

Spatial Variability of Chemical Element, Ash Content, and Calorific Value of Black Spruce (*Picea mariana*) from Labrador

by

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Abstract

Woody biomass residues from lumber production are an important renewable energy source, but their fuel quality depends on chemical composition and spatial variation. This study analyzed black spruce (*Picea mariana*) residues from Labrador to assess gross calorific value, carbon, hydrogen, and ash content. 14 trees provided 52 samples with triplicate tests. Variability was examined using fixed- and mixed-effects models, with paired t-tests and regression analyses applied to radial contrasts.

Results showed that radial effects were most consistent: inner wood averaged $\sim 0.3 \text{ MJ} \cdot \text{kg}^{-1}$ higher GCV, while outer wood contained $\sim 11\%$ more ash. Carbon decreased by $\sim 1.4\%$ from bottom to top, hydrogen remained stable (6.09–6.19%), and ash was $\sim 13\%$ higher in the top sections. Regression models explained little of the GCV variance ($R^2 < 0.1$). These findings indicate that elemental composition alone cannot fully predict energy potential but provide baseline data for evaluating lumber residues as solid biofuels in boreal forests.

Keywords: Black Spruce, Calorific value, Carbon Amount, Ash Content, Spatial Variability, Mixed-effect model, Labrador

Dedication

To my family, for their endless support and sacrifices, and to everyone who inspired my passion for forestry and research. This work is as much theirs as it is mine.

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List of Symbols, Nomenclature, or Abbreviation

ANOVA	Analysis of Variance
BTU/lb	British Thermal Unit per pound (1 BTU/lb= 2.326 MJ·kg ⁻¹)
CHS	Carbon, Hydrogen, and Sulfur
CI	Confidence Interval
CoV	Coefficient of Variation
CRM	Certified Reference Material
df	Degrees of Freedom
FEM	Fixed Effects Model
GCV	Gross Calorific Value
MC	Moisture Content
MEM	Mixed Effects Model
MJ/kg	Megajoules per Kilogram
MFA	Microfibril Angle
MLR	Multiple Linear Regression
NCV	Net Calorific Value
ppm	Parts per Million

R^2	Coefficient of Determination
R	Pearson Correlation Coefficient
SD	Standard Deviation
SG	Specific Gravity
SO ₂	Sulfur Dioxide
WSTC	Wood Science and Technology Centre

1 Introduction

1.1 Background

With the growing urgency to transition toward sustainable and carbon-neutral energy systems, biomass has emerged as a promising renewable energy source. Among biomass feedstocks, woody materials are considered highly attractive due to their relatively high energy density, low sulfur content, and wide availability in boreal and temperate regions (Pandey & Erbaugh, 2024). In particular, solid biofuels from forest residues and stemwood offer a viable route for replacing fossil fuels in decentralized heating and power generation systems, especially in rural or remote areas (IPCC, 2023).

The combustion performance of wood biomass depends on its intrinsic chemical and physical properties. Parameters such as carbon (C), hydrogen (H), oxygen (O) content, sulfur (S), ash content, and heating value are key indicators of fuel quality (Lamlom & Savidge, 2003; Obernberger & Thek, 2004). Carbon, hydrogen and oxygen contribute directly to energy yield, while sulfur affects emission profiles. Ash content, comprising inorganic minerals, influences not only the net energy output but also fouling, slagging, and handling characteristics (Maj et al., 2025; Werkelin et al., 2005). To standardize these measurements, international norms such as ISO 16948:2015 (C, H, N determination), ISO 18122:2022 (ash content), and ISO 18125:2017 (calorific value) are commonly applied in laboratory evaluations of biomass fuels.

1.2 Organization of the Report

This report is organized into five chapters, followed by references and curriculum vitae.

- Chapter 1 outlines the research background of this thesis work and the organization of this thesis report.
- Chapter 2 summarizes previous studies relevant to this research. It discusses wood biomass and its energy potential, properties affecting fuel quality, radial and vertical variations in wood, and the effects of CHS and ash content on calorific value. It also reviews statistical methods commonly used in biomass property evaluation, and concludes with the problem statement and research objectives.
- Chapter 3 details the sample design and preparation, experimental procedures for CHS, ash content, and calorific value determination, as well as the statistical approaches applied in the analysis.
- Chapter 4 presents the findings of the study. It begins with descriptive statistics and exploratory visualizations, then examines spatial variations in wood properties through fixed and mixed effects models. Supplementary analyses of bottom-only samples are followed by correlation and regression analysis for calorific value. Intra-tree variation in selected trees is then illustrated, and the chapter ends with an integrated discussion.
- Chapter 5 summarizes the major findings, highlights implications for biomass energy assessment, and provides suggestions for future research.

- The Bibliography lists all referenced works, and the Curriculum Vitae presents the academic background of the author.

2 Literature Review

2.1 Wood Biomass and Its Energy Potential

Forest-based biomass has become a central component of renewable energy portfolios aimed at mitigating climate change. According to the Intergovernmental Panel on Climate Change (IPCC, 2023), bioenergy derived from forest resources is vital for decarbonizing heating systems and supporting rural energy security, particularly in countries with extensive forest cover. The growing emphasis on circular economies and sustainable land use has further elevated the role of woody biomass as a low-carbon energy alternative.

Compared to herbaceous and agricultural biomass, woody biomass, especially from softwood species such as spruce and pine, offers several combustion-related advantages. These include high energy density, relatively low moisture and sulfur content, and lower ash yields, which contribute to improved thermal efficiency and reduced emissions (Obernberger & Thek, 2004; Werkelin et al., 2005). The gross calorific value (GCV) of coniferous wood typically ranges between 18 and 21 MJ/kg, depending on species, site conditions, and tissue type. These favorable properties make wood a preferred feedstock for densified fuels such as pellets and briquettes.

In the context of Canadian boreal forests, black spruce (*Picea mariana*) is one of the most widespread and economically significant softwood species. It stands as a common and valuable species across Newfoundland and Labrador, thriving particularly in wetland and nutrient-poor land (Sturtevant et al., 1996). The spread of black spruce extends to Northwestern Canada and goes as far as the northern tree line as Figure 2.1 shows. It dominates large tracts of forestland across Newfoundland and Labrador, contributing to

timber, pulp, and increasingly, biomass energy sectors. Despite its potential, relatively few studies have systematically evaluated the chemical element and energy properties of black spruce biomass, particularly in terms of spatial variation across and within trees. As Martin et al. (2018) emphasized, variation in traits such as carbon and ash content can significantly influence fuel quality, underscoring the importance of fine-scale analyses. The limited availability of such data poses challenges for accurate fuel classification and optimal utilization.

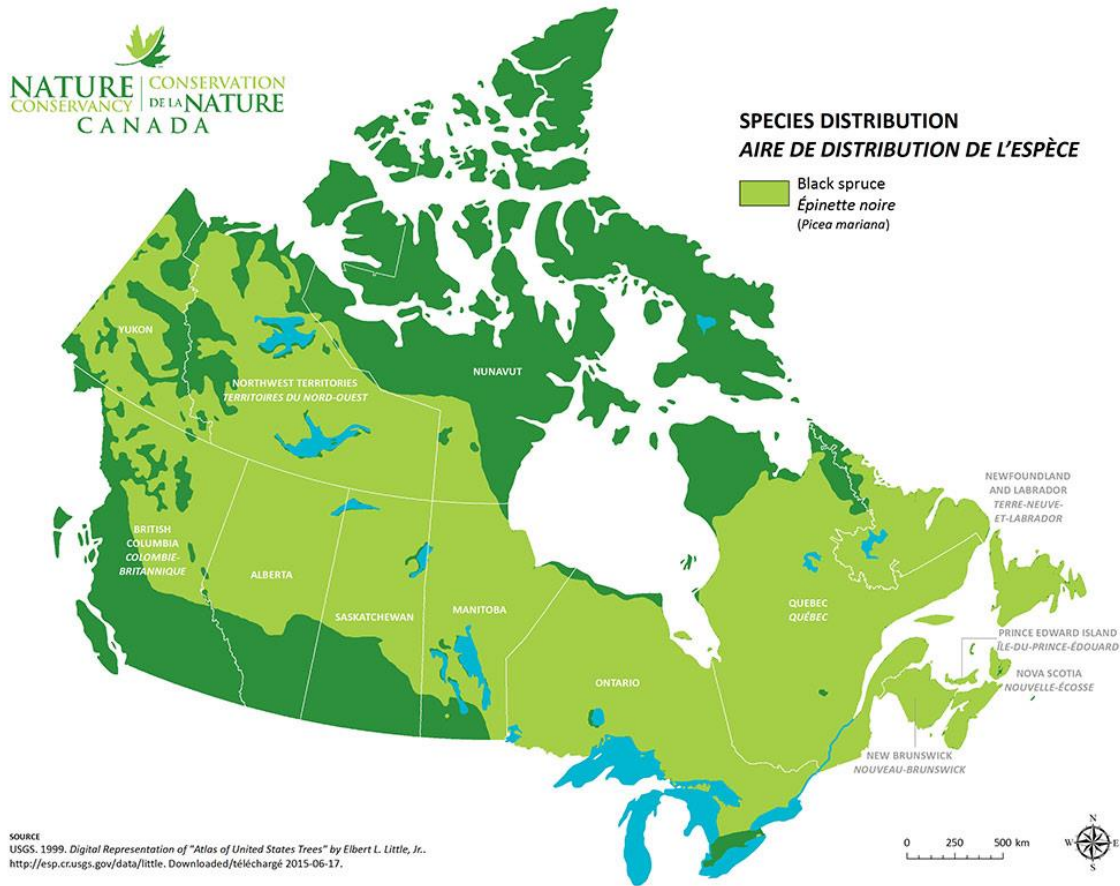


Figure 2.1 Distribution of black spruce across Canada (Nature Conservancy of Canada, n.d.)

