 2.2 Size and shape properties of ground chip and ground pellet particles using mechanical sieving and image analysis (mean ± standard deviation).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Ground chip particles</th>
<th>Ground pellet particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{gs}$ (mm)</td>
<td>3.2 6.3 12.7 25.4</td>
<td>3.2 6.3 12.7</td>
</tr>
</tbody>
</table>

### Mechanical sieving

<table>
<thead>
<tr>
<th>$f_{1mm}$ (%) (^1)</th>
<th>81.95 45.07 16.51 7.43</th>
<th>85.37 76.33 63.11</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_{2mm}$ (%) (^2)</td>
<td>99.31 87.53 44.58 22.09</td>
<td>99.93 97.44 88.09</td>
</tr>
<tr>
<td>$d_{sv}$ (mm)</td>
<td>0.58 ± 0.08 0.87 ± 0.10 1.59 ± 0.10 2.29 ± 0.12</td>
<td>0.50 ± 0.07 0.56 ± 0.06 0.64 ± 0.07</td>
</tr>
</tbody>
</table>

### Image analysis

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Ground chip particles</th>
<th>Ground pellet particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>W (mm)</td>
<td>1.03 ± 0.30 1.79 ± 0.54 3.11 ± 1.13 5.10 ± 2.50</td>
<td>1.54 ± 0.28 1.81 ± 0.61 2.41 ± 1.14</td>
</tr>
<tr>
<td>L (mm)</td>
<td>4.95 ± 1.46 8.28 ± 2.04 15.29 ± 4.74 25.55 ± 7.07</td>
<td>2.51 ± 0.57 3.11 ± 0.95 3.68 ± 1.03</td>
</tr>
<tr>
<td>AR</td>
<td>0.22 ± 0.09 0.22 ± 0.07 0.22 ± 0.09 0.21 ± 0.11</td>
<td>0.64 ± 0.16 0.62 ± 0.17 0.64 ± 0.18</td>
</tr>
<tr>
<td>$d_{eq}$ (mm)</td>
<td>1.71 ± 0.40 2.95 ± 0.72 5.19 ± 1.45 8.48 ± 2.94</td>
<td>1.79 ± 0.26 2.14 ± 0.60 2.75 ± 1.11</td>
</tr>
<tr>
<td>$W/d_{gs}$</td>
<td>0.32 ± 0.09 0.28 ± 0.08 0.24 ± 0.09 0.20 ± 0.10</td>
<td>0.48 ± 0.09 0.29 ± 0.09 0.19 ± 0.09</td>
</tr>
<tr>
<td>$L/d_{gs}$</td>
<td>1.55 ± 0.45 1.31 ± 0.32 1.20 ± 0.32 1.01 ± 0.28</td>
<td>0.78 ± 0.17 0.49 ± 0.15 0.29 ± 0.08</td>
</tr>
<tr>
<td>Sphericity</td>
<td>0.44 ± 0.08 0.44 ± 0.07 0.45 ± 0.09 0.44 ± 0.11</td>
<td>0.73 ± 0.09 0.70 ± 0.08 0.71 ± 0.11</td>
</tr>
<tr>
<td>Circularity</td>
<td>0.28 ± 0.08 0.27 ± 0.07 0.33 ± 0.10 0.32 ± 0.11</td>
<td>0.40 ± 0.13 0.38 ± 0.10 0.32 ± 0.07</td>
</tr>
<tr>
<td>Roundness</td>
<td>0.25 ± 0.09 0.26 ± 0.09 0.22 ± 0.09 0.21 ± 0.11</td>
<td>0.70 ± 0.21 0.62 ± 0.18 0.68 ± 0.20</td>
</tr>
</tbody>
</table>

\(^1\) $f_{1mm}$: Fraction of particles passed through the 1 mm sieve  
\(^2\) $f_{2mm}$: Fraction of particles passed through the 2 mm sieve
2.2.4 Pycnometer Density

The pycnometer density increased with the level of grinding (Table 2.3). Grinding breaks the structure of particles, opens the closed pores and increases the number of accessible pores for the pycnometer gas to penetrate. The density of ground chip particles increased from 1.05 to 1.33 g/cm³ when the grinder screen size was changed from 25.4 to 3.2 mm. The pycnometer density of ground pellet particles increased slightly from 1.40 to 1.43 g/cm³ when the grinder screen size was changed from 12.7 to 3.2 mm. There were two observed differences associated with the pycnometer densities of chip and pellet particles. Firstly, the grinding operation affected the density of chip particles more than pellet particles. This could be attributed to the fact that the internal particles of a pellet were ground before pelleting and further grinding of pellets did not change the pycnometer density significantly. Secondly, the density of pellet particles was higher than those of chip particles. It resulted from the structural transformation in the densification process. During pelleting, the applied force smashed the cellular structure of the fibers and reduced the pore volume of the particles and consequently less pore volume was accessible for pycnometer gas penetration. Figure 2.11 shows the SEM images of a single chip and a single pellet particle.

![Ground chip particle](image1.png)  ![Ground pellet particle](image2.png)

Figure 2.11 SEM images of a single ground pine chip and a single ground pine pellet particle.
2.2.5 Flow Characterization

The bulk density of pellet particles is greater than those of chip particles. Two reasons explain this observation. First, a single pellet particle is denser than a single chip particle. Second, chip particles are needle shape and their random arrangement in the bulk of particles made a more porous bulk than more-circular pellet particles (Table 2.3). By increasing the particle size, the bed porosity reduced and the loose bulk density of both chip and pellet particles increased.

Figure 2.12 depicts that HR and CCI values decreased with particle size. Larger particles had less tendency to make a compact bulk. During the tapping process, smaller particles compressed more and required more tapping to reach their final compaction. Smaller particles could fill small pores in the bulk and increase the bulk density. The same trend was also observed for the pellet particles, though the variation in the compressibility of pellet particles was less than chip particles.

In addition to the particle size, the level of bulk compression seems to be highly dependent on the shape of the particles. Greater length appears to promote the bulk compressibility. Chip and pellet particles subject to the 3.2 mm grinder screen had similar PSD. Yet, the chip particles compacted by 50%, which is significantly more than the pellet particles which compacted by 26%. Upon comparing the compressibility results, particle shape was confirmed to be more important than particle size in tapping compressibility. Empirical correlations also were developed to predict the HR and CCI values for the ground chip and ground pellet particles as a function of grinder screen size (Table 2.1).

Figure 2.13 shows the angle of repose (AOR) values of both chip and pellet particles. The AOR of chip particles was seen to decrease from 61.0° to 45.9° when grinder screen increased from 3.2 to 25.4 mm. It agrees with the literature that reported an increase in particle size is
accompanied by a decrease in cohesiveness and hence AOR [74, 95]. Small particles have a higher specific surface area that boosts the contact and cohesiveness among the particles. Due to the similar PSD of pellet particles, the AOR values of pellet particles were practically independent of grinder screen size. Similar to the results pertinent to compressibility, the effect of particle shape was more significant than particle size. Chip and pellet particles ground with 3.2 mm grinder screen had AOR values of 61.0° and 48.0°, respectively. The difference between AOR of chip and pellet particles having the same PSD could be explained by their different particle shapes. More-spherical pellet particles tend to roll over on each other and flow easier than longer and thinner chip particles that show a high level of interlock and poor flowability.

Figure 2.12 Hausner ratio (HR) and Carr-compressibility index (CCI) of ground chip and pellet particles.
Table 2.3 Flow properties of ground chip and ground pellet particles (mean ± standard error).

<table>
<thead>
<tr>
<th>Material</th>
<th>( d_{50} ) (mm)</th>
<th>Densities (g/cm(^3))</th>
<th>( \varepsilon_b ) (%)</th>
<th>Compressibility properties</th>
<th>Flow class (HR/CCI)</th>
<th>AOR (degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground chip</td>
<td>3.2</td>
<td>1.33 ± 0.01</td>
<td>0.13 ± 0.00</td>
<td>0.22 ± 0.01</td>
<td>89.6 ± 2.1</td>
<td>1.57 ± 0.01</td>
</tr>
<tr>
<td>Particle</td>
<td>6.3</td>
<td>1.32 ± 0.01</td>
<td>0.14 ± 0.01</td>
<td>0.21 ± 0.01</td>
<td>89.1 ± 1.9</td>
<td>1.45 ± 0.14</td>
</tr>
<tr>
<td></td>
<td>12.7</td>
<td>1.26 ± 0.01</td>
<td>0.14 ± 0.01</td>
<td>0.19 ± 0.01</td>
<td>88.5 ± 1.1</td>
<td>1.29 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>25.4</td>
<td>1.05 ± 0.01</td>
<td>0.16 ± 0.01</td>
<td>0.19 ± 0.01</td>
<td>85.0 ± 1.0</td>
<td>1.20 ± 0.03</td>
</tr>
<tr>
<td>Ground pellet</td>
<td>3.2</td>
<td>1.43 ± 0.01</td>
<td>0.39 ± 0.00</td>
<td>0.49 ± 0.01</td>
<td>72.7 ± 0.9</td>
<td>1.27 ± 0.03</td>
</tr>
<tr>
<td>Particle</td>
<td>6.3</td>
<td>1.42 ± 0.01</td>
<td>0.40 ± 0.00</td>
<td>0.49 ± 0.01</td>
<td>71.6 ± 1.1</td>
<td>1.22 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>12.7</td>
<td>1.40 ± 0.01</td>
<td>0.42 ± 0.00</td>
<td>0.50 ± 0.01</td>
<td>69.9 ± 0.7</td>
<td>1.19 ± 0.02</td>
</tr>
</tbody>
</table>

Figure 2.13 Angle of repose (AOR) of ground chip and ground pellet particles.
2.2.6 Similar Analysis on Pulverized Pellet Particles – Follow up with OPG

Ontario Power Generation (OPG) is a corporation that operates the industrial power plants under pellet combustion process. OPG had the significant technical contributions in the process of defining the project, further analysis and verifying the results with their industrial pulverized samples. For the sake of consistent and systematic academic study in this PhD research, the pellets were ground using a hammer mill. But, the power plants that co-fire or burn pure pellet modify and use their existing coal pulverizer. Studying the differences of ground and pulverized pellet particles were necessary.

After doing the experiments with ground pellet particles, a set of pulverized samples were received from OPG (Atikokan power station). A similar set of size and shape analyses were conducted on the received samples. The purpose was to make sure that the tested samples in this PhD project are representative of the industrial pulverized materials. The received pellets were made from three species of spruce, pine and fir (SPF).

Figure 2.14 shows the particle size distribution of ground and pulverized pellet particles that were obtained by the laser diffraction method. The results show that the pulverized pellet particles were slightly smaller. There was about 2% difference in the size range of 1 mm. The average particle size of pulverized sample was about 5% smaller than the ground pellet particles.

The shape analysis (Table 2.4) showed that the pulverized pellet particles have a similar range of aspect ratio and circularity. The average length of pulverized sample was a little larger than ground particles. It must have been due to the different wood species used in the pellet and pre-processing prior pelletization. Further flowability analysis showed that the flowability indexes of pulverized pellet particles are already same as the ground pellet particles.
Figure 2.14 Particle size distribution of ground pellet particles and pulverized pellet particles (pulverized by an industrial coal pulverizer at Ontario Power Generation, OPG).

Table 2.4 Shape and flowability analysis of pulverized pellet particles.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Microscopic image analysis</th>
<th>Flow properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Width (mm)</td>
<td>Length (mm)</td>
</tr>
<tr>
<td>Pulverized pellet</td>
<td>1.19</td>
<td>2.32</td>
</tr>
</tbody>
</table>
2.3 Highlights of Chapter 2

Pelletization enhances the grindability. To produce the particles of ~1 mm, pellet needs around 1/7 of energy required to grind chip.

Ground pellet particles are smaller and have a narrower size distribution than chip particles. The size of pellet particles is less sensitive to the grinding level and is more predictable.

Pelletization reduces the variability in the physical properties of particles.

Pelletization changes the shape of particles from long and needle shape chip particles to irregular-round and more-spherical particles.

The evolution in shape of the particles during pelletization, reduces the compressibility and cohesion among the particles and facilitates their flowability properties.

The further physical and flow analyses on the industrial pulverized sample (Atikokan power station, OPG) showed that the results of this chapter are quite representative of industrial pulverized pellet particles.
Chapter 3: Thermogravimetric Analysis of Single Chip and Pellet Particles

In addition to particle size, biomass density influences heat and mass transfer rates during thermal treatment processes. Pine chip and pine pellet as two forms of the same biomass species with different density were used. In this chapter, mass loss of chip and pellet particles was determined in drying and pyrolysis stages of a ramped-temperature thermogravimetric analysis. The particles used in this chapter were cut to the similar dimensions. The specific tasks of the current chapter are presented as follows:

Determine the effects of particle size (0.25-5 mm) and heating rate (10-50 °C/min) on mass loss of particles in thermogravimetric analysis of single pine chip and pellet particles.

Analyze the structure of single particles during the drying and further pyrolysis stages.

Determine the kinetic parameters of drying and pyrolysis mass loss in a ramped-temperature thermal treatment.

3.1 Material and Methods

3.1.1 Sample Preparation

The obtained information from Ontario Power Generation (OPG) of Canada (Figure 1.5) shows that industrial pulverized pellet particles to be used in power generation purposes are smaller than 2 mm. This information was being used to define the range of particle size tested in this study. The dried and ground chip particles (explained in Section 2.1.1) were cut manually using a sharp knife into five particle sizes (almost a cube) of 1, 2, 3, 4 and 5 mm. The 0.25-mm particles were prepared by a lab-scale knife mill (Thomas Scientific, USA, Thomas Wiley® Mini-
Mill; Model: 3383-L10). Particles passed through a 0.35 mm screen and retained on top of 0.25 mm screen were classified as 0.25 mm particles. Pellets were also crushed cut by a knife to the desired particle sizes. Pellet particles of 4 and 5 mm size were too heavy for the TGA unit; thus, measurements were limited to the particles smaller than 3 mm. The prepared particles were exposed to the laboratory environment for three days. The later moisture content measurement showed that their moisture content increased to about 10± 1%. Figure 3.1 shows prepared particles of chip and pellet.

![Figure 3.1 Different sizes of pine chip and pellet particles.](image)

### 3.1.2 Proximate and Ultimate Analysis

Proximate analysis of chip and pellet particles was conducted using the ASTM D1762-84 standard. Briefly, pine chips and pine pellets were ground in a hammer mill with a screen size of 1.6 mm. Ground particles were dried at a temperature of 105 °C for 2 hours and its dry-basis moisture content was calculated. Particles were thermo gravimetrically treated in a 950 °C oxygen-
free environment for 10 minutes to measure dry-basis volatile content. Ground raw particles were combusted at 650 °C for 6 hours in an oven. The dry-basis ash content was calculated using the mass of remaining ash. The ultimate analysis of chipped pine and pine pellet particles was done in a Fisons-EA 1108 elemental analyzer (Thermo Scientific, Waltham, USA). Table 3.1 lists proximate and ultimate analyses results of raw pine wood. All the proximate and ultimate analyses were done in three replicates to show the reproducibility of results.