2.2 Key Properties Affecting Wood Fuel Quality

The quality of wood as a solid biofuel is determined by a combination of physical, structural, and chemical attributes. Among these, bulk density, moisture content, anatomical features such as cell wall thickness and microfibril angle (MFA), and the distribution of extractives and lignin play fundamental roles in combustion behavior and energy yield (Demirbas, 2002; Obernberger & Thek, 2004; Saha et al., 2017).

Wood specific gravity (SG) strongly affects volumetric energy yield, as denser wood with higher SG produces more energy per unit volume even when mass-based calorific values are similar. Mature wood, characterized by thicker cell walls and lower MFA, generally shows higher density and mechanical strength, making it more advantageous for energy applications. (Barnett & Jeronimidis, 2003; Zobel & van Buijtenen, 1989). Juvenile wood, by contrast, tends to be less dense and more porous, which may reduce its combustion efficiency.

Moisture content (MC) is another critical factor. Elevated moisture reduces the effective calorific value, as energy is expended evaporating water before combustion can proceed efficiently. Oven-dried wood generally presents GCVs in the range of 18–20 MJ/kg, whereas high-moisture samples may fall significantly below this threshold due to latent heat loss (Vassilev et al., 2010). Standard drying protocols (e.g., ISO 18134-3:2023) are thus essential for comparative analysis of fuel quality.

Anatomical and chemical characteristics also influence combustion dynamics. The presence of extractives (resins, tannins, oils) enhances flammability and ignition properties, particularly in heartwood and mature tissues. These compounds often have high energy

content and contribute to soot and volatile emissions (Amthor, 2010; Lamtom & Savidge, 2003). Similarly, lignin-rich tissues, especially in latewood, exhibit slower but more energy-intensive combustion due to their condensed aromatic structure (Ma et al., 2014).

While the elemental composition of wood, especially carbon, hydrogen, and ash, is a major determinant of its calorific potential, a more detailed discussion of their quantitative effects is presented in Section 2.4. Understanding the interplay between these properties is essential for optimizing biomass combustion systems, selecting suitable feedstocks, and developing predictive models for fuel performance.

2.3 Radial and Vertical Variation in Wood Properties

Radial and vertical variation in wood properties is a fundamental characteristic influencing both structural applications and the energy performance of biomass. Radially, wood transitions from juvenile to mature zones and from heartwood to sapwood, accompanied by distinct shifts in anatomical and chemical traits. Juvenile wood, typically located near the pith, is characterized by higher MFA, lower SG, and higher MC, leading to reduced mechanical strength and altered thermal behavior (Zobel & van Buijtenen, 1989). In contrast, mature wood near the bark generally exhibits greater fiber length, lower MFA, and improved stiffness (Barnett & Jeronimidis, 2003).

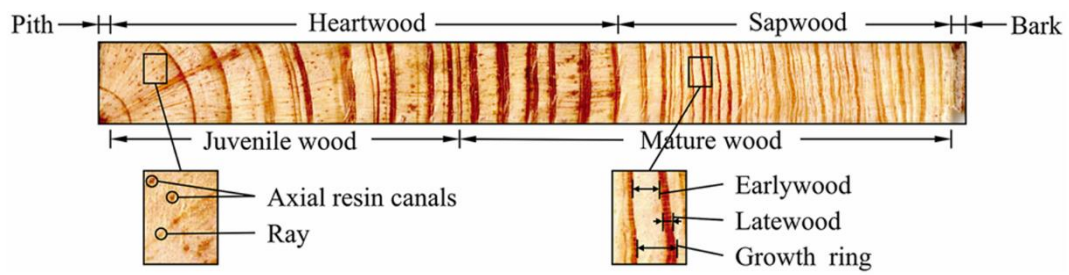


Figure 2.2 Cross-sectional image of Chinese pine (*Pinus tabulaeformis*) increment core (Wei et al., 2024)

Vertically, wood and lignification generally increase from the upper stem towards the base due to cambial maturation and gravitational adaptation (Larson, 1969; Plomion et al., 2001). This trend is accompanied by an increasing proportion of latewood and a reduction in growth ring width (Zobel & van Buijtenen, 1989), influencing not only physical properties such as shrinkage and mechanical strength but also chemical elemental composition relevant to combustion, most notably carbon concentration and ash content (Martin et al., 2018; Puri et al., 2024).

A representative example of radial variation is shown in Figure 2.2, which illustrates the transition from pith to bark in a Chinese pine (*Pinus tabulaeformis*) increment core. Distinct anatomical features such as axial resin canals, rays, earlywood–latewood boundaries, and the differentiation between juvenile and mature wood are clearly visible, providing a visual reference for the structural and chemical gradients described above (Wei et al., 2024).

2.4 Effects of CHS and Ash Content on Calorific Value

The elemental composition of wood, particularly the concentrations of carbon (C), hydrogen (H), sulfur (S), and ash content, exerts a decisive influence on its calorific value. Among these, carbon and hydrogen are the principal energy-contributing elements. Carbon, typically comprising 47–53% of oven-dry wood mass, is the dominant determinant of GCV, as it reflects the presence of energy-dense organic matter such as lignin and extractives (Lamlom & Savidge, 2003; Wei et al., 2024). Hydrogen content, generally ranging from 5.5% to 6.5%, also contributes positively, although to a lesser degree (Ma et al., 2014).

Numerous studies have demonstrated that elevated C and H contents are associated with increased GCV, whereas ash content has a negative effect, acting as a diluent that reduces the effective energy output per unit mass (Demirbas, 2002; Vassilev et al., 2010). Wood ash is composed of inorganic mineral residues, such as calcium, potassium, magnesium, and silica, that remain after combustion and do not contribute to energy production (Werkelin et al., 2005). While stem typically contains less than 1.0% ash, values exceeding 2.0% have been reported in bark, juvenile wood, and outer zones due to higher mineral deposition (Penninckx et al., 2001; Puri et al., 2024).

Although sulfur is present in trace amounts (usually <0.1%), its role is more environmental than energetic. During combustion, sulfur is converted into SO₂, contributing to acid gas emissions and potential corrosion in combustion systems (Koppejan & Schmidl, 2022). As such, minimizing sulfur is important for cleaner energy applications.

Empirical modeling further supports these relationships. Regression analyses often reveal that combinations of C, H, and ash content can explain a substantial portion of GCV

variation, with R^2 values exceeding 0.85 in some studies (Ma et al., 2014). Notably, the contribution of lignin and extractives, both of which are carbon-rich and exhibit calorific values as high as 63–88%, may also elevate GCV beyond what is predicted by CH analysis alone (Amthor, 2010; Lamtom & Savidge, 2003).

Therefore, assessing the interplay between CHS elements and ash content is crucial for understanding spatial variation in wood energy potential. Differences across radial and vertical positions within a tree—driven by physiological processes such as lignification, resin accumulation, and mineral transport—may lead to localized fluctuations in calorific performance. Incorporating these parameters into combustion modeling enhances the accuracy of biomass evaluation and supports more targeted utilization strategies.

2.5 Statistical Methods for Biomass Property Evaluation

Evaluating wood biomass as a renewable fuel source requires not only a detailed understanding of its chemical and physical properties, but also the application of robust statistical techniques to analyze variation, infer causal relationships, and develop predictive models. Given the inherent spatial heterogeneity in wood, across radial directions, vertical stem positions, and individual trees. Statistical frameworks must accommodate hierarchical data structures and multivariate relationships among fuel-relevant traits (Harrison et al., 2018; Searle et al., 2009).

One commonly adopted approach for assessing variation across multiple spatial scales is the fixed effects linear model (FEM), which treats experimental factors as fixed and enables direct estimation of their main and interaction effects. Such models are effective for detecting systematic spatial trends in biomass properties, particularly when applied to balanced datasets covering multiple tree compartments and radial zones (Kharrat et al., 2019; Wei et al., 2024).

Where non-independence among samples occurs, such as repeated measurements within trees or partial nesting—linear mixed-effects models (MEMs) offer greater flexibility. By incorporating both fixed effects (e.g., eco-block, stem position) and random effects (e.g., tree identity), MEMs allow researchers to control for inter-tree variability while accommodating unbalanced designs and technical replicates (Nakagawa & Schielzeth, 2013; Zuur et al., 2009). These models have been widely used in forest biomass research to improve inference reliability when hierarchical or repeated-measures structures are present (Harrison et al., 2018; Wei et al., 2024).

In addition to model-based approaches, paired t-tests are frequently used for focused comparisons, such as evaluating radial differences (inner vs. outer) within specific stem sections. This method provides a straightforward means of testing localized contrasts that may not emerge as significant in multi-factor models (Ruxton, 2006).

To investigate how chemical elemental composition influences combustion performance, multiple linear regression (MLR) is often employed. MLR models GCV as a function of elemental composition—most notably carbon (C), hydrogen (H), and ash content, which are key predictors of biomass energy potential (Demirbas, 2002; Ma et al., 2014; Vassilev et al., 2010). Regression coefficients quantify the direction and strength of each predictor's effect, while metrics such as the coefficient of determination (R^2) and residual analysis assess model fit and validity. High R^2 values (often >0.85) reported in temperate and boreal species highlight the predictive value of elemental composition for biomass fuel characterization (Amthor, 2010; Lamtom & Savidge, 2003).

Collectively, these statistical frameworks, ranging from fixed and mixed-effects models to pairwise tests and regression analyses, provide a versatile toolkit for understanding biomass variability. Their combined use enables researchers to partition variation across biological levels, identify key compositional drivers of fuel quality, and develop models that link wood chemistry to energy performance.

2.6 Problem Statement

However, wood is inherently variable. Its chemical elemental composition changes both longitudinally and radially, influenced by anatomical differences such as juvenile versus mature wood and sapwood versus heartwood. These anatomical gradients are typically reflected along both the vertical axis of the stem and the radial axis from pith to bark, making them ideal targets for sampling and comparative analysis. Previous studies have shown that these spatial variations can significantly affect carbon concentration, ash deposition, and energy yield (Martin et al., 2018; Wei et al., 2024; Zobel & van Buijtenen, 1989). Yet, most biomass classification systems and many scientific evaluations still rely on species-level averages or bulked composite samples, which may obscure these internal patterns and lead to inaccurate assessments of fuel quality.

This limitation is particularly relevant in Canada's boreal region, where black spruce (*Picea mariana*) dominates vast tracts of managed forestland. Despite its ecological and economic importance, systematic data on spatial variability in fuel-relevant traits, particularly CHS elements, ash content, and calorific value, remain limited for this species. Based on this context and the experimental design of the current study, the following research problems are identified:

1. The extent to which eco-block, tree identity, stem section, radial position and their interactions affect the chemical element and energy properties of black spruce.
2. Whether predictive models can be developed based on CHS and ash content to accurately estimate gross calorific value for biomass classification.
3. How spatially informed models may support improved biomass selection strategies by identifying high-energy-yield segments within or among trees.

2.7 Objectives and Scope of Work

In response to the research problems outlined above, the objectives and scope of this study were defined as follows:

This study aimed to evaluate the combustion-relevant properties of black spruce (*Picea mariana*) biomass from boreal forests in Labrador, with particular emphasis on spatial variation in chemical composition and energy potential. By examining carbon (C), hydrogen (H), sulfur (S) content, ash content, and gross calorific value (GCV), the study sought to understand how these parameters vary across different hierarchical levels ecological eco-block, tree identity, stem section, and radial direction and how such variability may affect the performance and classification of wood.

However, the scope of this study was restricted to evaluating the combustion-related properties of residual wood materials from the production of the lumber sampled from Labrador. Therefore, the research focused on the potential utilization of available residues rather than representing the overall biomass energy potential of Labrador's black spruce forests.

To achieve this, the study employed a combination of mixed-effect modeling and linear regression to unravel complex patterns of inter- and intra-tree variability and to identify statistically significant factors influencing fuel quality. In addition to quantifying these sources of variation, the research explored the feasibility of constructing predictive models for calorific value based on carbon, hydrogen and ash content, with the goal of informing rapid biomass assessment protocols.

The analytical framework and sampling design were intentionally developed with practical applicability in mind, aiming to guide more targeted biomass utilization strategies. By identifying high-energy-yield zones within individual trees and across broader tree populations, this approach enhanced the precision of biomass resource management. Through the integration of spatially explicit sampling and rigorous statistical modeling, the study established an empirical basis for more accurate assessment, classification, and strategic deployment of forest biomass as a sustainable renewable energy source.

3 Materials and Methods

3.1 Sample Design and Preparation

The black spruce (*Picea mariana*) samples were obtained from the two districts of Labrador: CC19005 and CC19011 as shown in Figure 3.. From both locations, enough lumbers can be acquired and marked with the corresponding sign to distinguish between each other and good for the following mechanical experiments. More specifically, Block CC19005 encompasses 18 stands over 365 hectares, with a total volume of 3,086 m³ and an average yield of 8.5 m³/ha. CC19011, under a Timber Sale Agreement, includes 15 stands over 140 hectares, contributing 21,598 m³ in total—20,983 m³ of softwood and 615 m³ of hardwood.

These two blocks were selected to represent variability in site conditions. Within each block, trees were selected from multiple spatially separated locations to capture within-site heterogeneity. After harvest, each tree stem was cut into sequential 12-foot logs starting from the base. For this study, only the lowest 2-foot segment from the bottommost 12-foot log of each tree was used. A quarter section was then excised from this 2-foot segment to serve as the standardized test specimen for further analysis.

A total of 52 samples were prepared from 14 trees using a two-batch design, as shown in Figure 3.2. Batch 1 consisted of 6 trees, from which samples were collected at three vertical stem positions: bottom, middle, and top. At each height, two subsamples were taken along the radial direction, one near the bark and one near the pith, resulting in 36 samples. Batch 2 included 8 additional trees sampled only at the bottom position, also with two radial

subsamples per tree, yielding an additional 16 samples. In total, 52 wood samples were prepared for laboratory analysis.

All test specimens were prepared from residual quarters of lumber logs collected from two eco-blocks examined. These materials were derived from lumber production residues rather than from trees harvested specifically for biomass fuel testing.

All the test work was carried out at the Wood Science and Technology Centre (WSTC), the University of New Brunswick (UNB), Fredericton, Canada, detailed experimental investigations are introduced as follows.

In addition to the chemical and thermal analyses, basic information of the sampled trees was also recorded to provide background on stand characteristics. Tree age was determined through ring counts, and the diameter at breast height was calculated as the average of the large- and small-end diameters of the logs. As shown in Table 3-1, the sampled trees ranged from 175 to 216 years in age, reflecting the old-growth nature of these eco-blocks. The breast height values varied between 18.0 and 28.3 cm, consistent with the slow-growing black spruce stands in Labrador. These values were derived from inventory records reported by Gong et al. (2025) in the Spiral Grain project, which was conducted in the same eco-blocks used for this study.

Tree ID	Tree age (years)	breast height (cm)
N-6	175	22.8
N-8	187	18.0
N-17	207	22.8
S-2	199	27.0
S-16	216	22.8
S-19	180	28.3
Average	194.0	23.62

Table 3-1 Tree age and diameter at breast height of the black spruce trees sampled from two eco-blocks in Labrador.

Note: Tree age values were obtained from ring counts, while breast height values were calculated as the average of large and small end diameters of logs reported in the referenced report (Gong et al., 2025).

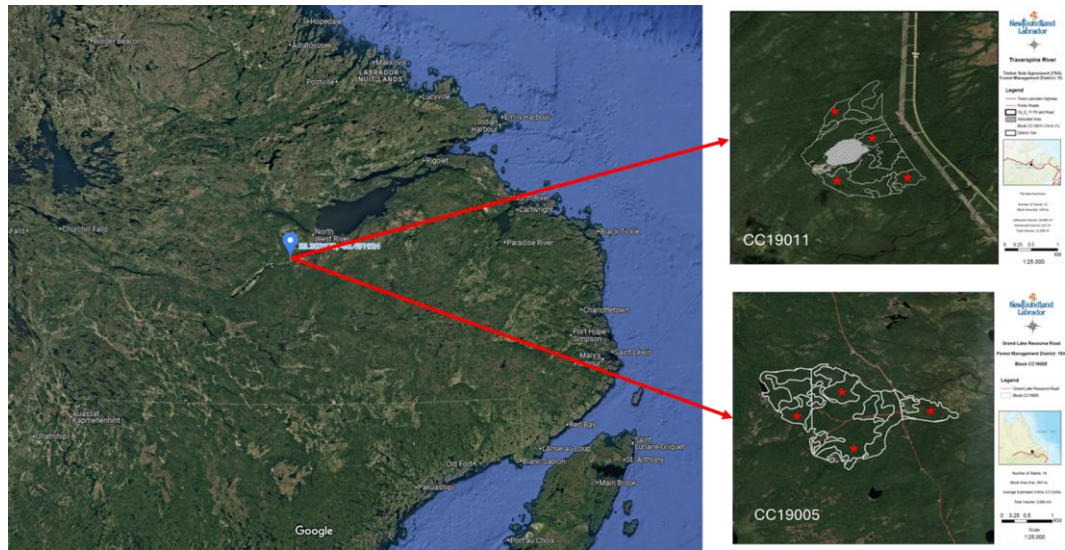


Figure 3.1 Sampling locations in Goose Bay, Labrador



Figure 3.1 Raw quartered logs of Batch 1 and Batch 2

Radial subsampling was performed by measuring 20 to 25 millimeters inward from the bark surface using a flexible measuring tape and a permanent marker, allowing consistent differentiation between outer wood and inner wood eco-blocks. This radial division threshold (20–25 mm) was based on preliminary observations of growth ring density and spacing, which were used to approximate the transition from the outer (denser) to inner (less dense) eco-blocks of the wood. Although not a strict anatomical juvenile-mature boundary, this distance was selected to capture potential radial differences in chemical and thermal properties, while maintaining consistency across all samples.