### Table 3.1 Proximate and ultimate analyses of chip and pellet particles of pine (mean ± variation).

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Chip particles</th>
<th>Pellet particles</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Proximate analysis</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moisture</td>
<td>11.22±0.10</td>
<td>9.80±0.07</td>
</tr>
<tr>
<td>Volatile</td>
<td>87.68±0.25</td>
<td>87.62±0.25</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>11.93±0.45</td>
<td>12.21±0.35</td>
</tr>
<tr>
<td>Ash</td>
<td>0.086±0.01</td>
<td>0.091±0.01</td>
</tr>
<tr>
<td><strong>Ultimate analysis</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon</td>
<td>48.02±0.03</td>
<td>48.08±0.08</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>6.14±0.07</td>
<td>6.26±0.02</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>Not detected</td>
<td>Not detected</td>
</tr>
<tr>
<td>Oxygen</td>
<td>45.85±0.05</td>
<td>45.65±0.02</td>
</tr>
</tbody>
</table>

1 Dry basis (wt.%); 2 Below 0.5 wt.%; 3 By difference

#### 3.1.3 Thermogravimetric Analysis

Thermogravimetric analysis was performed using a TGA (Model TGA-50H, Shimadzu Corporation, Japan). An alumina cup (Shimadzu Corporation, Japan) with an inside diameter of 6 mm and wall height of 3 mm held the particles. A thermocouple beneath the sample cup recorded the temperature of the nearest location of the sample. Ultra-pure nitrogen (99.999%) with a flow
rate of 50 ml/min provided an inert environment around particles and swept away the released volatiles. The furnace temperature increased from room temperature (~25 °C) to 600 °C with a constant heating rate \( \frac{dT}{dt} = \beta \) for each individual test. Experiments were done in two replicates to confirm the reproducibility of data.

A few preliminary tests were done to determine the effect of number of particles placed in the crucible. The tests conducted with 2, 4 and 10 particles of 2 mm particles. The tests were carried out at a heating rate of 50 °C/min. The tests showed that the effect of the initial number of particles inside the crucible on instantaneous mass of the sample was insignificant. Based on the preliminary test results and low range balance of the TGA unit, one particle was placed in the crucible for tests using 3, 4 and 5 mm particles. For 2 mm particles, four separated particles were placed in the crucible. For 0.25 and 1 mm particles, the pan was loosely filled with particles. Figure 3.1 shows the population of the particle(s) in the TGA crucible.

3.1.4 Data Reduction

The data from the TGA experiments were obtained as mass loss versus time (temperature). The TGA data were normalized to mass ratio \( \frac{m}{m_{25}} \) versus temperature. \( m \) and \( m_{25} \) (kg) are instantaneous mass of particle at temperatures of \( T \) and 25 °C, respectively. The mass values at the beginning and at the end of both drying and pyrolysis cycles were extracted from the experimental data. The mass loss for either drying or pyrolysis were calculated using equations (3.1) and (3.2).

Drying mass loss (%) = \( \frac{m_{25} - m_{150}}{m_{150}} \times 100 \)  \hspace{1cm} (3.1)

Pyrolysis mass loss (%) = \( \frac{m_{200} - m_{600}}{m_{200}} \times 100 \)  \hspace{1cm} (3.2)
where \( m_{25}, m_{150}, m_{200} \) and \( m_{600} \) (kg) are the mass of particles at the temperatures of 25, 150, 200 and 600 °C, respectively. It was necessary to monitor the time when drying and pyrolysis started and finished. For the sake of consistency, a set point was defined using the first-order mass loss equation, \( m/m_0 = \exp(-k.t) \). By substituting \( t = 1/k \), the value of \( m/m_0 \) is equal to \( 1/e \) or 0.37. Drying time was defined from the beginning of process until the time that moisture ratio reached to 0.37. Pyrolysis time was defined from the dry particle at 200 °C until the time the normalized mass ratio reached to 0.37.

### 3.1.5 Process Formulation

#### 3.1.5.1 Drying Formulation

The mass loss data in the temperature range of 25-150 °C were converted to moisture ratio data. Moisture ratio (MR) was calculated using the following equation [13, 113, 116, 141, 143].

\[
MR = \frac{M - M_e}{M_0 - M_e}
\]  

(3.3)

where \( M \), \( M_0 \), and \( M_e \) (kg water/kg dry material) are instantaneous moisture content, initial moisture content at the temperature of 25 °C and final moisture content at a temperature of 150 °C, respectively. As most of the moisture is removed during high drying temperatures, \( M_e \) is assumed zero [116]. Drying curves of moisture ratio versus temperature were fitted with two mathematical drying models listed in Table 3.2. For a constant heating rate analysis, \( dT/dt = \beta \). The model parameters were determined using the Levenberg-Marquardt non-linear regression method.
Table 3.2 Two drying models for a non-isothermal process.

<table>
<thead>
<tr>
<th>Model names</th>
<th>Non-isothermal drying model</th>
<th>Parameters</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Newton</td>
<td>$MR = \exp[-k_d(T - T_0/\beta)]$</td>
<td>$k_d$</td>
<td>[116]</td>
</tr>
<tr>
<td>Page</td>
<td>$MR = \exp[-k_d(T - T_0/\beta)^{n_p}]$</td>
<td>$n_p, k_d$</td>
<td>[141]</td>
</tr>
</tbody>
</table>

3.1.5.2 Pyrolysis Formulation

The thermal decomposition started from a temperature of 200 °C and prolonged to 600 °C. The kinetics formulation of a single step pyrolysis reaction is written as equation (3.4) [12, 15, 141, 144-149].

$$\frac{dX}{dt} = k_p \cdot f(X)$$

(3.4)

where $X$ is dimensionless conversion ratio and constant $k_p$ (1/s) is the temperature dependent reaction rate constant, defined by the Arrhenius equation (3.6).

$$X = \frac{m_{200} - m_f}{m_{200} - m_{600}}$$

(3.5)

$$k_p = k_{0p} \cdot \exp\left(-\frac{E}{RT}\right)$$

(3.6)

where $m_{200}$, $m$, and $m_{600}$ (kg) are masses of particles at temperatures of 200, $T$ and 600 °C, respectively. $T$ is a temperature between 200 and 600 °C. $k_0$ (1/s) is pre-exponential factor, $E$ (J/mol) is activation energy and $R$ (8.314 J/mol.K) is the universal ideal gas constant. Vlaev et al. [12] demonstrated that the equation (3.4) for a first-order pyrolysis reaction would be manipulated to equation (3.7). For a first-order reaction, $f(X)$ is equal to $(1-X)$ [150].

$$\ln(g) = \ln\left[-\frac{\ln(1-X)}{T^2}\right] = \ln\left[\frac{k_0 R}{\beta E} - \frac{E}{RT}\right]$$

(3.7)
A plot of $\ln[-\ln(1-X)/T^2]$ versus $(1/T)$ gives a straight line with slope of $(-E/R)$ and intercept of $\ln(k_oR/\beta E)$. For the sake of simplicity, $\ln[-\ln(1-X)/T^2]$ is shown as $\ln(g)$ in results. To eliminate the effect of heat transfer limitation on kinetics, the particle size should be small enough to neglect its internal temperature gradient. The heating rate should be slow enough to make sure that particle’s temperature is equal to the TGA furnace temperature. A set of preliminary tests, using saw dust (<125 µm) and heating rates of lower than 10 °C/min, were conducted. Preliminary test results showed that mass loss of 0.25 mm particle at heating rate of 10 °C/min represent the pure kinetics. However, for comparison purpose, the kinetic formulation was conducted on mass loss data of all particles. In this paper, the mass loss data at a heating rate of 10 °C/min in a temperature range of 200-600 °C were transformed to corresponding $\alpha$ values. Integral kinetic analysis was conducted to calculate the activation energies and pre-exponential factors.

### 3.2 Results and Discussion

To investigate the density of chip and pellet particles, 50 of each one were measured. Table 3.3 lists the measured size of particles, average mass and their variations of single particles for both chip and pellet particles. It seems that pellet particles are about 3-4 times denser than chip particles.

Figure 3.2 shows TGA analysis of 0.25 mm chip and pellet particles at a heating rate of 50 °C/min. There were two distinct regions of mass loss and two peaks in the mass loss rate data. The first region was drying that happened in the temperature range of 25-150 °C. The second region was pyrolysis that happened in the temperature range of 200-600 °C. Drying and pyrolysis
processes strongly depend on the temperature profile inside the particle [133, 151]. The combined effect of particle size, particle density and operating conditions like temperature and heating rate significantly change the temperature profile inside the particles [152]. The experimental results (Table 3.4 and Table 3.5) confirmed that particle size, heating rate and particle density affected the rate and duration of both drying and pyrolysis stages.

Table 3.3 Particle size, average mass, and their variations for single particles of both chip and pellet particles (50 particles of each size).

<table>
<thead>
<tr>
<th>Average and variation of particle size (mm)</th>
<th>Average and variation of mass of single ground particles (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Chip particles</td>
</tr>
<tr>
<td>0.25±0.13</td>
<td>0.03±0.02</td>
</tr>
<tr>
<td>1.00±0.25</td>
<td>0.16±0.06</td>
</tr>
<tr>
<td>2.00±0.49</td>
<td>0.95±0.11</td>
</tr>
<tr>
<td>3.00±0.66</td>
<td>6.04±0.37</td>
</tr>
<tr>
<td>4.00±0.63</td>
<td>8.33±0.45</td>
</tr>
<tr>
<td>5.00±0.53</td>
<td>16.25±1.75</td>
</tr>
</tbody>
</table>
3.2.1 Effect of Particle Size

The temperature at which the drying was finished changed with particle size. For example, at a heating rate of 20 °C/min, drying continued until 107, 110, 115, 125, 135 and 142 °C for chip particles of 0.25, 1, 2, 3, 4 and 5 mm in size, respectively. Pyrolysis started at around 200 °C and the major mass loss ended at 400-405 °C. Mass loss gradually continued till 600 °C when the particles lost 80% of their dry mass (\( m_{200} \)). The pyrolysis durations were similar for all particle sizes.

Larger particles have a larger internal and external heat and mass resistances. Demirbas [21] and NikAzar [25] hypothesized that the center of larger particles heats up slower than smaller particles. Our results confirm this hypothesis and show that drying time increased with increasing the particle size for both chip and pellet particles. Figure 3.3 plots drying mass loss of chip and
pellet particles that were dried with a heating rate of 30 °C/min. For pellet particles, smaller particles dried faster and lost more moisture. But, for chip particles, this was only observed up to a temperature of 100 °C. Due to a high specific surface area, the 0.25 mm particles were dried much faster than other particles and its drying ended at about 100 °C. For temperatures beyond 100 °C, three chip particle sizes of 3, 4 and 5 mm showed an accelerated mass loss. This trend was observed for all heating rates. Further drying tests were carried out and particles were pictures by a microscope before and after drying. Examinations showed that some cracks appeared in the structure of particles and the fibers got disintegrated. Figure 3.4 shows the microscopic pictures of particles before and after drying. It is speculated that surface evaporation of the large particles did set up a high moisture gradient from the interior to the surface. This was liable to cause an over-drying of surface and excessive shrinkage. The excessive shrinkage on the surface of the particle caused a high tension within the material and resulted the cracks [120]. The fractures in the structure of the particle must have increased the specific surface area. More accessible surface area boosts the convection heat transfer rate and facilitates the release of moisture. These cracks were not observed for smaller chipped particles and pellet particles.
Figure 3.3 Drying mass loss curve of chip and pellet particles (β=30 °C/min; temperature of up to 150 °C).

Figure 3.4 Microscopic surface picture of the 5-mm particle dried with heating rate of 20 °C/min and temperature of up to 150 °C; (a) & (b) before drying; and (c) & (d) after drying.
The pyrolysis durations (Table 3.4) show that the pyrolysis time was independent of particle size for both chip and pellet particles. Pyrolysis dry-basis mass loss varied randomly with particle sizes with no apparent trend. The differences of pyrolysis time among the particle sizes were not significant. Some studies in literature, like Şensöz et al. [67] and Encinar et al. [69], also showed that char yield is independent of particle size. Figure 3.5 and Figure 3.6 show the SEM micrographs of chip and pellet particles before and after pyrolysis. The SEM pictures show that the thermal decomposition during the pyrolysis broke the cell walls and large holes and cracks appeared inside the particle’s skeleton. Harsh thermal treatment enlarged the pores and connected the enclosed pores to many other open spaces. In this case, heat and volatiles must have diffused faster and resistances to transport must have decreased due to the structural changes in the particle.

3.2.2 Effect of Particle Structure

Particle structure and density affected the rate and duration of drying. Pellet particles needed 25%-88% more time to dry than the same sizes of chip particles. Pellet particles are denser and needed higher heat accumulation than chip particles to be heated up. Furthermore, pellet particles have random-oriented fibers which reduces the overall thermal conductivity of particles. Heat and mass diffusion orthogonal to fibers is slower than in the direction of fibers [153]. Higher density and lower overall thermal conductivity drop the thermal diffusivity \( \alpha = \frac{K_s}{\rho C_{ps}} \) significantly. During pyrolysis, the harsh thermal treatment decomposed the particles’ structure (Figure 3.5 and Figure 3.6). The evolution in particle structure after pyrolysis facilitated the devolatilization process and the structural differences of raw chip and pellet particles were not observed after pyrolysis. Dry-basis mass losses of both chip and pellet particles were about 80%. In addition, both chip and pellet particles turned into a carbon-rich solid after pyrolysis which had a much
higher thermal conductivity than raw wood. Thermal conductivity of char is in the range of 1.7 W/m.K and thermal conductivity of raw wood is in the range of 0.1-0.2 W/m.K.

Figure 3.5 Scanning electron microscopy pictures of raw and pyrolyzed chip particles (red dashed circles show the cracks in particle structure).

Figure 3.6 Scanning electron microscopy pictures of raw and pyrolyzed pellet particles (red dashed circles show the cracks in particle structure).
3.2.3 Process Modeling

Drying rate constants for pellet particles were lower than the drying rate constants of chip particles in both models (50-70% less). It corresponds to slower drying of pellet particles. As discussed earlier, thermal decomposition changed the structure of particles. Pyrolysis modeling also proved that the heat and mass diffused through the particles substantially easier when thermal decomposition happened. Figure 3.7 shows that the activation energy for the pyrolysis reaction of 0.25 mm pine chip particles at a heating rate of 10 °C/min dropped from 66.21 kJ/mol to 1.84 kJ/mol. A lower activation energy indicates that the devolatilization process happened faster. This phenomenon was reported by Vlaev et al. [12].

![Figure 3.7 Two-step pyrolysis kinetic model (particle size=0.25 mm; \( \beta = 10 \) °C/min).](image)

Some studies reported a phenomenon called “kinetic compensation effect” (KCE). The kinetic compensation effect states that there is a linear relationship between Arrhenius parameters...
\( \ln(k_0) \) and \( E \) for a family of related processes. It is a widely observed phenomenon in many areas of science, notably heterogeneous catalysis. KCE is caused by the exponential format of the Arrhenius equation and refers to the fact that the co-variability of parameters \( k_0 \) and \( E \) forces experimental data possibly to fit several models well with different \( f(X) \) [154]. This analysis shows that the appropriate \( f(X) \) is selected for the kinetic analysis. The similar results were also observed in this study, Figure 3.8.

![Graph showing variation of activation energy (E) versus \( \ln(k_0) \) (particle size=0.25 mm; \( \beta=10, 20, 30 \) and 50 \(^\circ\)C/min).](image)

**Figure 3.8** Variation of activation energy (E) versus \( \ln(k_0) \) (particle size=0.25 mm; \( \beta=10, 20, 30 \) and 50 \(^\circ\)C/min).
Table 3.4 Required time when moisture ratio in drying ($25 \, ^\circ\text{C} < T < 150 \, ^\circ\text{C}$) and dry mass ratio in pyrolysis ($200 \, ^\circ\text{C} < T < 600 \, ^\circ\text{C}$) reached to 37% of their initial values for chip and pellet particles.

<table>
<thead>
<tr>
<th>Heating rate ($^\circ\text{C}$/min)</th>
<th>Chip particle size (mm)</th>
<th>Pellet particle size (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.25 1 2 3 4 5</td>
<td>0.25 1 2 3 5</td>
</tr>
<tr>
<td>10</td>
<td>226 229 254 258 280 356</td>
<td>343 358 371 419</td>
</tr>
<tr>
<td>20</td>
<td>152 158 161 166 201 226</td>
<td>220 270 283 312</td>
</tr>
<tr>
<td>30</td>
<td>113 115 118 130 143 159</td>
<td>153 163 170 186</td>
</tr>
<tr>
<td>50</td>
<td>70 74 78 86 92 107</td>
<td>89 93 98 105</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Heating rate ($^\circ\text{C}$/min)</th>
<th>Chip particle size (mm)</th>
<th>Pellet particle size (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.25 1 2 3 4 5</td>
<td>0.25 1 2 3 5</td>
</tr>
<tr>
<td>10</td>
<td>1015 1016 1012 1022 1019 1021</td>
<td>1017 1019 1018 1017</td>
</tr>
<tr>
<td>20</td>
<td>547 548 549 546 546 549</td>
<td>540 542 541 543</td>
</tr>
<tr>
<td>30</td>
<td>383 384 386 383 388 383</td>
<td>379 383 379 377</td>
</tr>
<tr>
<td>50</td>
<td>246 248 248 248 250 248</td>
<td>247 244 243 246</td>
</tr>
</tbody>
</table>
Table 3.5 Parameters of Page drying models (25 °C < T < 150 °C) and of pyrolysis model (200 °C < T < 600 °C) of chipped and pellet particles at heating rate of 10 °C/min.

### Drying (Page model)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Chip particle size (mm)</th>
<th>Pellet particle size (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.25  1  2  3  4  5</td>
<td>0.25  1  2  3</td>
</tr>
<tr>
<td>$k_d$ (1/min)</td>
<td>0.05  0.04  0.04  0.05  0.05  0.02</td>
<td>0.02  0.02  0.01  0.01</td>
</tr>
<tr>
<td>$n_p$</td>
<td>2.07  2.16  2.32  2.11  2.15  2.37</td>
<td>2.25  1.97  2.30  2.28</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.90  0.98  0.96  0.99  0.99  0.99</td>
<td>0.98  0.99  0.99  0.99</td>
</tr>
</tbody>
</table>

### Pyrolysis (Non-isothermal model)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Chip particle size (mm)</th>
<th>Pellet particle size (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.25  1  2  3  4  5</td>
<td>0.25  1  2  3</td>
</tr>
<tr>
<td>$k_{0.1}$ (1/min)</td>
<td>0.12  0.24  0.28  1.15  1.16  1.43</td>
<td>0.33  0.24  0.32  0.47</td>
</tr>
<tr>
<td>$E_1$ (kJ/mol)</td>
<td>66.21  72.90  77.45  73.59  78.71  81.49</td>
<td>73.63  71.82  74.14  76.23</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.99  0.99  0.99  0.99  0.99  0.99</td>
<td>0.99  0.99  0.99  0.99</td>
</tr>
<tr>
<td>$T_{transition}$</td>
<td>374  374  373  374  375  374</td>
<td>372  374  373  374</td>
</tr>
<tr>
<td>$k_{0.2}$ (1/min)</td>
<td>15.42  4.02  16.82  18.39  57.05  11.75</td>
<td>0.14  0.14  0.16  0.09</td>
</tr>
<tr>
<td>$E_2$ (kJ/mol)</td>
<td>1.84  0.62  1.85  2.48  4.77  6.52</td>
<td>6.73  6.94  7.43  5.42</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.99  0.99  0.99  0.98  0.98  0.99</td>
<td>0.99  0.99  0.99  0.99</td>
</tr>
</tbody>
</table>
3.3 **Highlights of Chapter 3**

Pellet particles are about 3-4 times denser than chip particles with the same dimensions.

Drying of pellet particles took around 25%-90% more time than drying of chip particles.

Decomposition of particles in pyrolysis minimized their differences in the rate and duration of pyrolysis.

The pyrolysis stage showed a two-zone kinetic mass loss. Activation energies of first and second zones for 0.25 mm chip particles were 66.2 kJ/mol and 1.8 kJ/mol, respectively.
Chapter 4: Development of a Thin-Layer Thermogravimetric Analyzer

4.1 Experimental Procedure

A thin-layer thermogravimetric analyzer is designed and constructed to measure the mass of samples continuously during a thermal treatment test. Figure 4.1 shows the schematic picture of the constructed apparatus. The equipment consists of three sets of component parts: dryer/pyrolyzer section, instantaneous mass-measuring unit (Sartorius balance, Quintix 412-1S) and heating/controls system. The heating system includes an in-line preheater and an infrared heater. Figure 4.2 shows the in-line preheater, infrared heater, weight measuring system and the temperature controller panel.

The chamber is a rectangular box made of stainless steel with a cross section of 200 mm x 300 mm and a length of 400 mm. The sample holder (40 mm x 60 mm) inside the chamber rests on a stainless-steel mesh platform (50 mm x 70 mm). The platform has a fixed connection to a titanium rod (300 mm length). The rod lower-end rests on a digital balance located underneath the chamber. A small access door (50 mm x 70 mm) installed on the chamber front-wall is used to place or remove the sample from the chamber.

An infrared heater with a fused quartz surface (Omega, QC-061040-T) installed on top side of the vessel heated up the atmosphere inside the chamber to the targeted temperatures of 50-600 °C. The balance records the mass of the samples continuously. A continuous 3 L/min carrying gas passed through an in-line electrical pre-heater (Omega, AHP-7561). A K-type thermocouple recorded the temperature of the point of 10-mm distance from the sample holder and sent the signal to the temperature controller. The temperature controller kept the temperature of the monitoring point at the temperature set point. The biomass particles were spread as a thin layer on the sample
holder tray outside of the drying chamber prior to placing the sample holder with sample inside the heated dryer. The hot carrying gases passed over the particles, transferred the heat to the particles and carried the released moisture/volatiles out of the dryer. The balance transmitted the sample mass continuously to a computer receiver, recording the data in an excel file. The duration of thermal treatment of samples varied with the treatment temperature. The experiment were stopped when the mass of samples remained constant. Experiments were done in two replicates to confirm the reproducibility of data.

Figure 4.1 Schematic picture of the thin layer dryer/pyrolyzer (different parts are not in the same scale).
Figure 4.2 Picture of macro TGA equipment, showing preheater, infrared heater, weight-measuring system and temperature controller panel.
4.2 Transient and Steady-state Temperature Profile

The profile of temperature elevation in the output of in-line preheater and infrared heater surface and centerline of the vessel was recorded at several set points. Figure 4.3 shows the transient temperature elevation and the time when the samples were loaded. The temperature of chamber increased and kept constant at the set point. Figure 4.4 shows the temperature elevation of dryer/pyrolyzer section at the temperature set points of 200-500 °C. The uniformity of temperature in the center-axis of vessel was evaluated at all temperature set points (Figure 4.5). The temperature in the center-axis of vessel was measured using a 60-cm thermocouple. The recorded temperatures show that the temperature variation in the center-axis where the sample is located is constant at the temperature set point. Table 4.1 lists the temperature of in-line preheater, temperature of radiative heater and consuming energy of each heater to elevate the vessel temperature to the targeted temperature set points. Table 4.2 lists the center-axis temperature alongside the vessel. The analysis shows that there is a reduction of temperature in point 7, the output of vessel.

<table>
<thead>
<tr>
<th>Set point of vessel (°C)</th>
<th>50</th>
<th>100</th>
<th>150</th>
<th>200</th>
<th>300</th>
<th>400</th>
<th>500</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial temperature-drop due to door opening (°C)</td>
<td>± 1</td>
<td>± 2</td>
<td>± 2</td>
<td>± 2</td>
<td>± 3</td>
<td>± 4</td>
<td>± 5</td>
</tr>
<tr>
<td>Preheater exit gas (°C)</td>
<td>50</td>
<td>100</td>
<td>150</td>
<td>200</td>
<td>300</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>Infrared heater surface (°C)</td>
<td>135</td>
<td>214</td>
<td>335</td>
<td>414</td>
<td>551</td>
<td>672</td>
<td>800</td>
</tr>
<tr>
<td>Heat of inflow (W)</td>
<td>19.0</td>
<td>22.0</td>
<td>25.0</td>
<td>28.1</td>
<td>34.6</td>
<td>35.3</td>
<td>36.1</td>
</tr>
<tr>
<td>Heat of radiation (W)</td>
<td>32</td>
<td>57</td>
<td>121</td>
<td>181</td>
<td>317</td>
<td>471</td>
<td>670</td>
</tr>
</tbody>
</table>

Table 4.1 Steady-state temperature (°C) of heaters and dryer/pyrolyzer chamber.
Figure 4.3 Transient temperature profile of inflow gas, radiative heater and the chamber at set point of 500 °C.

Figure 4.4 Temperature elevation inside the dryer/pyrolyzer vessel at the temperature set points of 200-500 °C.
Figure 4.5 Uniformity of reactor temperature alongside of its central line at set point of 500 °C.

Table 4.2 Steady-state temperatures (°C) inside the dryer/pyrolyzer alongside the center axis (points are displayed in Figure 4.5).

<table>
<thead>
<tr>
<th>Set point of chamber (°C)</th>
<th>Point 1 (-20 mm)</th>
<th>Point 2 (0 mm)</th>
<th>Point 3 (10 mm)</th>
<th>Point 4 (15 mm)</th>
<th>Point 5 (20 mm)</th>
<th>Point 6 (30 mm)</th>
<th>Point 7 (40 mm)</th>
</tr>
</thead>
</table>
4.3 Specifications of Installed Parts

The designed and constructed equipment has various parts to measure and/or control the gas flow rate, temperature and mass of loaded sample. The specifications of assembled parts are explained as follow.

4.3.1 Flowmeter

Two flowmeters are installed. The first flowmeter is connected to a nitrogen gas cylinder. The second flowmeter is connected to the compressed air line. Table 4.3 lists the specifications of installed flow meters.

<table>
<thead>
<tr>
<th>Company</th>
<th>Part#</th>
<th>Flowing Gas</th>
<th>Maximum flow</th>
<th>Readability</th>
<th>Connection size</th>
</tr>
</thead>
<tbody>
<tr>
<td>OMEGA</td>
<td>FMA-A2408-SS-NIST5</td>
<td>Nitrogen</td>
<td>50 LPM</td>
<td>0.01 LPM</td>
<td>6.35 mm</td>
</tr>
<tr>
<td>OMEGA</td>
<td>FMA-A2317-NIST5</td>
<td>Air</td>
<td>50 LPM</td>
<td>0.01 LPM</td>
<td>6.35 mm</td>
</tr>
</tbody>
</table>

4.3.2 In-line Preheater

The AHP series in-line air heaters are used to heat up the clean and dry gas streams. AHP series air process heaters provide hot gas up to 500 °C with infinite control by varying the voltage and/or the air flow. Table 4.4 lists the specifications of in-line preheater. Closed loop control is achieved with temperature controllers and a “T-fitting” to mount a thermocouple. The T-fitting connected to the exit stream of heater and a thermocouple is mounted on it. The thermocouple measures the output temperature and sends the signal to the temperature controller to adjust the temperature of exit stream of in-line preheater. Figure 4.6 shows the T-fitting connection and
configuration of thermocouple installation. To be on the safe side, a maximum set point of 300 °C was set to avoid safety issues and burning the heater. Equation (4.1) calculates the consuming power of preheater as a function of flow rate and temperature rise.

\[
\text{Power (W)} = \text{Flow (SCFM)} \times \Delta T / 3
\]  

(4.1)

Figure 4.6 In-line preheater assembly, the heater (right) and thermocouple T-fitting (left) connected to the exit stream of heater (www.omega.ca).

Table 4.4 Specifications of the in-line preheater.

<table>
<thead>
<tr>
<th>Company</th>
<th>Part#</th>
<th>Voltage/Power</th>
<th>Heating length</th>
<th>Maximum gas flow</th>
<th>Diameter</th>
<th>Fitting size</th>
</tr>
</thead>
<tbody>
<tr>
<td>OMEGA</td>
<td>AHP-7562</td>
<td>240 Volts 750 W</td>
<td>140 mm</td>
<td>20 SCFM</td>
<td>19.75 mm</td>
<td>19.05 mm male NPT</td>
</tr>
</tbody>
</table>

4.3.3 **Infrared Heater**

OMEGA QH and QC Series quartz infrared radiant panel heaters have the most powerful power output of any infrared panel heater available. Table 4.5 lists the specifications of infrared radiative heater. The emitter surface is a fused quartz glass that is grooved to provide coil support. The glass face is cleanable and withstands a great thermal shock. The housing is made of aluminized steel with the electrical terminal housing on the back. A 3/16” i.d. quartz thermowell
is available for use with K-type thermocouples to monitor and control the temperature of quartz surface. Figure 4.7 shows the calibration curve of emitting energy from the surface of radiative heater as a function of heater surface temperature.

Table 4.5 Specifications of the infrared radiative heater.

<table>
<thead>
<tr>
<th>Company</th>
<th>Part#</th>
<th>Voltage/Power</th>
<th>Emitter face</th>
<th>Housing</th>
<th>Heated surface</th>
<th>Maximum temperature</th>
<th>Thermowell diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>OMEGA</td>
<td>QC-061040-T</td>
<td>480 Volts</td>
<td>98% pure fused quartz</td>
<td>Aluminized steel</td>
<td>15 mm x 25 mm</td>
<td>980 °C</td>
<td>4.75 mm</td>
</tr>
</tbody>
</table>

Figure 4.7 Calibration curve of emitting power versus surface temperature in the radiative heater.

4.3.4 Balance

The Quintix series of Sartorius balances is used to measure and record the mass of samples continuously during the thermal treatment experiments. Table 4.6 lists the specifications of digital balance. The maximum capacity of digital balance is 410 g. Its readability is 0.01 g and the
minimum recording interval is 1 second. Table 4.7 lists the calibration of digital balance using a wide range of calibration loads at various flow rates of carrying gas.

<table>
<thead>
<tr>
<th>Company</th>
<th>Part#</th>
<th>Capacity</th>
<th>Readability</th>
<th>Min. recording interval</th>
<th>Pan diameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sartorius</td>
<td>Quintix 412-1S</td>
<td>410 g</td>
<td>0.01 g</td>
<td>1 sec</td>
<td>180 mm</td>
</tr>
</tbody>
</table>

Table 4.7 Calibration of digital balance using calibration loads.

<table>
<thead>
<tr>
<th>Calibration loads (g)</th>
<th>Gas Flow (L/min)</th>
<th>0</th>
<th>1</th>
<th>3</th>
<th>5</th>
<th>10</th>
<th>25</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td></td>
<td>0.00</td>
<td>0.00</td>
<td>0.02</td>
<td>0.03</td>
<td>0.04</td>
<td>0.05</td>
<td>0.14</td>
</tr>
<tr>
<td>18.46</td>
<td></td>
<td>18.46</td>
<td>18.46</td>
<td>18.50</td>
<td>18.52</td>
<td>18.54</td>
<td>18.51</td>
<td>18.63</td>
</tr>
<tr>
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<td>27.71</td>
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<td>27.73</td>
<td>27.74</td>
<td>27.75</td>
<td>27.86</td>
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<tr>
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<td>36.95</td>
<td>36.96</td>
<td>36.97</td>
<td>36.98</td>
<td>37.09</td>
</tr>
<tr>
<td>46.18</td>
<td></td>
<td>46.18</td>
<td>46.18</td>
<td>46.18</td>
<td>46.19</td>
<td>46.20</td>
<td>46.21</td>
<td>46.30</td>
</tr>
<tr>
<td>55.43</td>
<td></td>
<td>55.43</td>
<td>55.43</td>
<td>55.43</td>
<td>55.44</td>
<td>55.45</td>
<td>55.45</td>
<td>55.54</td>
</tr>
</tbody>
</table>

4.4 Operating Manual

The procedure for conducting a drying and/or pyrolysis test and final shutting down of apparatus is as follow:

1. Open the carrying gas valve and regulate its flow to target value. Make sure to be consistent on gas flow to exclude the effect of gas velocity on balance.
2. Turn on the main temperature controller panel and set the temperature of inline preheater and chamber to target temperatures. To be on the safe side, do not set the temperature of inline preheater more than 300 °C.