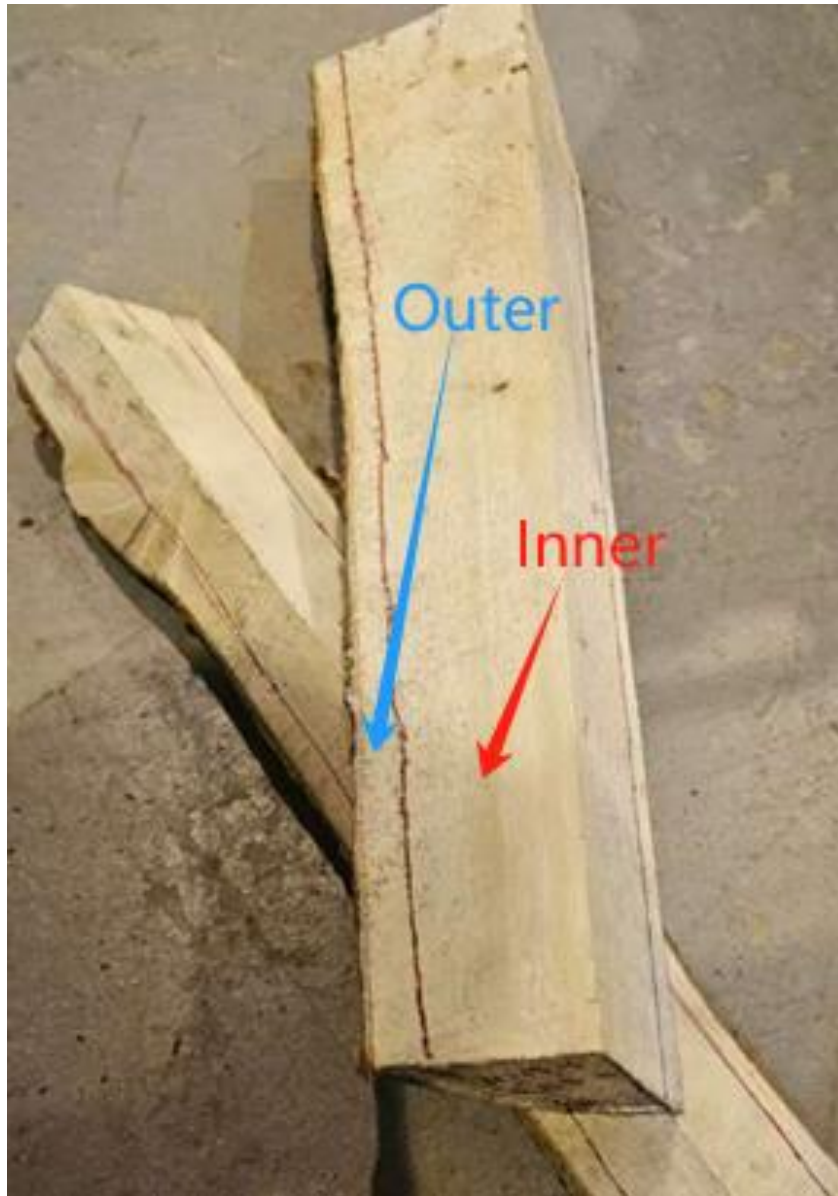


Figure 3.2 Marked division between inner and outer eco-blocks

The marked segments were then processed using a vertical band saw (GENERAL MFG CO. LTD., Model 490, Canada) to obtain narrow wood strips suitable for grinding. Each radial portion (inner and outer) from every quarter was cut separately to avoid cross-contamination and to maintain sample traceability, as shown in Figure 3.4.

These strips were then ground into fine powder using a Thomas Wiley Mill (Model 3379-K05, Arthur H. Thomas Co., USA) equipped with an internal mesh screen that ensures particle sizes of ≤ 1 mm (Figure 3.5). After grinding, the powder from each radial portion was thoroughly mixed to ensure homogeneity. A vacuum cleaner was used between samples to remove residual particles inside the grinder.

The ground material was weighed to ensure a sample mass of at least 20 g per portion, allowing for three replicate analyses per sample. No formal moisture correction or recording of initial/final weight was performed at this stage.



Figure 3.3 Band saw (Model: 490) and wood strips



Figure 3.4 Wiley Mill grinder (Model: 3379-K05) used for pulverizing samples

The powdered samples were then dried in a Fisher Isotemp laboratory oven (Model 30F) at a constant temperature of (103 ± 2) °C for 20–24 hours (Figure 3.6). This drying process followed the guidelines specified in ISO 18134-3 and ISO 16948:2015, ensuring consistency for elemental and thermal analyses.

After drying, each sample was sealed in a labeled Ziploc bag, indicating the tree number, batch, vertical section (top, middle, or bottom), and radial position (inner or outer). The sealed bags were stored in dry, shaded laboratory cabinets at the WSTC, without controlled temperature or humidity monitoring.

A total of 52 samples were prepared:

$(18 \text{ samples from Batch 1} + 8 \text{ samples from Batch 2}) \times 2 \text{ radial eco-blocks (inner and outer)}$
 $= 52 \text{ samples.}$

Each sample was assigned a unique identifier in the format “N/S -Y-Z-W_n,” where:

- “N/S-Y together represent the Tree ID, e.g., “N-6” for a tree from the North eco-blocks labeled as Tree 6;
- Z indicates the Stem Section, where 1 = Bottom, 2 = Middle, and 3 = Top;
- W refers to the Radial Position, with “H” for Inner and “S” for Outer;
- n denotes the replicate number (1–3).

Unless otherwise specified, all experimental procedures were conducted in 3 replicates for each sample. The average values were used for subsequent statistical analysis, with outlier values replaced by repeat tests if necessary.



Figure 3.5 Oven (Model: 30F) with temperature control for drying samples

3.2 Experimental Methods

3.2.1 Determination of Carbon, Hydrogen, and Sulfur (CHS)

The elemental composition of carbon (C), hydrogen (H), and sulfur (S) in the wood samples was determined using an ELTRA CHS 580 elemental analyzer (ELTRA GmbH, Germany), as shown in Figure 3.7, following the international standards ISO 16948:2015 (Solid biofuels — Determination of total content of carbon, hydrogen and nitrogen) and ISO 16994:2016 (Solid biofuels — Determination of total content of sulfur and chlorine).

Dried and milled samples (≤ 1 mm) were used directly without pelletizing. For each analysis, approximately 120–200 mg of sample powder was weighed using a Sartorius Practum124-1S analytical balance (0.0001 g resolution) and placed into ceramic crucibles.

The CHS 580 analyzer combusts samples at high temperature in an oxygen-rich environment, converting all carbon to CO₂, hydrogen to H₂O, and sulfur to SO₂. The resulting gases were separated and detected by infrared absorption. The system was operated under PC control, and all measurements were carried out in dry basis mode, with results reported as mass percentages (%) of the original oven-dried wood.

Instrument calibration was performed daily using certified reference materials (CRMs): AR4016 (Carbon and Sulfur in Soil, 2.05% each) and EDTA (AR2092), as shown in Figure 3.8. A blank run was also performed regularly to ensure baseline accuracy.



Figure 3.6 CHS analyzer (Model: ELTRA CHS 580) used for determining carbon, hydrogen, and sulfur content of wood samples



Figure 3.7 Certified reference materials used for calibration: AR4016 (C & S = 2.05%) and EDTA (AR2092)

3.2.2 Determination of Ash Content

The ash content of the wood samples was determined according to the procedures outlined in ISO 18122:2022 – Solid biofuels – Determination of ash content. Ash content is defined as the inorganic residue remaining after combustion of organic matter in a controlled environment.

Approximately 1.0000 ± 0.0010 g of oven-dried sample was weighed into pre-weighed porcelain crucibles with lids using a Mettler AT261 DeltaRange analytical balance (accuracy 0.01 mg). Each crucible was labeled to maintain traceability throughout the process.

The ash determination process was performed in a Fisher Scientific muffle furnace (Model 650-58) (Figure 3.9), equipped with automatic temperature control. The heating followed a two-stage program in compliance with ISO 18122:

1. The temperature was increased to 250 °C and held for 60 minutes to remove volatile components.
2. Then, the furnace was ramped up to 550 ± 10 °C and maintained for 120 minutes to complete the ash determination process.

After heating, crucibles were removed from the furnace and allowed to cool naturally to room temperature before final weighing. No desiccator was used. The ash content (% dry basis) was calculated using Eq. (1):

$$Ash (\%) = (m_2 - m_1) / m_0 \times 100 \quad \text{Eq. (1)}$$

where:

- m_1 = weight of empty crucible with lid
- m_0 = weight of the sample
- m_2 = weight of crucible, lid, and ash residue

Each batch included 9 to 12 crucibles, and each sample was processed in triplicate. If a replicate value significantly deviated from the others, it was discarded, and the sample was reprocessed.



Figure 3.8 Muffle furnace (Model: Fisher Scientific 650-58) used for ash determination of wood samples

3.2.3 Determination of Calorific Value

The GCV of each wood sample was determined using a Parr 6300 automatic bomb calorimeter (Parr Instrument Company, USA) (Figure 3.10), accordance with ISO 18125:2017 – Solid biofuels – Determination of calorific value.

Approximately 0.5000 ± 0.0010 g of oven-dried wood powder (previously dried at 103 °C) was weighed into a metal crucible using a Mettler Toledo analytical balance and placed inside the bomb chamber without pelletization. A cotton fuse wire was manually fixed between the ignition terminals and inserted partially into the sample to ensure complete combustion.

The bomb chamber was charged with oxygen at a pressure of 450 psi (~31 atm). Each test was initiated through the system's automatic ignition and control program. If any test resulted in incomplete combustion (misfire), it was discarded and repeated with a fresh sample.



Figure 3.9 Automatic bomb calorimeter (Model: Parr 6300) used to measure the GCV of wood samples.

Benzoic acid was used as the calibration standard. Multiple calibration runs were performed at the start of each test session, and the system was accepted only if the standard deviation of the calibration series was below 0.12%, as recommended by the manufacturer. The sample weight (in grams) was entered into the system, which automatically calculated the calorific value based on the observed temperature rise. No manual moisture correction or Net Calorific Value (NCV) adjustment was performed.

The calorific value was expressed in BTU per pound (BTU/lb) on an oven-dry basis. Conversions to other units (MJ/kg) were not performed in this section and will be discussed in later sections for comparative purposes.



Figure 3.10 Benzoic acid for standardization

3.3 Statistical Analysis

All data processing and statistical analyses were conducted using Microsoft Excel 365 and RStudio (Version 2024.12.0 + 467). Two main data tables were prepared to facilitate downstream analysis:

- The `ReplicatesData` contains all raw measurements from the three replicate tests for each sample, including values for carbon, hydrogen, sulfur, ash content, and gross calorific value. This dataset was used exclusively in Section 4.2 for both the fixed-effects linear model (FEM) (primary analysis) and the mixed-effects model (MEM) (supplementary analysis), as it preserves within-sample variability needed for these models.
- The `MeanData` contains the average value of each parameter for every unique sample ($n = 52$), calculated after removal of statistical outliers. This dataset was used for exploratory data visualization and for linear regression modeling, where a single representative value per sample was required.