3. In case of using nitrogen as carrying gas, sweep the chamber at least 20-30 minutes prior to the first run.

4. Turn on the computer and open an Excel file.

5. Turn on the digital balance. The balance needs about 15-30 minutes warm up time. So, make sure you turn on the balance around 30 minutes prior to your test. Please do not unplug the balance USB cable neither during the experiment nor before/after that.

6. Wait till both temperature controllers show your targeted temperatures on their screens.

7. Press the “Print” option on the balance screen to start recording the instantaneous mass on excel file.

8. Load the material into crucible (initial mass depends on thickness of material layer and its initial density), open the chamber’s door and put the crucible on mesh support plate.

9. After finishing the test at desired residence time, reduce the set point of both heaters and wait to carrying gas cool down the heaters and chamber environment.

10. Close the carrying gas valve and shut down the computer.

11. Turn off the temperature controller panel.
Chapter 5: Thin-Layer Drying Characterization of Ground Chip and Ground Pellet Particles

Initial moisture content of woody biomass significantly changes the efficiency of the thermal conversion process. Wood particles are dried prior to be fed to the pyrolysis/combustion chambers. In this chapter, the mass and volume shrinkages of ground chip and ground pellet particles of pine wood were studied when exposed to either air or pure nitrogen gas. The moistened particles were dried at a constant-temperature in a thin layer dryer set at the temperatures of 50-200 °C. The drying process was characterized in terms of the rate of moisture loss, moisture diffusion coefficient, duration of drying, particle degradation and volume shrinkage. The specific tasks of the current chapter are presented as follows:

Determine drying rates of ground chip and ground pellet particles in the temperature range of 50-200 °C and initial moisture contents of 0.10-0.50 (dry basis).

Develop empirical correlations to relate drying rate constants, moisture diffusion coefficient and drying time to drying temperature, initial moisture content and grinder screen size.

Determine the effect of carrying gas on drying rate, equilibrium moisture contents, degradation of particles and drying duration. The used carrying gases were dry nitrogen, dry air and atmospheric air.

Determine the particle and bulk volume shrinkage of ground chip and ground pellet particles.
5.1 Material and Methods

5.1.1 Sample Preparation

The full procedure of grinding pine chips and pine pellets using four grinder screen sizes of 3.2, 6.3, 12.7 and 25.4 mm is provided in Section 2.1.1. Calculated amounts of water were sprayed on the particles to adjust their initial moisture contents ($M_0$) to 0.10, 0.30 and 0.50 (dry-mass basis). Moistened particles were stored in sealed containers and kept in a refrigerator (~4-5 °C) for at least 3 days to reach a uniform moisture distribution prior to the drying tests.

5.1.2 Thin-Layer Drying

The description of the designed dryer and procedure of conducting a drying experiment is provided in Chapter 4. The targeted drying temperatures were 50, 100, 150 and 200 °C. Three different carrying gases were used to dry the particles in this work; 1) dry nitrogen (cylinder with purity of 99.998%, moisture-free, Praxair Company), 2) dry air (cylinder with a composition of 79% nitrogen and 21% oxygen, moisture-free, Praxair Company) and 3) utility air from UBC campus line (temperature=20 ± 5 °C; relative humidity of 70 ± 5%). Drying tests were stopped when the mass of the sample remained constant. Experiments were done in two replicates to confirm the reproducibility of data.

5.1.3 Drying Rate Equations

The mass loss data were smoothed and converted to the corresponding moisture ratio ($MR$) using equation (5.1).

$$MR = \frac{M - M_c}{M_0 - M_c}$$  \hspace{1cm} (5.1)
where $M$, $M_0$, and $M_e$ are instantaneous, initial and final moisture contents (kg water/kg dry matter), respectively. Drying rates $(-dM/dt)$ were calculated using the finite difference method. Moisture ratio data versus time were fitted with four semi-theoretical mathematical drying models listed in Table 5.1 [116].

Table 5.1 Semi-theoretical drying kinetics models for thin-layer isothermal drying condition.

<table>
<thead>
<tr>
<th>Model</th>
<th>Isothermal drying model</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Newton</td>
<td>$MR = \exp(-k_d t)$</td>
<td>$k_d$</td>
</tr>
<tr>
<td>Page</td>
<td>$MR = \exp(-k_d t^n)$</td>
<td>$n_p, k_d$</td>
</tr>
<tr>
<td>Henderson</td>
<td>$MR = b \exp(-k_d t)$</td>
<td>$b, k_d$</td>
</tr>
<tr>
<td>Logarithmic</td>
<td>$MR = a + b \exp(-k_d t)$</td>
<td>$a, b, k_d$</td>
</tr>
</tbody>
</table>

5.1.4 Moisture Diffusion Coefficient

The part of drying process that drying rate starts to decline is called the falling rate period. During this period, internal diffusion is the dominant mass transfer mechanism [112, 113, 117]. The moisture loss data in the falling rate period were fitted to the analytical solution of Fick’s second law to calculate the moisture diffusion coefficient. Fick’s second law showing in equation (5.2) is an unsteady-state diffusion mass transfer model.

$$\frac{\partial M}{\partial t} = D \frac{\partial^2 M}{\partial x^2}$$ (5.2)

where $t$ (s) is the process time, $x$ (m) is the distance and $D$ (m$^2$/s) is the moisture diffusivity inside the particle. The Fick’s model was solved analytically in the spherical coordinate. Based on the assumption that the moisture diffusion coefficient does not depend on the moisture content, equations (5.3) is the solution of diffusion equation in spherical coordinate.
\[ MR = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left[-\frac{n^2 \pi^2 D}{(d_p/2)^2} t\right] \]  

(5.3)

where \( d_p \) (m) is the equivalent diameter of a spherical particle. By truncating the right side of equation (5.3) to its first term, it reduces to equation (5.4). Moisture diffusion coefficients were determined using the Levenberg-Marquardt non-linear regression method.

\[ MR = \frac{6}{\pi^2} \exp\left(-\frac{\pi^2 D}{(d_p/2)^2} t\right) \]  

(5.4)

### 5.1.5 Particle and Bulk Volume Shrinkage

Shrinkage of a single particle is defined as the variation of its volume over its initial volume [139]. Because of the difficulty in volume measurement of small ground particles, the particle shrinkage in this study is defined as a reduction in average particle diameter of a sample during a drying process over initial average particle diameter. Bulk volume shrinkage is defined as the reduction in bulk volume of particles over initial bulk volume.

\[ S_b = \frac{V_{b,\text{moist}} - V_{b,\text{dry}}}{V_{b,\text{moist}}} \]  

(5.5)

\[ S_p = \frac{d_{p,\text{moist}} - d_{p,\text{dry}}}{d_{p,\text{moist}}} \]  

(5.6)

where \( S_b, S_p, V_{b,\text{moist}} \) (cm\(^3\)), \( V_{b,\text{dry}} \) (cm\(^3\)), \( d_{p,\text{moist}} \) (mm) and \( d_{p,\text{dry}} \) (mm) are shrinkage coefficient of bulk volume, shrinkage coefficient of particle size, bulk volume of moist particles, bulk volume of dry particles, average particle diameter of moist particles and average particle diameter of dry particles, respectively. Both ground chip and ground pellet particles were moistened to the initial moisture contents of 0.10-0.90 and dried at the temperature of 100 °C. Average diameter of
particles before and after drying were measured using the Malvern Mastersizer equipment, provided in Section 2.1.3.2. Each measurement was repeated three times.

5.1.6 Bulk Porosity

Bulk porosity was calculated using equation (5.7) [92, 139].

$$\varepsilon_b = 1 - \frac{\rho_b}{\rho_p}$$  \hspace{1cm} (5.7)

where $\varepsilon_b$, $\rho_b$ and $\rho_p$ are bulk porosity, bulk density (g/cm$^3$) and particle density (g/cm$^3$), respectively. Terms of $\rho_b$ and $\rho_p$ at a specific initial moisture content were calculated using equations (5.8) and (5.9), respectively.

$$\rho_b = \frac{m_b}{V_b} = \frac{m_{b,\text{dry}} (1 + M_b)}{V_{b,\text{dry}} (1 + S_b)}$$  \hspace{1cm} (5.8)

$$\rho_p = \frac{m_p}{V_p} = \frac{m_{p,\text{dry}} (1 + M_p)}{\pi/6 d_{p,\text{dry}}^3 (1 + S_p)^3} = \frac{m_{p,\text{dry}} (1 + M_p)}{V_{p,\text{dry}} (1 + S_p)^3}$$  \hspace{1cm} (5.9)

The particle shrinkage coefficient in this study is diameter-basis; therefore, the particles are assumed spherical and the particle volume is replaced with its diameter-basis definition. As a result, equation (5.7) reduces to equation (5.10).

$$\varepsilon_b = 1 - \frac{\rho_{b,\text{dry}} (1 + S_b)^3}{\rho_{p,\text{dry}} (1 + S_b)}$$  \hspace{1cm} (5.10)

Density of dry particles ($\rho_{p,\text{dry}}$) was determined using a gas pycnometer (Quantachrome Instruments, USA, model# MVP-D160-E) that is provided in Section 2.1.4.
5.1.7 **Analysis of Variance (ANOVA)**

The drying experiments were done using a full-factorial statistical method. The drying rate constants ($k_d$) were calculated using the Newton equation. To show the significance of the various factors ($T$, $M_0$, $d_{gs}$) on the drying rate constants ($k_d$), the Analysis of Variance (ANOVA) has been conducted using the Minitab software, version 17. The level of significance was set as 0.05. It means when the P-value of a factor is less than 0.05, its effect on the drying rate is significant. Comparing the F-values of all factors ($T$, $M_0$ and $d_{gs}$) shows that which factor had a greater contribution to the drying rate.

5.1.8 **Development of Empirical Correlations**

Two sets of empirical correlations are developed in the current chapter. First set predicts the drying rate constant ($k_d$, 1/min) and moisture diffusion coefficients ($D$, m$^2$/s) using a proposed exponential correlation, equation (5.11).

$$k_d \& D = \exp(aT_f +bM_0+cd_{gs}+d)$$  \hspace{1cm} (5.11)

where $T_f$ (°C) is fluid temperature, $M_0$ (kg water/kg dry material) is initial moisture content and $d_{gs}$ (mm) is grinder screen size. Grinder screen size is used as the particle size representative. The reason is that identifying a single particle size for a ground sample is not reliable and results a high sensitivity to the method that average particle size is obtained. Using the grinder screen size adds more stability and repeatability to the correlation. The second set predicts the shrinkage coefficients of particle and bulk volume, equation (5.12). The shrinkage coefficient followed an exponential trend.
where \( a \) is the fitting constant, SIP (kg water/kg dry material) is the shrinkage intersection point and \( S_{SIP} \) is the shrinkage coefficient of either particle size or bulk volume in SIP. In a drying process, both average particle size and bulk volume were expected to be constant first followed by a decreasing line. By monitoring the variation of average particle size of samples versus the moisture content, SIP was obtained by the intersection of initial plateau and the further decreasing line. In a drying process, SIP was defined as a moisture content that the shrinkage of particles started.

5.2 Results and Discussion

5.2.1 Drying Curves Characterization

The drying process showed three distinct periods (Figure 5.1): a rising rate period, a short constant rate period, and a falling rate period. During the rising rate, the particles warmed up and the drying rate increased to a maximum value. Higher moisture content, larger particle and lower drying temperature prolonged the warming time. In the constant rate period, the surface water evaporated. Part of the free water was expected to evaporate in the warm up period and resulted a short constant rate period. In the falling rate period, drying rate dropped down till the moisture approached zero. Unlike some earlier experiments reported on drying [110, 114], only one falling rate period was observed for ground pine chip and pellet particles with initial moisture contents of up to 0.50.
Figure 5.1 Moisture loss and drying rate of chip particles ($d_p = 3.2, 6.3, 12.7$ and $25.4$ mm; $M_0 = 0.50$; $T_f = 100$ °C).

For the sake of comparison with the literature, drying rate of chip particles was also experimented at initial moisture contents of 0.70 and 0.90, and displayed in Figure 5.2. Falling rate was divided into two distinct periods in moisture contents higher than 0.50. Migration of internal moisture to the particle surface during the first falling rate period occurs through moisture diffusion, capillary flow and internal pressure set up by shrinkage during drying [120]. In second falling rate period, the capillary flow of moisture was ceased and internal moisture diffusion controlled the rate of drying [110, 114, 120].
Critical moisture content \($M_{cr}\) is defined as the moisture content that constant rate period transitions to the falling rate period [120]. Critical moisture ratio \((M_{cr}/M_0)\) at the drying temperatures of 50-150 °C was in the range of 0.65-0.75 and this values was independent of particle size, temperature and initial moisture content. The acquired values agree with the numbers in literature [110, 113, 116, 119]. The critical moisture ratios at 200 °C drying was mostly in the range of 0.50-0.60. It could be explained by the slight degradation of biomass particles at 200 °C that lost their dry mass. Figure 5.3 shows small cracks appeared in the structure of particles that were dried at 200 °C. At 200 °C, smaller particles lost their moisture earlier and lost more of their dry mass (Figure 5.4). As explained in Chapter 2, pellet particles were generally smaller than chip particles and lost more of their dry mass at the temperature of 200 °C.
Figure 5.3 Scanning electron microscopic (SEM) picture of chip particles dried at temperature of 200 °C (red dashed circles show the cracks in structure of the particle).

Figure 5.4 Degradation of ground chip and ground pellet particles (M₀=0.30, Tᵣ=200 °C).

5.2.2 Thin-Layer Drying Models

The fitting analysis showed that the Page and then Newton models were the best-fitted models to the drying experimental data (Figure 5.5). In Page model, the power of $n$ changed
randomly with operating conditions in the range of 1-2 which changed the unit of drying rate constant. For the sake of consistency in unit, Newton model was used. However, drying of pine particles exhibited an initial warming up period followed by a short constant rate period that deviated from the first-order Newton model.

The drying rate constant \(k_d\) changed significantly with the drying temperature. The values of \(k_d\) increased by a factor of 2-3 by each 50 °C temperature increase. Density of a single biomass particle influenced the rate of drying, too (Figure 5.6). Drying rate constants \(k_d\) of chip particles were about twice of the ones for pellet particles in the same operating conditions (Table 5.3). Due to structural differences (explained in Chapters 2 and 3), moisture diffusion coefficients inside the chip particles were also about twice of the values inside the pellet particles, \((1-12.6)\times10^{-10} \text{ (m}^2\text{/s)}\).
versus \((0.5-7.5) \times 10^{-10} \text{ m}^2/\text{s}\), displayed in Figure 5.7. Empirical correlations are also developed to relate \(k_d \text{ (1/min)}\) and \(D \text{ (m}^2/\text{s})\) to operating conditions for both chip and pellet particles.

\[
k_{d,\text{chip}} = \exp[(0.013T_f) - (2.372M_0) - (0.035d_{gs}) - 2.095] \quad (5.13)
\]

\[
k_{d,\text{pellet}} = \exp[(0.012T_f) - (1.278M_0) - (0.034d_{gs}) - 2.533] \quad (5.14)
\]

\[
D_{\text{chip}} = 10^{-10} \exp[(0.013T_f) - (2.342M_0) + (0.077d_{gs}) + 0.671] \quad (5.15)
\]

\[
D_{\text{pellet}} = 10^{-10} \exp[(0.011T_f) - (1.139M_0) + (0.055d_{gs}) - 0.202] \quad (5.16)
\]

where \(T_f \text{ (°C)}\) is drying temperature, \(M_0 \text{ (kg water/kg dry material)}\) is initial moisture content and \(d_{gs} \text{ (mm)}\) is grinder screen size. Figure 5.8 shows the agreement of predicted \(k_d\) and \(D\) with the experimental values. The correlations are developed for the drying temperature range of 50-200 °C, initial moisture contents of 0.10-0.50, grinder screen size of 3.2-25.4 mm. The presented correlations do not reflect the effect of relative humidity of carrying gas and are developed for drying experiments in moisture-free carrying gas.

The analysis of variance (ANOVA) was conducted on the experimental-obtained drying rate constants (Table 5.2). The results reveal that although the effect of drying temperature was greater than other two factors \((M_0 \text{ and } d_{gs})\), the effects of all three parameters are significant. All three \(P\)-values are much less than 0.05 which fall in the significant zone.
Table 5.2 ANOVA table to show the significance of operating parameters on drying rate constant ($k_a$) of chip particles.

<table>
<thead>
<tr>
<th>Source</th>
<th>DF(^1)</th>
<th>Adj. SS</th>
<th>Adj. MS</th>
<th>F-value</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$</td>
<td>2</td>
<td>2.2437</td>
<td>0.74791</td>
<td>47.74</td>
<td>0.000</td>
</tr>
<tr>
<td>$M_0$</td>
<td>2</td>
<td>0.5920</td>
<td>0.29601</td>
<td>18.89</td>
<td>0.000</td>
</tr>
<tr>
<td>$d_{gs}$</td>
<td>3</td>
<td>0.3415</td>
<td>0.11385</td>
<td>7.27</td>
<td>0.001</td>
</tr>
<tr>
<td>Error</td>
<td>28</td>
<td>0.6110</td>
<td>0.01567</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>35</td>
<td>3.7883</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^1\) DF: Degree of Freedom

Figure 5.6 Moisture loss of ground chip and ground pellet particles ($M_0=0.30$; $T_f=50$, 100, 150 and 200 °C; carrying gas=atmospheric air).
Figure 5.7 Effect of initial moisture content and drying temperature on moisture diffusion coefficient (d_p=3.2 mm).

Figure 5.8 Agreement of the predicted drying rate constants and moisture diffusion coefficients with experimental values for ground chip and pellet particles.
Table 5.3 Drying rate constants (k_d, 1/min) for drying of ground chip and ground pellet particles (d_{gs}=3.2 mm) in dry nitrogen, dry air and atmospheric air carrying gases.

<table>
<thead>
<tr>
<th>M_0</th>
<th>Carrying gas</th>
<th>Ground chip particles</th>
<th>Ground pellet particles</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>50 °C</td>
<td>100 °C</td>
</tr>
<tr>
<td>0.1</td>
<td>Nitrogen</td>
<td>0.150</td>
<td>0.363</td>
</tr>
<tr>
<td></td>
<td>Atmospheric Air</td>
<td>0.102</td>
<td>0.364</td>
</tr>
<tr>
<td>0.3</td>
<td>Nitrogen</td>
<td>0.096</td>
<td>0.268</td>
</tr>
<tr>
<td></td>
<td>Atmospheric Air</td>
<td>0.066</td>
<td>0.271</td>
</tr>
<tr>
<td>0.5</td>
<td>Nitrogen</td>
<td>0.070</td>
<td>0.201</td>
</tr>
<tr>
<td></td>
<td>Atmospheric Air</td>
<td>0.053</td>
<td>0.210</td>
</tr>
<tr>
<td></td>
<td>Dry air</td>
<td>0.068</td>
<td>0.210</td>
</tr>
</tbody>
</table>

5.2.3 Drying Time

The drying time is defined as the time when the particles lost 90% of their initial moisture content (MR =0.10). Higher temperature transferred a larger inward heat flux to particle’s surface and accelerated the drying process (Figure 5.9). Larger particles had a lower specific surface area and longer path of moisture diffusion that prolonged the drying process consequently.

Pellet particles needed more time to dry than chip particles with the same size. The moisture diffusion coefficient inside the chip particles were twice of the ones in pellet particles. As around 70% of drying processes took place during falling rate, the pellet particles took more time to dry than chip particles. Drying of similar PSD chip and pellet particles (d_{gs}=3.2 mm) with initial moisture content of 0.50 showed that the pellet particles needed 93%, 56%, 46% and 37% more time to dry than chip particles in the drying temperatures of 50, 100, 150 and 200 °C, respectively. The same trend was also observed for chip and pellet particles ground with 6.3 mm grinder screen, although the pellet particles were smaller than chip particles ground with 6.3 mm screen. For
particles ground with 12.7 mm screen, a meaningful drying time difference between chip and pellet particles was not observed.

Figure 5.9 Drying duration of ground chip and ground pellet particles (d_\text{g}=3.2 \text{ mm}, M_0=0.50).

5.2.4 Effect of Drying Gas

The carrying gas seemed not to have any significant effect on the rate and duration of drying at the temperatures of higher than 100 °C. At 50 °C, the rate of drying in atmospheric air was lower than the rate in dry gas (Table 5.3). Higher relative humidity of atmospheric air (RH of 70±5% versus moisture-free gases) reduced the driving force of moisture evaporation and increased the equilibrium moisture content (Table 5.4). Equilibrium moisture content at temperatures higher than 50 °C was zero. The larger values of the activation energy for drying in atmospheric air compared to moisture-free gases showed that the atmospheric air drying process was more
sensitive to the drying temperature (higher activation energy in Table 5.5). Chip and pellet particles had the same activation energy; however, their pre-exponential factors were different.

Table 5.4 Equilibrium moisture contents of drying tests at 50 °C (M_e at higher temperatures were zero).

<table>
<thead>
<tr>
<th>M_0</th>
<th>Carrying gas</th>
<th>Ground chip particles</th>
<th>Ground pellet particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>Nitrogen</td>
<td>0.001</td>
<td>0.001</td>
</tr>
<tr>
<td></td>
<td>Atmospheric Air</td>
<td>0.003</td>
<td>0.005</td>
</tr>
<tr>
<td>0.3</td>
<td>Nitrogen</td>
<td>0.001</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td>Atmospheric Air</td>
<td>0.009</td>
<td>0.035</td>
</tr>
<tr>
<td>0.5</td>
<td>Nitrogen</td>
<td>0.003</td>
<td>0.005</td>
</tr>
<tr>
<td></td>
<td>Atmospheric Air</td>
<td>0.015</td>
<td>0.040</td>
</tr>
<tr>
<td></td>
<td>Dry air</td>
<td>0.002</td>
<td>-</td>
</tr>
</tbody>
</table>

The temperature at which degradation of particles started reduced by the oxygen content air (Figure 5.10). Start of particle degradation was defined as the time when mass of particle dropped below its dry mass. Particle degradation started at 150 °C with nitrogen gas and at 200 °C with air. Degradation of the particles at 150 °C air stream started slightly after 10 minutes. The level of degradation after 30 minutes was about 1-2% and the SEM micrographs did not show any clear change in the structure of particles dried at 150 °C. Drying at 150 °C nitrogen stream did not degrade the particles, at least after 30 minutes. At 200 °C of both carrying gases, particles started to degrade after 1.5-2.0 minutes. Both chip and pellet particles lost about 7-8% of their dry mass after 30 minutes in either nitrogen or air stream of 200 °C.
Table 5.5 Activation energy ($E$, kJ/mol) and pre-exponential factor ($k_0$, 1/min) of drying tests.

<table>
<thead>
<tr>
<th>$M_0$</th>
<th>Carrying gas</th>
<th>Ground chip particles</th>
<th>Ground pellet particles</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$E$ (kJ/mol)</td>
<td>$k_0$ (1/min)</td>
</tr>
<tr>
<td>0.10</td>
<td>Nitrogen</td>
<td>19.60</td>
<td>216.85</td>
</tr>
<tr>
<td></td>
<td>Atmospheric Air</td>
<td>23.04</td>
<td>576.40</td>
</tr>
<tr>
<td>0.30</td>
<td>Nitrogen</td>
<td>19.80</td>
<td>157.48</td>
</tr>
<tr>
<td></td>
<td>Atmospheric Air</td>
<td>23.17</td>
<td>413.68</td>
</tr>
<tr>
<td>0.50</td>
<td>Nitrogen</td>
<td>18.41</td>
<td>70.76</td>
</tr>
<tr>
<td></td>
<td>Atmospheric Air</td>
<td>20.69</td>
<td>138.05</td>
</tr>
<tr>
<td></td>
<td>Dry air</td>
<td>19.66</td>
<td>106.48</td>
</tr>
</tbody>
</table>

Figure 5.10 Effect of drying temperature on mass loss of ground chip particles ($d_{50}=3.2$ mm; $M_0=0.30$; $T_f=50$, 100, 150 and 200 °C; carrying gas=dry nitrogen (left), atmospheric air (right)).

5.2.5 Volumetric Shrinkage

Figure 5.11 shows the reduction of average particle diameter of the chip and pellet particles as their moisture drops. From $M_0$ of 0.90 down to 0.50, a slight reduction in $d_p$ happened. Below 0.50, the diameter of both chip and pellet particles dropped sharply. It seems that particles were
completely saturated with water at initial moisture content of 0.50 (and higher). The breakthrough point of \( M_0 = 0.50 \) is called “shrinkage intersection point (SIP)” [120]. The data in Figure 5.11 was used to calculate the particle shrinkage coefficient in equation (5.6). The variation of \( d_p \) with moisture content was fitted to a power-law empirical correlation.

\[
d_p = a(M)^b
\]  \hspace{1cm} (5.17)

Figure 5.11 Variation of average particle size of samples as a function of moisture content.

Figure 5.12 shows the total shrinkage in particle size and bulk volume of chip and pellet particles at various initial moisture contents. Initial moisture content of particles influenced the total shrinkage in either single particle size or volume of the bulk. Chip and pellet particles showed a similar amount of particle shrinkage at all initial moisture contents. Shrinkage in particle size increased with initial moisture content and leveled off at an initial moisture content of 0.50.
Shrinkage in bulk volume of the particles comes from two sources: shrinkage in individual particles and reduction in their bulk porosity. The similar trend of increasing bulk volume shrinkage with initial moisture content resulted from the shrinkage in particle size. Similar to particle shrinkage, the reduction in bulk porosity at moisture contents higher than 0.50 was constant. The difference between bulk volume shrinkage of the chip and pellet particles came from their difference in bulk porosity.

Figure 5.13 shows that the bulk porosity of the pellet particles reduced significantly after drying, whereas the bulk porosity of the chip particles decreased slightly. The maximum reduction in bulk porosity was 3% for chip particles and 17% for pellet particles which happened at moisture contents higher than SIP. Different reduction in the bulk porosity of chip and pellet particles despite of similar single particle shrinkage may be explained by their different particle shape and fiber orientation. Chip particles are needle shape and fibers are longitudinal, whereas pellet particles are closer to spherical shape and have a random orientation of fibers. Literature clearly established that shrinkage happens mostly in a direction normal to the microfibril direction [120, 122, 123]. Therefore, shrinkage-induced changes in volume of needle-shape particles happened only on the thickness and length reduction was negligible. On the other hand, the size of more-spherical pellet particles with a random orientation of fibers changed in all directions. In a random packing situation, pellet particles exhibited a larger reduction in their bulk porosity than those of chip particles.

Developed empirical correlation relate the shrinkage coefficients (both particle size and bulk volume) to the initial moisture content ($M_0$, kg water/kg dry material), shrinkage intersection
point (SIP, kg water/kg dry material) and total shrinkage at shrinkage intersection point ($S_{SIP}$).

Table 5.6 lists the statistical results of correlation fittings.

<table>
<thead>
<tr>
<th>Shrinkage coefficient</th>
<th>SIP</th>
<th>Shrinkage @ SIP</th>
<th>a</th>
<th>$R^2$</th>
<th>$\chi^2$</th>
<th>RMSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_{p,chip}$</td>
<td>0.50</td>
<td>0.18</td>
<td>1.96</td>
<td>0.95</td>
<td>3.43E-4</td>
<td>1.85E-2</td>
</tr>
<tr>
<td>$S_{p,pellet}$</td>
<td>0.50</td>
<td>0.18</td>
<td>2.02</td>
<td>0.95</td>
<td>2.86E-4</td>
<td>1.69E-2</td>
</tr>
<tr>
<td>$S_{b,chip}$</td>
<td>0.50</td>
<td>0.40</td>
<td>1.94</td>
<td>0.93</td>
<td>2.32E-3</td>
<td>4.81E-2</td>
</tr>
<tr>
<td>$S_{b,pellet}$</td>
<td>0.50</td>
<td>0.66</td>
<td>2.22</td>
<td>0.93</td>
<td>6.81E-3</td>
<td>8.25E-2</td>
</tr>
</tbody>
</table>

$^{1}$SIP: shrinkage intersection point (kg water/kg dry material)

![Graph showing total shrinkage in bulk volume and particle size of ground chip and ground pellet particles.](image)

Figure 5.12 Total shrinkage in bulk volume and particle size of ground chip and ground pellet particles.
5.2.6 Effect of Shrinkage on Drying Rate

As provided in Section 5.1.4, moisture diffusion coefficient was calculated using the fitting of experimental data in falling rate period with the solution of Fick’s second law. Based on the assumption that the moisture diffusion coefficient does not depend on the moisture content, the first term of solution of Fick’s second law is linearized and reduced to equation (5.18).

\[
\ln(MR) = \ln(A) - \frac{4\pi^2 D}{d_p^2} t
\]  \hspace{1cm} (5.18)

The experimental drying data were analyzed using equation (5.18) to estimate the moisture diffusion coefficient in two cases. Case 1 is when the particle dimension is fixed during drying and case 2 is when particle shrinks and its dimension changes. The independent variable is \( t \) for the
former case and $t/d_p^2$ for the latter case, respectively. The slope of the linearized equation is $-4 \pi^2 D/d_p^2$ for the former case and $-4 \pi^2 D$ for the latter case, respectively.

Table 5.7 lists the estimated parameters of D and A using the data presented in Figure 5.6 and Figure 5.11. The fitting evaluation coefficients ($R^2$, $\chi^2$ and RMSE) are also given in Table 5.7. The values of coefficient A was supposed to be close to unity since MR=1 at the beginning of process (t=0). By knowing this fact and looking at fitting evaluation coefficients ($R^2$, $\chi^2$ and RMSE) shows that the first order drying equation with variable radius fitted the experimental data better that the equation with a fixed radius. The estimated moisture diffusion coefficients for the chip and pellet particles were $7.69-9.09*10^{-11}$ and $3.13-4.59*10^{-11}$, respectively. It confirms that the dense structure of pellet particles reduces the rate of moisture diffusion compared to the chip particles. Moisture diffusivity in case of fixed radius was a little higher than those in case of variable radius. It is concluded that shrinkage during a drying process reduces the moisture diffusion coefficients. The similar conclusion was drawn for drying of agricultural materials by Fusco et al. [155]. No specific trend in D with increasing initial moisture content was detected.
Table 5.7 Estimated diffusion coefficient \( (D, \text{m}^2/\text{s}) \) and constant A.