In RStudio, data manipulation was conducted using the *dplyr* and *tidyr* packages, including filtering, grouping, and summarizing datasets to create both `ReplicatesData` and `MeanData` tables. Visualization of exploratory plots and model outputs was performed with *ggplot2*.

For statistical modeling, the base `lm()` function was used to fit fixed-effects linear models assessing the effects of eco-block, stem section, and radial position on gross calorific value (GCV), carbon, hydrogen, and ash content. The *lmerTest* package was used to fit linear mixed-effects models (`lmer()` function), which incorporated `TreeID` as a random effect to account for within-tree correlation. Supplementary paired comparisons, such as inner vs.

outer radial positions in the bottom stem section, were conducted using `t.test()` in R. MLR models of GCV as a function of carbon, hydrogen, and ash content were also fitted using `lm()`. Model diagnostics, including variance inflation factors, residual plots, and assumption checks, were performed with the *car* (`vif()`, `Anova()`) and *performance* (`check_model()`) packages.

Descriptive statistics (mean, standard deviation, coefficient of variation), preliminary plots, and figure formatting were prepared in Microsoft Excel, whereas all inferential statistical analyses were conducted in R.

4 Results and Discussion

All measurements for Heat, Carbon (C), Hydrogen (H), and Ash content were recorded in triplicate for each sample (TreeID $\times$ Section $\times$ Radial). The mean values of these replicates were calculated to form the primary dataset for analysis (MeanData), resulting in 52 observations. Sulphur (S) content was only detected in two replicates from a single sample (N-6-1-H) at concentrations in parts per million (ppm), significantly lower than other elemental levels. Due to its negligible abundance and sparse detection, S was excluded from all subsequent statistical analyses and visualizations. SG data were obtained from WSTC for the same batch of wood materials. These SG values were measured independently by WSTC and provided as a single rough mean value for each sample, without replicate measurements; therefore, SG was only used descriptively and was not subjected to replicate-based statistical tests. Unless otherwise specified, all descriptive statistics and inferential analyses in Sections 4.1, 4.3–4.5 were based on the processed MeanData ($n = 52$). In Section 4.2, the full replicate dataset (ReplicatesData, $n = 152$) was used to fit both FEMs and MEMs.

4.1 Descriptive Statistics and Data Overview

4.1.1 Statistics Summary

The descriptive statistics presented in Table 4-1 provide an overview of the measured wood fuel properties used in this study, including Carbon (C), Hydrogen (H), Ash content, GCV, and SG. These values were derived from the mean of three replicate measurements for each sample (TreeID $\times$ Section $\times$ Radial), resulting in a dataset of 52 observations. SG values were obtained from the WSTC as single mean measurements for the same set of samples. Sulphur (S) content was excluded from further analysis due to negligible abundance and sparse detection. The table reports the mean, standard deviation (SD), minimum, maximum, range, and coefficient of variation (CoV) for each variable, providing a quantitative baseline for subsequent spatial variation analyses.

Table 4-1 presents the descriptive statistics for the measured wood fuel properties, including C, H, Ash content, GCV, and SG. Carbon and Hydrogen exhibited relatively low variability, with CoV values of 2.18% and 2.05%, respectively, indicating stable elemental composition across the sampled trees. GCV also showed low variation (CoV = 1.45%), suggesting consistent calorific value. In contrast, Ash content displayed the highest variability (CoV = 19.86%), reflecting greater heterogeneity in mineral content. SG values ranged from 0.39 to 0.51, with a moderate CoV of 6.09%.

Variable	Unit	Mean	SD	Max	Min	Range	CoV (%)
Carbon (C)	% dry weight	50.32	1.09	52.13	47.93	4.21	2.18
Hydrogen (H)	% dry weight	6.17	0.13	6.51	5.99	0.52	2.05
Ash content	% dry weight	0.330	0.070	0.609	0.213	0.395	19.86
Gross calorific value (GCV)	MJ/kg	18.92	0.27	19.83	18.51	1.33	1.45
Specific gravity (SG)	none	0.43	0.03	0.51	0.39	0.12	6.09

Table 4-1 Descriptive Statistics of Wood Samples (n = 52).

Note: Values are based on the mean of three replicate measurements for each sample (TreeID × Section × Radial). Specific gravity (SG) values were provided by WSTC as single mean measurements for each sample. Coefficient of variation (CoV) was calculated as $(SD / \text{Mean}) \times 100\%$.

4.1.2 Group-wise Mean $\pm$ SD Plots

While Table 4-1 summarizes the overall distribution and variability of each property across all samples, it does not reveal how these properties vary among specific spatial factors. To provide a clearer visual understanding, Figures 4.1 to 4.5 present the mean values and standard deviations of C, H, Ash, GCV and SG for each combination of Eco-block, Section, and Radial position ($2 \times 3 \times 2 = 12$ groups). The figures are arranged in the order of their direct or indirect influence on fuel quality, beginning with GCV, followed by Carbon, Hydrogen, Ash content, and SG. These visualizations allow for preliminary observations of potential spatial patterns, which will be statistically evaluated in Section 4.2.

All bar charts presented in this section (Figures 4.1 to 4.5) display mean $\pm$ standard deviation values based on three replicate measurements per sample. For the Bottom section, $n = 7$ per bar was used by combining data from both Batch 1 and Batch 2 (14 trees $\times$ 2 radial positions). For the Middle and Top sections, $n = 3$ per bar was used, as these positions were only available in Batch 1 (6 trees $\times$ 2 radial positions).

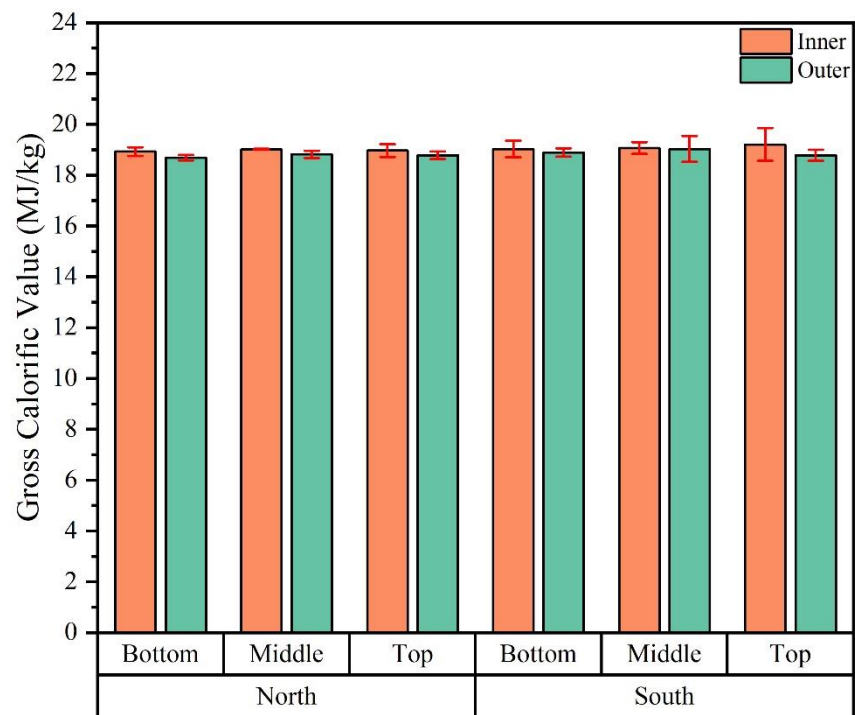


Figure 4.1 Mean $\pm$ SD of GCV (MJ/kg) by Eco-block, Section, and Radial position.

GCV ranged from approximately 18.5 to 19.8 MJ/kg across the 12 spatial groups. Visual inspection indicates minimal variation between two eco-blocks, with slightly higher values observed in the South bottom section compared to other sections. Differences between radial positions were generally small, though inner samples tended to have marginally higher GCVs in several sections. Standard deviations were low for all groups, consistent with the low CoV (1.45%) reported in Table 4-1, suggesting overall stability in calorific value across the sampled trees. These preliminary observations will be formally evaluated in Section 4.2 using both FEMs and MEMs.

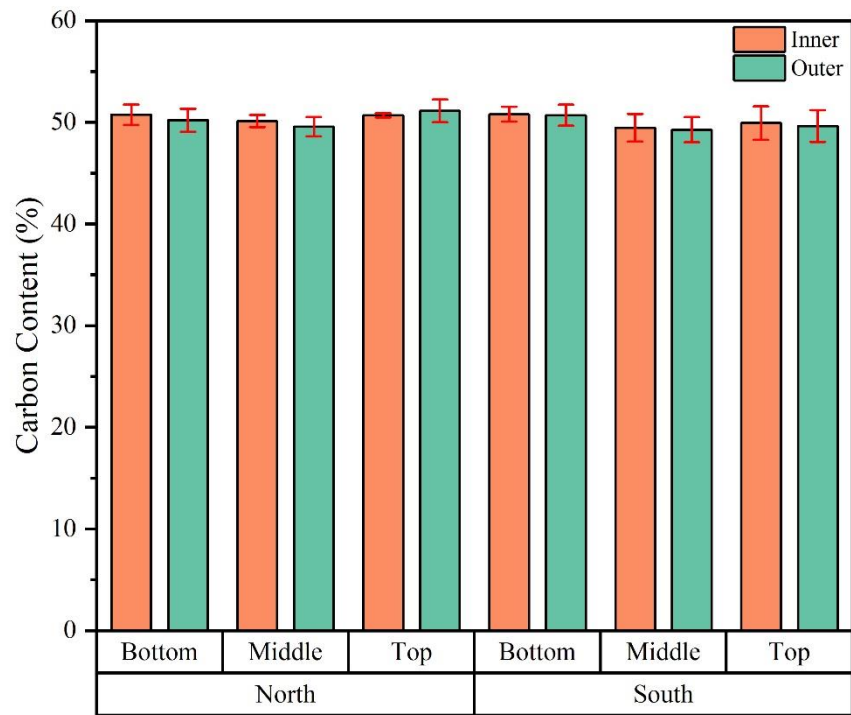


Figure 4.2 Mean $\pm$ SD of carbon content (% dry weight) by Eco-block, Section, and Radial position.