<table>
<thead>
<tr>
<th></th>
<th>( M_0 )</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.10</td>
<td>0.30</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>Fixed radius</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ground chip particles</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D (m(^2/\text{s}))</td>
<td>1.39E-10</td>
<td>1.87E-10</td>
<td>1.46E-10</td>
</tr>
<tr>
<td>A</td>
<td>1.76</td>
<td>3.92</td>
<td>2.83</td>
</tr>
<tr>
<td>( d_p ) (mm)</td>
<td>0.773</td>
<td>0.853</td>
<td>0.888</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.974</td>
<td>0.961</td>
<td>0.983</td>
</tr>
<tr>
<td>( \chi^2 )</td>
<td>0.018</td>
<td>0.050</td>
<td>0.0150</td>
</tr>
<tr>
<td>RMSE</td>
<td>0.135</td>
<td>0.225</td>
<td>0.123</td>
</tr>
<tr>
<td>Variable radius</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D (m(^2/\text{s}))</td>
<td>8.33E-11</td>
<td>9.09E-11</td>
<td>7.69E-11</td>
</tr>
<tr>
<td>A</td>
<td>1.09</td>
<td>1.06</td>
<td>1.14</td>
</tr>
<tr>
<td>( d_p ) (mm)</td>
<td>0.925(M)(^{0.073})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.989</td>
<td>0.998</td>
<td>0.994</td>
</tr>
<tr>
<td>( \chi^2 )</td>
<td>0.007</td>
<td>0.002</td>
<td>0.004</td>
</tr>
<tr>
<td>RMSE</td>
<td>0.087</td>
<td>0.051</td>
<td>0.070</td>
</tr>
<tr>
<td>Ground pellet particles</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Fixed radius</td>
<td></td>
<td></td>
</tr>
<tr>
<td>D (m(^2/\text{s}))</td>
<td>6.13E-11</td>
<td>7.6E-11</td>
<td>9.21E-11</td>
</tr>
<tr>
<td>A</td>
<td>1.657</td>
<td>1.963</td>
<td>3.950</td>
</tr>
<tr>
<td>( d_p ) (mm)</td>
<td>0.686</td>
<td>0.740</td>
<td>0.777</td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.973</td>
<td>0.973</td>
<td>0.973</td>
</tr>
<tr>
<td>( \chi^2 )</td>
<td>0.033</td>
<td>0.036</td>
<td>0.038</td>
</tr>
<tr>
<td>RMSE</td>
<td>0.181</td>
<td>0.189</td>
<td>0.196</td>
</tr>
<tr>
<td>Variable radius</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D (m(^2/\text{s}))</td>
<td>3.13E-11</td>
<td>4.59E-11</td>
<td>4.47E-11</td>
</tr>
<tr>
<td>A</td>
<td>1.03</td>
<td>1.05</td>
<td>1.17</td>
</tr>
<tr>
<td>( d_p ) (mm)</td>
<td>0.802(M)(^{0.070})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( R^2 )</td>
<td>0.984</td>
<td>0.992</td>
<td>0.999</td>
</tr>
<tr>
<td>( \chi^2 )</td>
<td>0.031</td>
<td>0.007</td>
<td>0.001</td>
</tr>
<tr>
<td>RMSE</td>
<td>0.178</td>
<td>0.084</td>
<td>0.036</td>
</tr>
</tbody>
</table>
5.3 Highlights of Chapter 5

Pellet particles were denser and dried slower than the chip particles. The moisture diffusion coefficient inside the chip particles are about twice of those inside the pellet particles.

Drying process was strongly function of the drying temperature and was significantly prolonged at temperatures of lower than 50 °C.

At drying temperature of 50 °C, higher relative humidity of atmospheric air prolonged the drying duration. At higher temperatures, effect of relative humidity of carrying gas was insignificant and the drying temperature was dominant.

Particle shrinkage of chip and pellet particles was similar, but bulk of the pellet particles shrank significantly more than bulk of the chip particles.

The variable-radius drying model fitted better with experimental data than the fixed-radius model.
Chapter 6: Thin-Layer Pyrolysis of Ground Chip and Ground Pellet Particles

In this chapter, a one-dimensional heat transfer model coupled with a kinetic model was used to predict the overall pyrolysis mass loss of a single wood particle. The kinetic parameters were determined experimentally and a two-zone kinetic mechanism was presented. Developed model was validated with experimental pyrolysis data obtained in a thin layer pyrolyzer. The regime and characteristics of the conversion were evaluated in terms of the particle size and reactor temperature. Empirical correlations were also developed to predict the pyrolysis mass loss of moist ground chip and pellet particles. The specific tasks of the current chapter are presented as follows:

Determine the kinetic parameters for pyrolysis of pine wood particles.

Develop a detailed model to predict the overall mass loss of single wood particles in a constant-temperature pyrolysis process.

Conduct pyrolysis experiments at various particle sizes and operating temperatures to validate the developed model.

Determine the range of particle size valid for intrinsic kinetic model and simplified lumped model.

Develop empirical correlations to predict the pyrolysis mass loss of moist ground chip and pellet particles.
6.1 Material and Methods

6.1.1 Sample Preparation

The received pine chips and commercial pine pellets were dried down to 4-5% moisture content and three sets of samples were prepared. Figure 6.1 shows the preparation procedure of three sets of sample. First set of samples is ground pine chip particles that were sieved using various sieve sizes (0.125, 0.25, 0.5, 0.85, 1, 2 and 5 mm) and was used to validate the model at a specific particle size. Second set of samples is ground pine chip particles and have a wide size distribution. Set 2 of particles were pyrolyzed to evaluate the applicability of the developed model for ground and wide-distributed particles. Third set is moist ground chip and ground pellet particles.

![Figure 6.1 Procedure of preparing three sets of samples.](image-url)
6.1.2 Pyrolysis Experiments

The full description of the designed pyrolyzer and procedure of conducting a pyrolysis experiment are given in Chapter 4. The targeted pyrolysis temperatures were in the range of 300-550 °C. Nitrogen (purity of 99.998%, moisture-free, Praxair Company) was used as the carrying gas to create an oxygen-free environment. Pyrolysis tests were stopped when the mass of sample remained constant. Experiments were done in two replicates to confirm the reproducibility of data.

6.1.3 Model Development

The rate of pyrolysis mass loss strongly depends on the temperature distribution inside the particle. Temperature distribution also depends on instantaneous particle density. Therefore, the kinetic model needs to be solved in conjunction with the heat transfer model. The complexity of the heat transfer model strongly depends on the particle size. In this study, a transient one-dimensional thermal diffusion equation has been solved instantaneously with a proposed kinetic model. To simplify the numerical analysis of wood pyrolysis process, the following assumptions are made:

- Thermophysical properties of wood particles vary with the local temperature. The correlations are taken from published literature and the conducted experiments in this study. The correlations are listed in Table 6.1.
- Particles are assumed spherical with the equivalent diameter of \( d_p \). Heat transfers only in the radial direction.
- Heat transfers from the hot gas to the surface of particles by a combination of heat convection and radiation.
• Structure of wood particles is assumed homogenous. An overall heat conduction inside the particle with an effective thermal conductivity of $K_s$ represents both convection (between the volatiles and the solid in the pores of the particle) and conduction [132, 133, 136].

• Dimensions and shape of particles do not vary during the thermal decomposition. The propagation of pyrolysis fronts starts from the particle surface and move toward the center. The core of the particle is raw wood which shrinks during the process. Therefore, the particle has a constant volume during the process and core raw wood is shrinking. This approach is called “Shrinking Core Model” [128, 130, 133, 136] (Figure 6.2).

• Within the range of used particle size, mass transfer inside the particles is assumed to be fast compared to heat transfer [127-134]. It means that the produced volatiles leave the particle without any interaction and secondary reactions are excluded [25]. The heat transfer and mass loss kinetic control the rate of devolatilization.

Figure 6.2 Schematic picture of shrinking core concept in a pyrolyzing wood particle.
Table 6.1 Thermophysical properties used in the numerical simulation.

<table>
<thead>
<tr>
<th>Property</th>
<th>Temperature range (°C)</th>
<th>Correlation/Value(^1)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrolyzing particle thermal conductivity, (K_s) (W/m.K)</td>
<td>(300 \leq T \leq 550)</td>
<td>(0.13 + 3 \times 10^{-4}T)</td>
<td>[130, 136]</td>
</tr>
<tr>
<td>Pyrolyzing particle heat capacity, (C_{p,s}) (J/kg.K)</td>
<td>(300 \leq T \leq 550)</td>
<td>(1112 + 4.85T)</td>
<td>[130, 136]</td>
</tr>
<tr>
<td>Initial particle density, (\rho_0) (kg/m(^3))</td>
<td>-</td>
<td>500</td>
<td>[17]</td>
</tr>
<tr>
<td>Biochar density ratio, (\rho_e/\rho_0)</td>
<td>(300 \leq T \leq 550)</td>
<td>(80.51T_f^{-0.94})</td>
<td>Experimental correlation (Section 6.2.2)</td>
</tr>
<tr>
<td>Heat of reaction, (q) (J/kg)</td>
<td>(300 \leq T \leq 550)</td>
<td>0</td>
<td>Preliminary model tuning (Section 6.2.2)</td>
</tr>
</tbody>
</table>

Heat transfer parameters

<table>
<thead>
<tr>
<th>Heat transfer coefficient, (h) (W/m(^2).K)</th>
<th>(T \leq 400)</th>
<th>5</th>
<th>[28]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(T &gt; 400)</td>
<td>10</td>
<td>[130]</td>
</tr>
<tr>
<td>Emissivity, (\varepsilon)</td>
<td>(100 \leq T \leq 550)</td>
<td>0.3</td>
<td>Preliminary model tuning (Section 6.2.2)</td>
</tr>
<tr>
<td>Stefan-Boltzmann constant, (\sigma) (W/m(^2).K(^4))</td>
<td>(100 \leq T \leq 550)</td>
<td>(5.67 \times 10^{-8})</td>
<td>[152]</td>
</tr>
</tbody>
</table>

\(^1\) The unit of temperature in the correlations is °C.

6.1.3.1 Pyrolysis Mass Loss Kinetic

The first step in developing a particle model is to derive a kinetics model for the reaction taking place during biomass pyrolysis. When the rate of heat transfer (both internal and external) is fast compared to rate of reaction, the particle temperature is uniform and equal to the hot gas temperature around the particles. In this case, the kinetics control the rate of mass loss. Pyrolysis reaction is represented by an overall single-step reaction in current study, describing by the following scheme.

\(\text{Biomass} \rightarrow \text{Char} + \text{Volatile}\)
This model indicates that raw biomass particles decompose to the char and volatile. The rate of mass loss per unit volume, \(-d\rho/dt\) (kg/m\(^3\).s), is assumed to follow a single step \(n\)th-order kinetics. As the particle shrinkage is neglected in this study and the particle volume is assumed to be constant during the treatment, the unit of mass loss rate is presented by (kg/s). The kinetic equation for the proposed mechanism is presented by equation (6.1).

\[
-r_p = -\frac{d\rho}{dt} = k_p (\rho - \rho_e)^n
\]

(6.1)

where \(\rho\) (kg/m\(^3\)) is instantaneous density of the particle, \(\rho_e\) (kg/m\(^3\)) is the final density of the particle, \(n\) is the order of pyrolysis mass loss. Literature [109, 156, 157] used mostly a first-order for the current reaction scheme. Although, in this study the order of mass loss is determined using the experimental pyrolysis data. \(k_p\) (1/kg\(^{n-1}\).s) is the pyrolysis rate constant. Pyrolysis rate is a strong function of the local temperature and is described by the Arrhenius relationship, equation (6.2).

\[
k_p = k_0 \exp(-E/RT)
\]

(6.2)

where \(k_0\) (1/kg\(^{n-1}\).s) is the pre-exponential factor, \(E\) (J/mol) is the activation energy, \(R\) (J/mol.K) is the universal gas constant and \(T\) (K) is the absolute local temperature.

6.1.3.2 Heat Transfer Model

Balancing energy on a differential control volume inside a spherical particle and applying the listed assumptions and assuming a radial coordinates and single heat transfer direction result a partial differential equation to describe the temperature distribution inside a solid particle, equation
Bird et al. [152] explained the fundamental of differential control volume energy balance in various coordinates.

\[ \rho C_{p,s} \frac{\partial T}{\partial t} = K_s \left( \frac{b}{r} \frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial r^2} \right) + (-q)(-\frac{d\rho}{dt}) \]  

(6.3)

where \( C_{p,s} \) (J/kg.K) is the particle specific heat capacity, \( K_s \) (W/m.K) is the spatially averaged particle thermal conductivity, \( r \) (m) is the radial position starting from particle center. \( b \) is the geometrical factor; equal 0, 1 and 2 for cartesian, cylindrical and spherical coordinates, respectively. \( q \) (J/kg) is the heat of pyrolysis reaction which is locally consumed/produced by pyrolysis reaction. The left-hand side term represents the transient temperature within the particle. The first term on the right-hand side shows the effective heat conduction inside the particle. The particles are assumed as spheres in the current study (\( b=2 \)). The second term on the right-hand side is the heat exchanging in the pyrolysis reaction. Equation (6.3) requires one initial condition and two boundary conditions. The initial condition indicates the particle has an initial uniform temperature of \( T_0 \) and an initial density of \( \rho_0 \), given by equations (6.4) and (6.5).

\[ T(0,r) = T_0 \]  

(6.4)

\[ \rho(0,r) = \rho_0 \]  

(6.5)

Symmetry of temperature profile with respect to the center of particle gives the first boundary condition in equation (6.6) [132, 136, 158].

\[ \frac{\partial T(t,0)}{\partial r} = 0 \]  

(6.6)

The term \( \frac{1}{r}(\partial T/\partial r) \) in equation (6.3) is indeterminate at \( r=0 \) which is physically not possible. This issue is soothed by using L’Hospital’s rule, showing in equation (6.7).
\[ \lim_{r \to 0} \frac{1}{r} \frac{\partial T}{\partial r} = \frac{\partial^2 T(t,0)}{\partial r^2} \]  

(6.7)

Then, the first boundary condition at particle center reduces to equation (6.8).

\[ \rho C_{ps} \frac{\partial T(t,0)}{\partial t} = K_s (b + 1) \frac{\partial^2 T(t,0)}{\partial r^2} + (-q)(-\frac{d\rho}{dt}) \]  

(6.8)

Boundary condition 2 is defined from the assumption that the heat flux to the particle’s surface is a combination of convection and radiation heat transfer, equation (6.9) [132, 133, 136, 158].

\[ K_s \frac{\partial T(t,d_p/2)}{\partial r} = h[T_f - T(t,d_p/2)] + \sigma \varepsilon [T_h^4 - T(t,d_p/2)^4] \]  

(6.9)

where \( T_f \) (K) is the fluid temperature around the particle, \( T_h \) (K) is the temperature of radiant surface, \( h \) (W/m\(^2\).K) is the convective heat transfer coefficient, \( \varepsilon \) is emissivity and \( \sigma \) (W/m\(^2\).K\(^4\)) is Stefan-Boltzmann constant. It is assumed that the temperature of radiant surface is equal to the fluid temperature.

The second boundary condition has a non-linear term of \( T^4 \) which should be linearized. To solve this issue, an overall convective heat transfer coefficient has been defined. The combination of convection and radiation heat transfer to the particle surface is assumed to be equal to an overall convection heat transfer, with an overall heat transfer coefficient of \( H \), showing in equation (6.10).

\[ H(t) = h + \sigma \varepsilon [T(t,d_p/2)^3 + T(t,d_p/2)^2 T_f + T(t,d_p/2) T_f^2 + T_f^3] \]  

(6.10)

The differential equations have been converted to the linear algebraic equations using the pure implicit scheme of finite difference formulations that provide an unconditionally stable solution. This method does not require any restriction on temporal and spatial step sizes. The finite difference formulations of developed models are explained in Appendix B.
6.1.4 Experimental Kinetic Parameters

The first step to determine the kinetic parameters is to calculate the order of mass loss. To determine the order of mass loss, the conversion-basis reaction rate equation is linearized, equation (6.11) [12, 15, 141, 144-149].

\[
\ln\left(\frac{dX}{dt}\right) = \ln(k_p) + n\ln(1 - X)
\]

(6.11)

where \(X\) is the dimensionless conversion ratio and is defined by equation (6.12).

\[
X = \frac{\rho_0 - \rho}{\rho_0 - \rho_e}
\]

(6.12)

Due to constant-volume assumption of particles during the pyrolysis process, the mass of samples was replaced with density in equation (6.12). The mass loss data were smoothed and converted to conversion versus time data. The plot of \(\ln(dX/dt)\) versus \(\ln(1 - X)\) gives a straight line with a slope of \(n\) (order of mass loss).