Carbon content ranged from approximately 47.93% to 52.13% across the 12 spatial groups. Visually, carbon content appeared relatively consistent between two eco-blocks, with a slight tendency for higher values in the bottom and middle sections of the South eco-block. Differences between radial positions were minor, although inner samples in several sections exhibited marginally higher carbon content compared to outer samples. The relatively small standard deviations across groups correspond to the low CoV (2.18%) reported in Table 4-1, indicating stable carbon composition across the sampled trees. These preliminary spatial patterns will be further examined in Section 4.2 through fixed and mixed effects modeling.

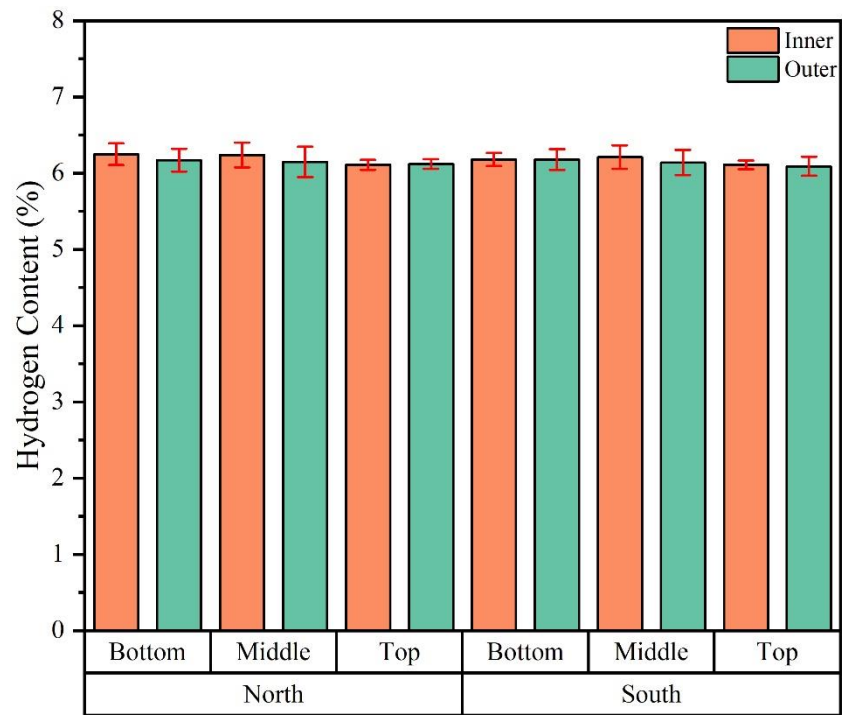


Figure 4.3 Mean $\pm$ SD of hydrogen content (% dry weight) by Eco-block, Section, and Radial position.

Hydrogen content ranged from approximately 5.99% to 6.51% across the 12 spatial groups. Visual inspection suggests minimal differences between two eco-blocks, with slightly higher hydrogen levels in the bottom section of the South eco-block. Variation between radial positions was limited, though in certain sections, inner samples displayed marginally higher hydrogen content than outer samples. Standard deviations were consistently low, matching the low CoV (2.05%) reported in Table 4-1, indicating a stable hydrogen composition in the sampled trees. These observed patterns will be formally tested in Section 4.2 using both FEMs and MEMs.

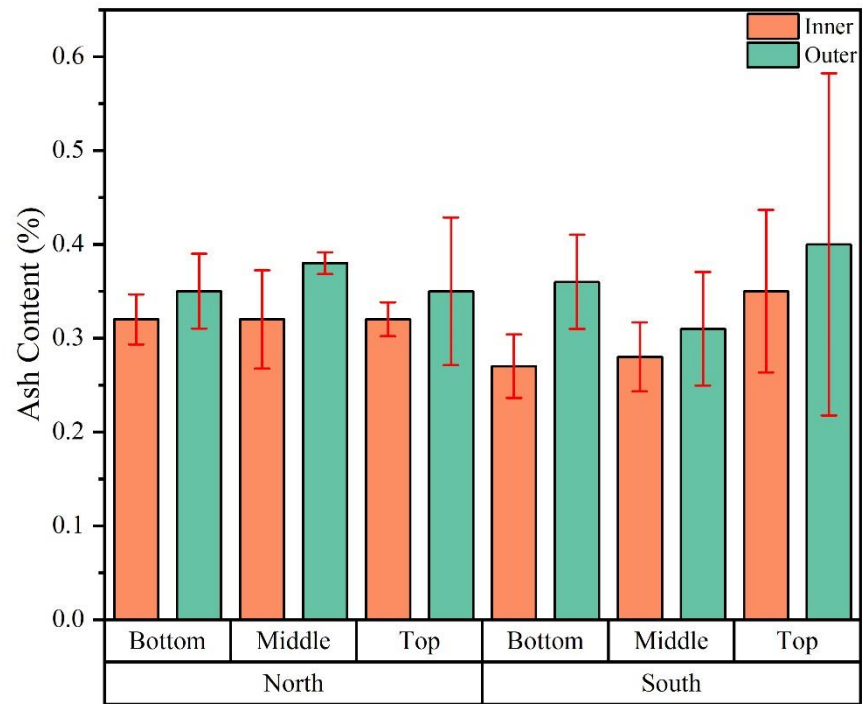


Figure 4.4 Mean $\pm$ SD of ash content (% dry weight) by Eco-block, Section, and Radial position.

Ash content ranged from approximately 0.213% to 0.609% across the 12 spatial groups, representing the largest relative variability among all measured properties (CoV = 19.86% in Table 4-1). Visual inspection suggests higher ash content in the bottom section of the South eco-block, particularly in outer radial samples. Differences between radial positions were more noticeable than for other variables, with outer samples often exhibiting higher ash content than inner samples. Standard deviations were relatively large compared to the mean values, reflecting the heterogeneous distribution of mineral content within and between trees. These preliminary spatial trends will be examined in detail in Section 4.2 through fixed and mixed effects models.

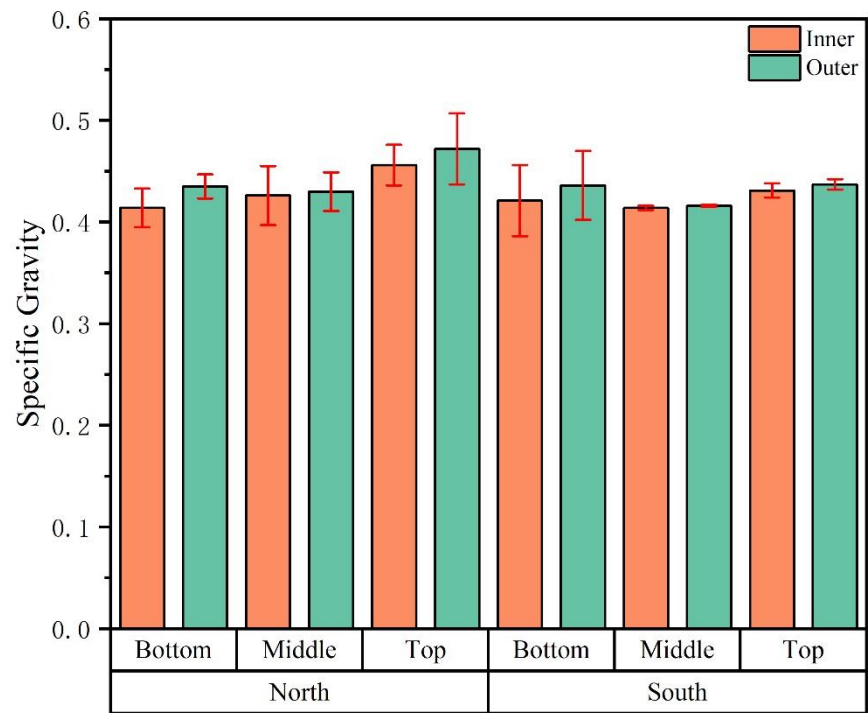


Figure 4.5 Mean $\pm$ SD of SG by Eco-block, Section, and Radial position.

Specific gravity ranged from 0.39 to 0.51 across the 12 spatial groups, with a moderate relative variability ($\text{CoV} = 6.09\%$ in Table 4-1). Visual inspection shows that SG tended to be slightly higher in the bottom sections for both eco-blocks, with marginally greater values in the South eco-block overall. Differences between radial positions were minimal, though in some sections outer samples exhibited slightly lower SG values than inner samples. Given that SG values were derived from external measurements without replicates, the observed variation reflects broader physical differences among samples rather than measurement precision. These preliminary spatial patterns will be further explored in Section 4.2.

Overall, the descriptive statistics and visual assessments in this section indicate that GCV, C, and H content were relatively stable across the sampled trees, whereas ash content exhibited substantial variability. SG showed moderate variation, with some spatial patterns observable across eco-blocks, sections, and radial positions. These preliminary observations suggest potential influences of spatial factors on wood fuel properties, which will be formally tested using fixed and mixed effects models in Section 4.2.

4.2 Spatial Variation in Wood Property

To evaluate how spatial factors influence wood combustion properties, this section investigates the effects of Eco-block (North vs South), Section (Bottom, Middle, Top), and Radial position (Inner vs Outer) on four response variables: GCV, Carbon, Hydrogen, and Ash content.

Two statistical modeling approaches were applied to each variable. First, Fixed Effects Linear Models (FEMs) were constructed to estimate the main effects of the three spatial factors. The significance of each factor was assessed using Type II ANOVA. Second, to account for the repeated measures and nested structure of the data (i.e., multiple samples from the same tree), Mixed Effects Models (MEMs) were fitted by including TreeID as a random effect, and Type III ANOVA was used for significance testing.

This dual-model framework allows for comparison between population-level fixed effects and within-tree variability. The results of both models are presented and compared for each wood property in the following subsections (4.2.1–4.2.4), followed by an integrated summary in 4.2.5.

To provide an overview of the spatial patterns prior to the detailed statistical analysis, Figures 4.6 and 4.7 summarize the mean values of wood properties across vertical (top, middle, bottom) and radial (inner, outer) positions for the North and South eco-blocks, respectively. These schematic diagrams offer an intuitive visualization of intra-tree variability, showing, for example, slightly higher carbon content and calorific value in the inner wood, and consistently elevated ash content in the outer wood. Such general patterns provide context for the statistical evaluations presented in Sections 4.2.1–4.2.4.

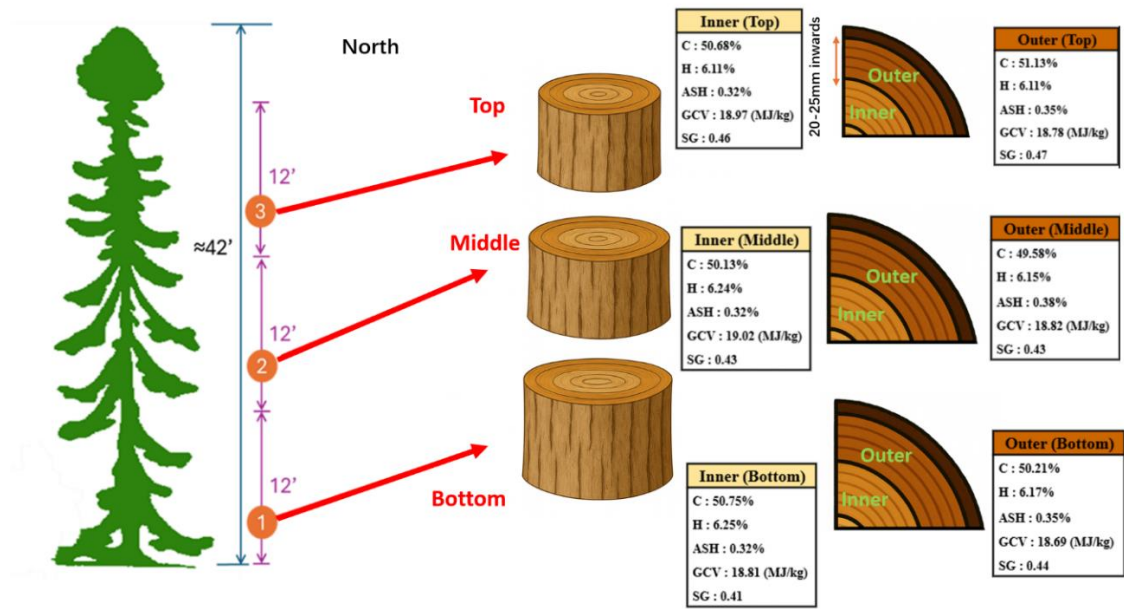


Figure 4.6 Mean values of C, H, Ash, GCV, and SG across vertical and radial positions in the North eco-block

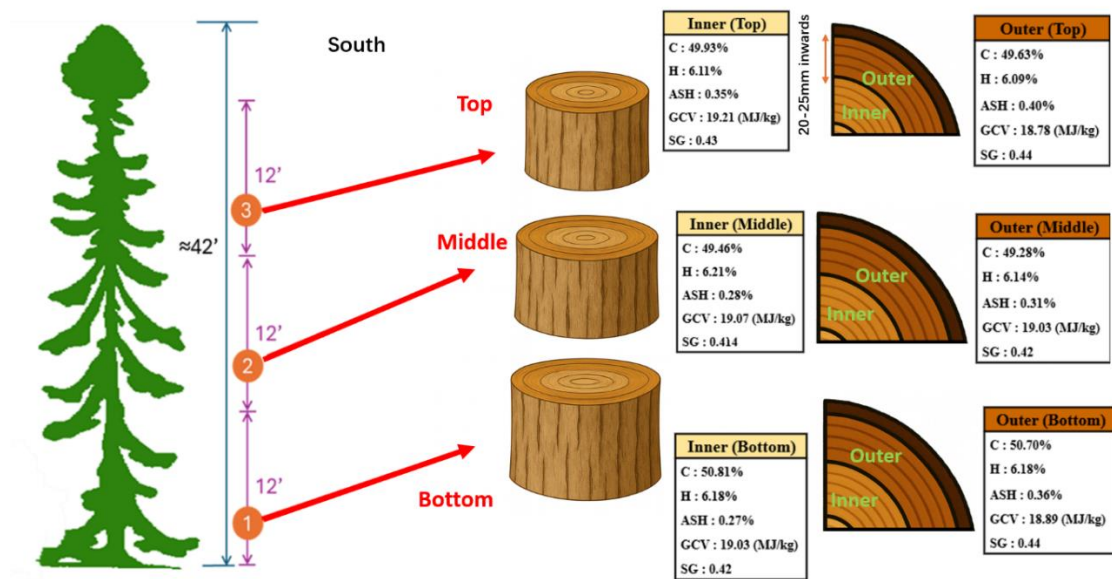


Figure 4.7 Mean values of C, H, Ash, GCV, and SG across vertical and radial positions in the South eco-block

4.2.1 Variations in Calorific Value

Calorific value is a key indicator of biomass energy performance and serves as the primary response variable in this study. All calorific value data analyzed here refer to experimentally determined GCV. To evaluate how calorific value varies with tree spatial characteristics, both FEM and MEM were applied taking Eco-block, Section, and Radial position as predictors.

The FEM revealed that both Eco-block and Radial position had significant effects on GCV, whereas Section was not significant (Table 4-2). Samples from outer radial positions exhibited significantly lower GCV than those from inner positions (Estimate = $-0.204 \pm 0.048 \text{ MJ}\cdot\text{kg}^{-1}$, $p < 0.001$), representing the largest single-factor effect in the model. This negative coefficient indicates that outer wood has, on average, $0.204 \text{ MJ}\cdot\text{kg}^{-1}$ lower GCV than inner wood, suggesting a possible association with changes in chemical elemental composition during radial growth. By contrast, samples from the South Eco-block had moderately higher GCV than those from the North (Estimate = $0.139 \pm 0.048 \text{ MJ}\cdot\text{kg}^{-1}$, $p = 0.0048$), reflecting potential site or block differences in growth conditions or resource allocation.

The vertical Section factor did not show a statistically significant influence ($p = 0.085$ for Middle; $p = 0.365$ for Top relative to Bottom), indicating that vertical variation in GCV was relatively small compared to radial or Eco-block differences.

Term	Estimate $\pm$ SE	p-value	Significance
Eco-block South	0.139 $\pm$ 0.048	0.0048	**
SectionMiddle	0.104 $\pm$ 0.060	0.085	
SectionTop	0.055 $\pm$ 0.060	0.365	
RadialOuter	-0.204 $\pm$ 0.048	< 0.001	***

Table 4-2 Fixed-Effect Estimates for GCV Model

Note: Significance codes: *** $p < 0.001$, ** $p < 0.01$, * $p < 0.05$

Factor	Chi ²	df	p-value	Significance
Eco-block	1.64	1	0.2007	
Section	0.88	2	0.6424	
Radial	28.01	1	1.21e-07	***

Table 4-3 Type III ANOVA for GCV (MEM)

Note: Significance codes: *** $p < 0.001$, ** $p < 0.01$, * $p < 0.05$

As shown in Figure 4.1 (Section 4.1), Outer samples had notably lower GCVs than Inner samples, a trend confirmed by both statistical models.

When TreeID was added as a random effect in the MEM, Radial remained highly significant, but the effect of Eco-block became non-significant (Table 4-3). This suggests that the difference in eco-block observed in the fixed model may be due to inter-tree variability rather than true spatial differences. Section remained non-significant in both models.

These results indicate that Radial position is the most consistent and significant spatial factor influencing the GCV of black spruce wood, whereas Eco-block and Section show limited or inconsistent effects. The next section (4.2.2) examines whether similar patterns of spatial variation are observed in the carbon content of black spruce wood.

4.2.2 Variations in Carbon Content

Carbon is a key chemical component influencing the energy yield of biomass combustion. To assess how spatial factors affect carbon content in black spruce wood, both FEM and MEM were applied.

The FEM (Table 4-4) identified SectionMiddle as the only significant factor ($p < 0.001$). Specifically, samples from the middle section of the stem contained, on average, $1.007 \pm 0.232\%$ less carbon than those from the bottom section, representing the largest observed effect among all tested predictors. This negative estimate suggests a notable depletion of carbon content in the mid-stem eco-block, which may be linked to variation in growth rates or changes in wood formation patterns along the stem height.

In contrast, neither Eco-block nor Radial position showed significant effects ($p > 0.1$), with effect sizes being relatively small (e.g., RadialOuter: $-0.240 \pm 0.186\%$). The absence of significant eco-block or radial variation implies that carbon distribution in black spruce is more strongly influenced by vertical position than by geographic or radial factors.