To conduct the kinetic analysis, the particles should be bone-dried and small enough to be isothermal of the hot pyrolysis environment. The first set of samples that were passed through a 0.125 mm sieve was used to conduct kinetic analysis experiments. The samples were pyrolyzed at 11 different temperatures in the range of 300-550 °C. All experiments were done in constant-temperature operation. The linearized form of kinetic relation was applied for all constant-temperature pyrolysis tests in the temperature range of 300-550 °C. The tests were done twice to confirm the repeatability of results. After obtaining the order of mass loss, the reaction rate constants \((k_p)\) were determined and were fitted to the Arrhenius relation and the activation energy \((E)\) and pre-exponential factor \((k_0)\) were calculated.
6.2 Results and Discussion

6.2.1 Experimental Kinetic Parameters

The order of mass loss for each constant-temperature pyrolysis experiment was determined (Figure 6.3). The reaction had a mass loss order of $n=0.95-1.0$ in the temperature range of 300-350 °C. The value of $n$ dropped significantly to about $n=0.6$ at the pyrolysis temperature of 375 °C and stayed constant at $n=0.50-0.55$ at the pyrolysis temperatures of 400-550 °C.

![Figure 6.3 Order of pyrolysis mass loss at the pyrolysis temperatures of 300-550 °C.](image)

In this research, $n$ represents the combination of all individual thermal reactions and is called the order of overall pyrolysis mass loss. Pyrolysis process includes numerous individual reactions happening in parallel and/or in series. The most important ones are degradation of hemicellulose, cellulose and lignin which have different reactivities at a range of temperature. Individual reactions in the pyrolysis process may have various orders of reaction. Rajeswara Rao and Sharma [159]
showed that the order of reactions in pyrolysis of hemicellulose, cellulose and lignin depend on the process temperature. The order of reaction of hemicellulose, cellulose and lignin changed at 270, 350 and 390 °C, respectively. It seems that the transition temperature of cellulose corresponds to the transition temperature observed in this study. The same results were also observed by Vlaev et al. [12] and Rezaei et al. [160] in a ramped-temperature pyrolysis. It has been observed that the mechanism of mass loss changes at a transition temperature which is specific for each biomass species. This transition temperature was about 350-370 °C for pine wood [160]. Although, Vlaev et al. [12] and Rezaei et al. [160] assumed a first-order mass loss and calculated the activation energy for two regimes of temperatures.

To determine the values of $k_p$ with consistent units, the values of $n$ should have been kept constant. The order of mass loss was taken as $n=1$ in the temperature range of 300-350 °C (zone 1), and $n=0.5$ in the temperature range of 375-550 °C (zone 2). To calculate the activation energy (E) and pre-exponential factors ($k_0$) in both temperature zones, the linearized form of Arrhenius relation was used. Table 6.2 lists the kinetic parameters and governing equations obtained for two temperature zones.

<table>
<thead>
<tr>
<th>Zone #</th>
<th>Temperature range (°C)</th>
<th>$k_0$ (1/kg$^{n-1}$s)</th>
<th>E (kJ/mol)</th>
<th>$n$</th>
<th>$R^2$</th>
<th>Governing equations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zone 1</td>
<td>300 - 350</td>
<td>51.28</td>
<td>48.05</td>
<td>1.0</td>
<td>0.99</td>
<td>$-\ln(1 - X) = k_p \cdot t$</td>
</tr>
<tr>
<td>Zone 2</td>
<td>375 - 550</td>
<td>13.28</td>
<td>27.41</td>
<td>0.5</td>
<td>0.99</td>
<td>$-2(1 - X)^{0.5} = k_p \cdot t$</td>
</tr>
</tbody>
</table>
6.2.2 Tuning Model Parameters

6.2.2.1 Biochar Density ($\rho_e$)

There were a few parameters in the model which needed to be tuned. The physical properties and their dependency on the pyrolysis temperature were taken from the literature, as listed in Table 6.1. The kinetic equation needed the final biochar density ($\rho_e$) to calculate the rate of mass loss in each time step. The final biochar density was determined by the acquired experimental data. In this study, the thermal treatment process was always continued until the steady-state mass was reached; therefore, the final biochar density was practically independent of particle size but varied significantly with the pyrolysis temperature ($T_f$). Figure 6.4 plots the final biochar density ratio versus pyrolysis temperature. The biochar density ratio was correlated with treatment temperature as a power-law relation.

$$\rho_e/\rho_0 = 80.51 T_f^{-0.94}$$

Figure 6.4 Experimental biochar density pyrolyzed at the temperatures of 300-550 °C.
6.2.2.2 Emissivity (ε)

The second parameter to be tuned was emissivity (ε). The value of emissivity depends on the radiant surface, the material that absorbs the radiative energy and how the material sees the radiant surface. In modeling a single particle in literature, the particle mostly was hanged in the middle of a circular furnace that makes the emissivity around 0.95. In this study, the particles were poured as a thin layer in a crucible. Therefore, only half of the particles’ surface was seen by the radiative source. A value of ε = 0.3 is assumed (ε = 0.6-0.7 for fused quartz).

6.2.2.3 Equivalent Particle Diameter (d_p)

The particles are assumed spherical, so an equivalent particle diameter (d_p) was identified for each sample. Particles obtained from set 1 were fractionated narrowly, then the opening size of sieves are assumed to be equal to d_p. Particles obtained from sets 2 and 3 have a wide size distribution and grinder screen opening size (d_{gs}) is not representative of particle size. To solve this, image processing was conducted to measure the actual dimensions of the particles and identify a d_p. Theoretically, the thickness of a particle is the shortest dimension and controls the rate of heat transfer. In picturing a particle using the microscope, the particle rests on the surface in a way that measuring its thickness was not practical. Their width and length were only measured. In this study, width was used as the representative of d_p. However, using width instead of particle thickness would be a source of uncertainty.
6.2.2.4 Heat of Reaction (q)

Another parameter to tune was the heat of reaction. Because of the difficulty of measuring and simplicity of calculations, it is usually considered as an adjustable parameter [138]. The values in the range of +100 to -250 kJ/kg has been used commonly in the literature [128, 129, 136]. Some published literature also showed that the effect of heat of reaction on the predicted mass loss is quite negligible compared to the convection and radiation heat sources [132, 133, 156, 161]. Pyle et al. [133] examined the effect of heat of reaction in the range of 0 to -210 kJ/kg and suggested that the effective enthalpy of reaction could be zero in the model. The preliminary modeling results in this study (Figure 6.5 and Figure 6.6) showed that the effect of heat of reaction on the temperature distribution inside the particle and the overall mass loss is quite negligible. Therefore, the heat of pyrolysis reaction is taken zero. It seems that the heat transfer on the particle boundary is fast enough to give the required heat or take the released heat.

By substituting \( q = 0 \), the heat transfer model is divided into two zones: 1) when the local temperature of the particle is less than the pyrolysis temperature \( (T(t,r) < T_f) \), and 2) when the local temperature of the particle is equal to the pyrolysis temperature \( T(t,r) = T_f \). In the first zone, the heat that transfers to the particle through convection and radiation mechanisms warms up the particle to the pyrolysis temperature. Energy balance determines the local temperature as a function of time and radius which affect the instantaneous rate of reaction, particle density and the thermophysical properties of particles. In the second zone, the temperature of the particle is maintained constant and the heat transfer model will be de-coupled from the kinetic model and a pure kinetic equation determines the mass loss.
Figure 6.5 Effect of heat of reaction on temperature distribution of a 1-mm particle pyrolyzing at 500 °C.
6.2.3 Model Validation

Figure 6.7 displays the experimental and model-fitted mass loss of ground pine chip particles. The numerical solution agreed well with the experimental mass loss. Larger particles had an internal heat transfer limitation and an initial thermal lag was observed. The model fitted the mass of smaller particles better than large particles. It may be due to various reasons; such as the representative particle diameter used in the model and/or the physical property correlations that may not predict the properties of a particle during the whole pyrolysis process accurately. The ground particles are a mixture of various particle sizes and defining a unique particle diameter representing the whole mixture is challenging. However, the overall agreement of the model with the data over a wide range of particle sizes was acceptable.

Figure 6.8 shows that the variable order of the mass loss kinetics model helped to predict the overall mass loss accurately. The model captured the initial lag in low temperatures. Figure 6.9
shows the conversion time of particles passing through a 0.125 mm sieve ($d_p=0.125$ mm) and ground particles ($d_{gs}=3.2$ mm) at different pyrolysis temperatures. Conversion time is the time that particles took to reach the conversion ratio of $X=0.9$. The predicted conversion time of the numerical model was also plotted and it showed a good agreement with the experimental conversion duration data. The conversion time reduced drastically when the pyrolysis temperature changed from 300 °C to 375 °C. The conversion time reduced with a smoother slope at pyrolysis temperatures higher than 375 °C. The results show that the rate of mass loss in the temperature range of 300-350 °C is more sensitive to the pyrolysis temperature than in the range of 400-550 °C. The higher activation energy in zone 1 also confirms this observation.

Figure 6.7 Effect of particle size on pyrolysis mass loss of ground particles ($T_f=500$ °C).
Figure 6.8 Effect of temperature on pyrolysis mass loss of ground chip particles ($d_{gs}=3.2$ mm, $T_f=300$-$550$ °C).

Figure 6.9 Effect of pyrolysis temperature and particle size on conversion time (when $X=0.9$; $d_p=0.125$ mm, $d_{gs}=3.2$ mm; $T_f=300$-$550$ °C).
6.2.3.1 Critical Particle Sizes Free of Internal Heat Transfer Limitation

It has always been important to define the range of particle sizes free of internal heat transfer limitations. In this range, the decomposition rate is only controlled by the kinetics of mass loss. To determine the range of particles free of internal heat transfer limitation, the conversion time approach has been used. Conversion time was defined as the time that \( X = 0.9 \). The first set of prepared samples was pyrolyzed at a temperature of 500 °C. Figure 6.10 shows the experimental and predicted values of conversion time versus the inverse of particle diameter. The variation of conversion time in the particle size range of 0.125-0.5 mm was insignificant. The conversion time suddenly increased for particles larger than 0.5 mm. It seems that the pyrolysis of particles smaller than 0.5 mm was controlled by reaction kinetics, while the pyrolysis of particles larger than 0.5 mm was limited by the internal heat transfer. The developed model captured the conversion time of particles properly.

![Figure 6.10 Evolution of conversion time versus inverse of particle size (d_p=0.125-5 mm; T_f=500 °C).](image)
6.2.3.2 Particle Size Region of Lumped Approach

When the rate of internal heat transfer is fast compared to the external heat transfer, it is safe to assume a negligible temperature gradient inside the particle, and the particle may be presented by a uniform temperature that changes with time. The process is controlled by the external heat transfer and the mass loss kinetic. Lumped approach facilitates the formulation of the process, as the control volume is the whole particle, $T(t)$ and $\rho(t)$, and needs less time and effort to solve the mathematical model at the particle level. In the case of pure convection boundary condition, Biot number ($Bi = h d_p / K_s$) analysis evaluates the lumped particle size zone. When the boundary condition is the combination of convection and radiation, $Bi$ is calculated by the overall heat transfer coefficient, $H$. Although it has been found in the current study that this approach is not applicable, too. According to equation (6.10), the value of $H$ depended on the surface temperature which changed with time (re-calculated in each time step). Therefore, the value of $Bi$ changed with time and there was not a single $Bi$ representing the whole system.

In this study, the direct output of temperature distribution inside the particle was used to identify the lumped zone. Particle density was decreased during the pyrolysis and the heat transfer was facilitated. To be on the safe side, the decomposition rate was excluded and the original density of wood particle remained constant in this analysis. Figure 6.11 shows the theoretical temperatures of particle surface ($T_s$) and particle center ($T_c$) at the fluid temperatures of $T_f = 100-500$ °C for a 10-mm particle. Higher fluid temperature elevates the particles surface temperature faster than lower fluid temperature, and a sharper temperature gradient inside the particle was observed in higher fluid temperature, specifically in the early times of the process.
Figure 6.11 Theoretical temperature profile at center ($T_c$) and surface ($T_s$) of a particle ($d_p=10$ mm, $T_f=100-500$ °C).

Figure 6.12 Theoretical temperature difference inside the particles ($T_s-T_c$) ($d_p=0.25-10$ mm, $T_f=500$ °C).
Figure 6.12 shows the temperature difference from the particle surface to its center \((T_s - T_c)\) for a wide particle size range of 0.25-10 mm and environment temperature of 500 °C. The magnified part of the graph in Figure 6.12 shows that the temperature difference for the small particles (<0.5 mm) was quite negligible. Figure 6.13 shows the maximum temperature difference inside the particles (peaks is Figure 6.12) versus the particle size. To be on the safe side, the acceptable maximum temperature difference from the particle surface to its center was taken as 2% of the whole expected temperature elevation. It means that the acceptable maximum temperature difference inside the particles are 1.5, 3.5, 5.5, 7.5 and 9.5 °C at the treatment temperatures of 100, 200, 300, 400 and 500 °C, respectively. The black dots in Figure 6.13 show \(0.02(T_f - T_0)\) which made the critical line. The particle sizes below the critical line in Figure 6.13 have quite a negligible internal temperature gradient.

![Image](image.png)

**Figure 6.13** Theoretical maximum temperature difference from surface to center of the particle.
6.2.4 Effect of Particle Density - Chip Particles vs. Pellet Particles

Experimental results in Figure 6.14 showed that a higher density of pellet particles caused an initial lag in pyrolysis mass loss. At pyrolysis temperatures of <350 °C, it seems that the total pyrolysis mass loss of pellet particles is slightly less than total pyrolysis mass loss of chip particles (~5%). At temperatures of >400 °C, pellet particles showed an initial lag in mass loss and reached a similar mass loss of chip particles. Despite of drying that structure of particles does not change, the structure of particles undergoing a pyrolysis process decomposes significantly and the difference in initial density of particles is negligible.

![Figure 6.14 Experimental mass loss of dry ground chip and ground pellet particles (d_p=3.2 mm; T_f=300-550 °C).](image)

6.2.5 Pyrolysis of Moist Particles

The ground chip and ground pellet particles were moistened (sample set 3) and pyrolyzed at the fluid temperatures of 300, 400 and 500 °C. Figure 6.15 and Figure 6.16 show the experimental
pyrolysis mass loss (and mass loss rate) of the moist ground chip and pellet particles (sample set 3) with initial moisture contents of 0.10, 0.30 and 0.50 at 500 °C.Unlike the reported slow pyrolysis results in the literature, no constant mass was observed after the drying stage. Due to the sudden exposure of moist particles to the hot environment, the drying and pyrolysis happened simultaneously and two zones of drying and pyrolysis were not distinctly identifiable. Figure 6.16 shows that the rate of drying of pellet particles was much lower than the drying rate of chip particles. In pyrolysis stage, the decomposition of particle structure caused that there was not a significant difference in rate of pyrolysis and temperature played the main role. A similar behavior in drying and pyrolysis of dry pine particles was observed in the previous Chapters 3 and 4.

Figure 6.15 Pyrolysis mass loss of moist ground chip and moist ground pellet particles (dₚ=3.2 mm; Mₒ= 0.10, 0.30 and 0.50; Tᵣ=500 °C).
The overlap of the drying and pyrolysis stages and the lack of reliable physical properties and drying kinetics at high temperatures made the rigorous modeling of this process challenging. A large number of assumptions were used in the literature to facilitate the development of the model for the pyrolysis of moist particles [162-165]. In this study, empirical correlations have been developed to relate the mass loss rate constants of drying and pyrolysis zones \((k_d \text{ and } k_p, \text{1/min})\) to pyrolysis temperature \((T_f, ^\circ \text{C})\), initial moisture content \((M_0, \text{kg water/kg dry material})\) and grinder screen size \((d_{gs}, \text{mm})\). The overall mass loss in pyrolysis of moist particles was divided into two hypothetical zones of drying and pyrolysis. Each zone was assumed to show a first order \((n=1)\) mass loss. Therefore, the overall mass loss curve of each sample was modeled using two
constants, a drying rate constant \((k_d)\) and a pyrolysis rate constant \((k_p)\). The correlations are developed for both moist ground chip and moist ground pellet particles. The functionality of both drying and pyrolysis constants to fluid temperature, initial moisture content and grinder screen size followed an exponential form, equation (6.13).

\[ k_d & k_p = \exp(aT_f + bM_0 + cd_{gs} + d) \]  

\( \text{(6.13)} \)

Table 6.3 lists the parameters of the equation (6.13) and the statistical results for drying and pyrolysis zones of both ground chip and ground pellet particles. Figure 6.17 shows the deviation of predicted \(k_d\) and \(k_p\) from experimental values. It shows that the empirical correlations had an acceptable agreement with the experiments.

<table>
<thead>
<tr>
<th>Material</th>
<th>Drying zone, ( k_d )</th>
<th>Pyrolysis zone, ( k_p )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Constants</td>
<td>( R^2 )</td>
</tr>
<tr>
<td>Ground chip particles</td>
<td>a = 0.005</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>b = 1.040</td>
<td></td>
</tr>
<tr>
<td></td>
<td>c = -0.030</td>
<td></td>
</tr>
<tr>
<td></td>
<td>d = -3.599</td>
<td></td>
</tr>
<tr>
<td>Ground pellet particles</td>
<td>a = 0.005</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>b = 1.801</td>
<td></td>
</tr>
<tr>
<td></td>
<td>c = -0.013</td>
<td></td>
</tr>
<tr>
<td></td>
<td>d = -4.233</td>
<td></td>
</tr>
</tbody>
</table>
Figure 6.17 Agreement of drying and pyrolysis constants between empirical correlations and experimental values in pyrolysis of moist particles.

The experimental results of this part were numerically analyzed using the analysis of variance (ANOVA), explained in Section 5.1.7. The output of statistical analysis in ANOVA table, Table 6.4 and Table 6.5, reveals that the effects of all factors in the drying stage were significant, although the effect of temperature was greater. In drying stage, all three P-values are much lower than 0.05 which fall in the significant zone. In pyrolysis stage, the effect of temperature was quite significant and dominant. The P-values of $M_0$ and $d_g$ are larger than 0.05 which shows their influence on the rate of pyrolysis mass loss is insignificant.
Table 6.4 ANOVA table to show the significance of operating parameters on drying rate constant ($k_d$) of chip particles.

<table>
<thead>
<tr>
<th>Source</th>
<th>DF(^1)</th>
<th>Adj. SS</th>
<th>Adj. MS</th>
<th>F-value</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>2</td>
<td>0.27008</td>
<td>0.135042</td>
<td>106.37</td>
<td>0.000</td>
</tr>
<tr>
<td>M(_0)</td>
<td>2</td>
<td>0.06733</td>
<td>0.033663</td>
<td>26.51</td>
<td>0.000</td>
</tr>
<tr>
<td>d(_gs)</td>
<td>3</td>
<td>0.08846</td>
<td>0.029488</td>
<td>23.23</td>
<td>0.000</td>
</tr>
<tr>
<td>Error</td>
<td>28</td>
<td>0.03555</td>
<td>0.001270</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>35</td>
<td>0.46142</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^1\)DF: Degree of Freedom

Table 6.5 ANOVA table to show the significance of operating parameters on pyrolysis rate constant ($k_p$) of chip particles.

<table>
<thead>
<tr>
<th>Source</th>
<th>DF(^1)</th>
<th>Adj. SS</th>
<th>Adj. MS</th>
<th>F-value</th>
<th>P-value</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>2</td>
<td>7.06723</td>
<td>3.53362</td>
<td>649.74</td>
<td>0.000</td>
</tr>
<tr>
<td>M(_0)</td>
<td>2</td>
<td>0.01680</td>
<td>0.00840</td>
<td>1.54</td>
<td>0.231</td>
</tr>
<tr>
<td>d(_gs)</td>
<td>3</td>
<td>0.01199</td>
<td>0.00400</td>
<td>0.74</td>
<td>0.540</td>
</tr>
<tr>
<td>Error</td>
<td>28</td>
<td>0.15228</td>
<td>0.00544</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>35</td>
<td>7.24830</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^1\)DF: Degree of Freedom
6.3 Highlights of Chapter 6

Particles smaller than 0.5 mm do not have significant internal heat transfer limitation.

A two-zone kinetic model fitted better with the experimental data. The order of mass loss and kinetic parameters switched at the pyrolysis temperature of 350 °C.

The developed model predicts the overall mass loss accurately. The model captures the initial warm-up period of particles well.

Image processing of particles helped to identify the characteristic length of particles.

The maximum particle size valid for lumped formulation depends on operating temperature, 0.9-1.0 mm at 100 °C and 0.6-0.7 mm at 500 °C.

Pellet particles have a small initial delay in their mass loss compared with chip particles. A harsh thermal treatment (pyrolysis temperatures of >400 °C) minimizes the effect of initial particle density.
Chapter 7: Conclusions and Recommendations

7.1 Conclusions

Wood chip and wood pellet as two woody feedstocks in the market are available to replace coal and/or feed the biomass conversion plants (e.g. pyrolysis, gasification and combustion). In this thesis, ground chip and ground pellet particles of pine wood were investigated with respect to their size, shape, density, energy input for size reduction, flow properties, the rate of drying and further pyrolysis. The new data generated in this investigation leads to an improved understanding about handling and transporting of particles in thermochemical and biochemical conversion plants. The unique knowledge gained from this research increases the operational efficiency and reduces the probability of stoppage in feeding systems; thus, contributes to a reduction in the cost of conversion products (chemicals, biofuels, heat and power). Another contribution of this study is designing a thin-layer constant-temperature thermogravimetric analyzer. The designed apparatus produces reliable experimental data that can be used in further single particle modeling. The developed pyrolysis model contributes to an improved prediction of conversion rates as a function of particle size and temperature. Major findings of this thesis are summarized below.

Wood pellet consumed significantly less grinding energy than wood chips. To produce the similar PSD that is desirable for thermal conversion (<1 mm), wood chips took about 7 times more energy to be ground than wood pellets did. No matter what grinder screen was used (in the range of 3.2-25.4 mm), more than 90% of pellet particles passed through a 2-mm sieve that makes the ground pellet appropriate for thermal conversion processes. Pellet particles were smaller, denser and had a narrower PSD than ground chip particles. Wood chips should be ground with grinder screens of <6 mm to produce an appropriate PSD for thermal conversion. However, chip particles
ground with screens of <6 mm seems to have flow issues. Pellet particles produced with all screens were in the range of good flowability based on Hausner ratio and Carr-compressibility index.

Pelletization reduced the variability in size distribution, particle shape and flow properties of ground particles. Pellet particles were more spherical shape and had the aspect ratios (W/L) of about 3 times of needle-shape chip particles. Shape of the chip particles caused higher bulk compressibility. The analysis of flow properties showed that pellet particles are less cohesive and flow easier than chip particles. Small ground chip particles may cause flow issues in a bulk of the particles. Flow characterization showed that the effect of particle shape (geometry) on flow properties of particles is more than the particle size.

A critical moisture ratio of 0.70 showed that 70% of moisture, in both chip and pellet particles, evaporates by the moisture diffusion mechanism. Denser structure and random orientation of fibers in pellet particles reduced the rate of moisture diffusion. Moisture diffusion coefficient inside the chip particles were up to twice of the moisture diffusivity inside the pellet particles. That is why the chip particles dried faster than pellet particles.

Drying medium (nitrogen or air) influence two aspects of drying process. First, at temperatures higher than 100 °C, the temperature was a dominant parameter and the drying gas did not influence the diffusion coefficient and rate of drying. At 50 °C, the higher relative humidity of atmospheric air reduced the drying rate and consequently prolonged the drying process significantly. Second, particle degradation started at 200 °C in a nitrogen environment and at 150 °C in an air environment. Degradation started after 10 minutes at 150 °C and after 2-2.5 minutes at 200 °C. The particles lost about 3%-7% of their dry mass at 200 °C.

Both chip and pellet particles showed a similar level of shrinkage in size of single particles. Unlikely, the bulk of pellet particles shrank more than the bulk of chip particles. Due to the
spherical shape of pellet particles, they shrank in all directions, whereas chip particles shrank only in their thickness. Pellet particles exhibited a larger reduction in bulk porosity than the chip particles. The volumetric shrinkage increased with moisture content and leveled off at a moisture content of 0.50. It seems that particles were saturated at moisture content of 0.5 (and higher).

A mathematical model was developed to predict the overall pyrolysis mass loss of a single wood particle. The developed model used a two-stage kinetics that predicted the effect of pyrolysis temperature and particle size with a good agreement with acquired experimental data. The transition temperature in the kinetic model was at the temperature of around 350 °C. The width of particles as a representative of particle size fitted the experimental data best. Particles smaller than 0.5 mm did not exhibit an internal heat transfer limitation within the range of these drying and pyrolysis conditions. Due to combined and transient boundary conditions, application of Biot number could not be applied because the boundary conditions included radiation heat transfer. A lumped assumption for small particles was justified based on observing the transient one-dimensional solutions to heat conduction equations. The critical particle size for assuming lump heat transfer was 0.6-0.7 mm at the fluid temperature of 500 °C and 0.9-1.0 mm at the fluid temperature of 100 °C.
7.2 Recommendations

A summary of recommendations is listed below.

The main goal of designing and building the thin layer dryer/pyrolyzer in this research was to measure the mass of particles continuously in a wide operating temperature range. The amount of used material for each test was adequate for the kinetic study purposes. However, the reactor configurations and the amount of pyrolyzed material was not enough to collect a reliable amount of pyrolysis bio-oil. It is recommended to design and construct a larger reactor to be able to collect and condense the produced volatiles. For this purpose, designing a volatile collection kit is suggested.

It is also recommended to characterize the pyrolysis by-product in terms of their physical properties. The composition of permanent gases which are flammable helps to conduct a reliable energy balance for the whole system. The adsorption capability of produced biochar is addressed in the literature. The biochar samples were collected in this research, but are not characterized. It is recommended to characterize the biochar in terms of its adsorption properties and feasibility of biochar upgrading to increase its adsorption capacity.

Flow properties of ground particles are determined using the angle of repose and compressibility methods in this research. The mentioned methods are static analyses which are strong enough for comparing the flowability of various samples. However, it is highly recommended to design a series of dynamic experiments using other techniques. The complimentary experiments may consist of 1) pressure drop in a bed of particles, 2) fluidization properties of particles, 3) pneumatic transportation of particles in pipe lines, and 4) shear analysis to measure the cohesion among the particles in a moving bulk.
References


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Appendices

Appendix A - Commercial Pellet versus BBRG-made Pellet

Commercial pine chips and pellets were used in all parts of this project. In addition, the ground chip particles were pelletized and a set of flowability experiments were conducted on the prepared pellets. The results were compared with the commercial pine pellet particles. The pine pellets were produced in Pellet Laboratory of Biomass and Bioenergy Research Group (BBRG) at the University of British Columbia. To produce pellet, the dried pine chips were ground in a hammer mill installed with a 3.2 mm grinder screen. The ground particles were moistened to around 12%. No additives or chemicals were added to the particles. The prepared particles were pelletized in a CPM pellet mill (California Pellet Mill, USA; Model: CL-3 3HP). Thereafter, the produced pine pellets were ground using the same hammer mill installed with the grinder screen size of 3.2 mm.

Table A.1 lists the flow properties of ground particles coming from commercial pine pellet and BBRG-produced pine pellet. Ground commercial pellet have better flowability; however, the same ground chip particles were pelletized in both sources of pellet. The compressibility and angle of repose of BBRG pellet particles were higher than those of commercial pellet particles. It must be due to the different level of compression to produce commercial pellet and to produce pellet in the laboratory-scale CPM pellet mill. Lower loose and tapped bulk density of BBRG pellet particles confirm that the BBRG pellet particles were less compressed than the commercial ones.
Table A.1 Flow properties of ground commercial pellet particles and ground BBRG pellet particles (dₕ=3.2 mm) (mean ± standard error).

<table>
<thead>
<tr>
<th>Material</th>
<th>Loose bulk density (g/cm³)</th>
<th>Tapped bulk density (g/cm³)</th>
<th>HR</th>
<th>CCI (%)</th>
<th>AOR (degree)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground pellet particles (commercial)</td>
<td>0.39 ± 0.00</td>
<td>0.49 ± 0.01</td>
<td>1.27 ± 0.03</td>
<td>20.98 ± 1.97</td>
<td>48.0 ± 0.7</td>
</tr>
<tr>
<td>Ground pellet particles (BBRG-produced)</td>
<td>0.32 ± 0.00</td>
<td>0.42 ± 0.00</td>
<td>1.30 ± 0.03</td>
<td>21.81 ± 1.8</td>
<td>50.1 ± 0.2</td>
</tr>
</tbody>
</table>
Appendix B - Finite Difference Formulation of Heat Transfer Model

The differential energy balance equation, equation (6.3), along with the initial and boundary conditions, equations (6.4), (6.7) and (6.8), are converted to the linear algebraic equations using the pure implicit scheme of finite difference formulations. The pure implicit scheme is an unconditionally stable method. There is no restriction on time and radius step sizes. The final finite difference form of equations (6.3) is shown in equation (B.1).

\[ T_i^j = -Fo(1 - \frac{b}{2i})T_{i-1}^{j+1} + (1 + 2Fo)T_i^{j+1} - Fo(1 + \frac{b}{2i})T_{i+1}^{j+1} - \alpha dt(-q)(-\frac{d\rho}{dt}) \]  

(B.1)

where \( i \) is the numerator in radius direction and \( j \) is the numerator in time direction. \( \alpha \) and \( Fo \) are thermal diffusivity and Fourier number, respectively, and defined in equations (B.2) and (B.3).

\[ \alpha = \frac{K_s}{\rho C_{p,s}} \]  

(B.2)

\[ Fo = \frac{\alpha dt}{dr^2} \]  

(B.3)

where \( dt \) and \( dr \) are the time and radius step sizes, respectively. The finite difference form of first boundary condition is shown in equation (B.4).

\[ T_i^j = (1 + 2Fo(1 + b))T_i^{j+1} - 2Fo(1 + b)T_{i+1}^{j+1} - \alpha dt(-q)(-\frac{d\rho}{dt}) \]  

(B.4)

where \( i = 1 \) is the node in the particle center. The finite difference form of the second boundary condition is given by equation (B.5).

\[ T_m^j = (-2Fo)T_{m-1}^{j+1} + (1 + 2Fo(1 + Bi(1 + \frac{b}{2m})))T_{m}^{j+1} - 2Bi.Fo(1 + \frac{b}{2m})T_i - \alpha dt(-q)(-\frac{d\rho}{dt}) \]  

(B.5)

where \( m \) is the number of nodes in radius and \( i = m \) shows the node on the particle surface. \( Bi \) is the Biot number that is defined in equation (B.6).

\[ Bi = H.dr/K_s \]  

(B.6)