Term	Estimate $\pm$ SE	p-value	Significance
Eco-block	-0.221 $\pm$ 0.186	0.237	
South			
SectionMiddle	-1.007 $\pm$ 0.232	< 0.001	***
SectionTop	-0.275 $\pm$ 0.232	0.237	
RadialOuter	-0.240 $\pm$ 0.186	0.199	

Table 4-4 Fixed-Effect Estimates for Carbon Model

Note: Significance codes: *** $p < 0.001$

Factor	Chi ²	df	p-value	Significance
Eco-block	0.01	1	0.9370	
Section	12.60	2	0.0020	**
Radial	2.90	1	0.0909	

Table 4-5 Type III ANOVA for Carbon (MEM)

Note: Significance codes: ** $p < 0.01$

In the MEM (Table 4-5), Section remained a significant predictor of carbon content ($p = 0.0024$), with the middle section containing significantly lower carbon than the bottom section. Radial position approached significance ($p = 0.0909$), suggesting a possible tendency for lower carbon content in outer wood, while Eco-block remained non-significant ($p = 0.9370$). These results confirm that vertical variation in carbon content is robust even after accounting for between-tree variability.

4.2.3 Variations in Hydrogen Content

Hydrogen content contributes to combustion characteristics such as ignition and burn rate. Although its proportion in biomass is relatively small, it can influence thermal degradation patterns and energy release dynamics. In this study, both FEM and MEM were applied to examine spatial variation in hydrogen content across Eco-block, Section, and Radial position.

The FEM (Table 4-6) indicated that SectionTop had a significant negative effect on hydrogen content ($p = 0.0019$), with an estimate of $-0.087 \pm 0.028\%$. This result suggests that wood from the upper portion of the stem contains, on average, 0.087% less hydrogen than wood from the bottom section, potentially reflecting changes in moisture-related compounds or structural carbohydrates with height. RadialOuter was marginally significant ($p = 0.0532$), showing a tendency for outerwood to contain slightly less hydrogen than innerwood, possibly due to differences in lignification and extractive deposition during radial growth.

The Eco-block factor did not exhibit a significant effect ($p = 0.275$), indicating that hydrogen distribution is relatively uniform between the North and South eco-blocks. Overall, these findings highlight that vertical position within the stem is the primary driver of hydrogen variation, with a secondary trend suggesting lower hydrogen in outerwood.

Term	Estimate $\pm$ SE	p-value	Significance
Eco-block South	-0.024 $\pm$ 0.022	0.275	
SectionMiddle	-0.008 $\pm$ 0.028	0.765	
SectionTop	-0.087 $\pm$ 0.028	0.0019	**
RadialOuter	-0.043 $\pm$ 0.022	0.0532	

Table 4-6 Fixed-Effect Estimates for Hydrogen Model

Note: Significance codes: ** $p < 0.01$

Factor	Chi ²	df	p-value	Significance
Eco-block	0.163	1	0.686	
Section	14.644	2	0.00066	***
Radial	7.162	1	0.0074	**

Table 4-7 Type III ANOVA for Hydrogen (MEM)

Note: Significance codes: *** $p < 0.001$, ** $p < 0.01$

In the MEM (Table 4-7), both Section and Radial position were statistically significant ($p = 0.0011$ and $p = 0.0074$, respectively). Specifically, hydrogen content was lower in the upper portion of the stem and in outerwood compared to their respective reference categories. These patterns may be related to differences in moisture content, cell wall chemistry, or tissue composition along the vertical and radial axes of the tree.

In summary, vertical position (Section) and radial position jointly influenced hydrogen content, whereas Eco-block had no detectable effect.

4.2.4 Variations in Ash Content

Ash content reflects the amount of inorganic residue in biomass after combustion and plays an important role in determining combustion quality and slagging potential. High ash content is typically associated with lower fuel quality.

The FEM (Table 4-8) indicated that both SectionTop and RadialOuter had significant positive effects on ash content ($p = 0.0117$ and $p < 0.001$, respectively), showing that samples from the upper stem and outerwood contained higher proportions of ash. Eco-block had no significant effect.

These patterns were corroborated by the MEM (Table 4-9), in which SectionTop remained significant and RadialOuter was highly significant ($p < 0.001$). Eco-block again showed no detectable influence. The agreement between the two models suggests that the observed variation is consistent across trees and not driven by individual-tree effects.

Overall, ash content tended to increase toward the stem periphery and upper sections, likely reflecting differences in mineral accumulation, bark content, or the physiological maturity of cells. Among the spatial factors, radial position emerged as the most consistent and influential predictor, mirroring the patterns observed for GCV.

The relatively high variability in ash content may partly reflect sample preparation issues, such as the inadvertent inclusion of fine dust particles, as well as potential instrument sensitivity limits. Given the small absolute magnitude of ash fractions, even minor handling differences could lead to amplified relative variation.

Term	Estimate $\pm$ SE	p-value	Significance
Eco-block South	-0.015 $\pm$ 0.011	0.159	
SectionMiddle	0.002 $\pm$ 0.013	0.881	
SectionTop	0.034 $\pm$ 0.013	0.0117	*
RadialOuter	0.054 $\pm$ 0.011	< 0.001	***

Table 4-8 Fixed-Effect Estimates for Ash Content

Note: Significance codes: *** $p < 0.001$, * $p < 0.05$

Factor	Chi ²	df	p-value	Significance
Eco- block	2.01	1	0.1576	
Section	9.77	2	0.0076	**
Radial	23.74	1	1.08e-06	***

Table 4-9 Type III ANOVA for Ash Content (MEM)

Note: Significance codes: *** $p < 0.001$, ** $p < 0.01$

4.2.5 Summary and Comparison of Models

Response Variable	Model Type	Eco- block	Section	Radial
GCV	Fixed	**		***
	Mixed			***
Carbon	Fixed		***	
	Mixed		**	
Hydrogen	Fixed		**	
	Mixed		***	**
Ash Content	Fixed		*	***
	Mixed		**	***

Table 4-10 Summary of Spatial Factor Significance in FEMs and MEMs

Note: Significance codes: *** $p < 0.001$, ** $p < 0.01$, * $p < 0.05$

The results of the fixed and mixed effects models are summarized in Table 4-10. Across all four wood properties, Radial position emerged as the most consistently significant spatial factor, particularly for GCV and Ash content, which are directly related to combustion performance. This effect remained highly significant even after accounting for inter-tree variability in the MEMs.

Section showed variable influence depending on the response variable. For Carbon and Hydrogen, significant or near-significant effects were observed, especially in the middle and top portions of the stem. The influence of Section was generally retained in the MEMs, suggesting that vertical position affects certain chemical properties.

In contrast, Eco-block did not show consistent significance in any model, and its effects disappeared entirely in the MEMs, implying that eco-block differences are likely confounded by individual tree variability rather than systematic spatial effects.

Overall, the spatial analysis revealed clear trends in how tree position affects wood properties. Radial variation emerged as the most robust and consistent factor, influencing both GCV and ash content, while vertical section contributed to chemical differences such as carbon and hydrogen levels. These findings provide a strong spatial foundation for evaluating wood combustion performance in black spruce.

Given that radial position was found to be the most significant and stable factor in the previous analyses, and that the bottom section provides the largest sample size across trees, Section 4.3 focuses exclusively on bottom-only samples to further examine radial variation under controlled vertical conditions.

4.3 Bottom-Only Supplementary Analysis

To further validate the influence of radial position on wood properties, this section focuses on a subset of samples collected exclusively from the bottom section of the stem. This bottom-only dataset includes the 6 full-tree samples from Batch 1, together with 8 additional trees from Batch 2 that each contributed both inner and outer samples at the bottom position. In total, the dataset comprises $14 \text{ trees} \times 2 \text{ radial positions} \times 3 \text{ replicates}$, resulting in 84 observations.

As reported in Section 4.2, radial position (inner and outer) was the most consistently significant factor affecting both GCV and ash content. However, those results were derived from a full factorial model that simultaneously considered eco-block, vertical section, and radial position, meaning that vertical variation could partially interact with radial effects. By restricting the analysis to the bottom section, vertical position is held constant, thereby eliminating this potential confounding source of variability.

Given the paired nature of the inner–outer observations within each tree, a paired t-test was selected to directly compare mean values between radial positions. This approach allows a focused assessment of whether the radial trends identified in the comprehensive analysis remain detectable under a fixed stem position, thereby providing a targeted validation of radial effects in the absence of vertical variation.

4.3.1 Overall Paired t-test for Bottom-only Samples

Variable	t value	df	p value	Mean diff	95% CI lower	95% CI upper	Sig.
GCV	3.104	13	0.00838	0.193	0.059	0.328	**
Carbon	1.070	13	0.30400	0.321	-0.327	0.968	
Ash	-3.755	13	0.00241	-0.061	-0.096	-0.026	**
Hydrogen	1.999	13	0.06690	0.042	-0.003	0.088	
SG	-4.972	13	0.00025	-0.018	-0.026	-0.010	***

Table 4-11 Paired t-test Results for Bottom-only Samples (Inner vs Outer) across Trees

Note: Significance codes: *** $p < 0.001$, ** $p < 0.01$

Paired t-tests on the bottom-only dataset revealed significant radial differences in several wood properties (Table 4-3). For GCV, Outer wood exhibited a significantly higher mean value than Inner wood ($t(13) = 3.104$, $p = 0.00838$), with an average difference of 0.193 MJ kg^{-1} (Outer – Inner) and a 95% confidence interval (CI) from 0.059 to 0.328 MJ kg^{-1} .

Ash content was significantly lower in Outer wood compared to Inner wood ($t(13) = -3.755$, $p = 0.00241$), with a mean difference of -0.061% and a CI from -0.096 to -0.026% . It should be noted that this result contrasts with the overall radial trend reported in Section 4.2.1, where outer wood exhibited lower GCV than inner wood across the full tree height. This reversal in the bottom-only dataset likely reflects vertical variation in radial effects, whereby radial patterns at the bottom section differ from those observed in the middle and top sections. By restricting the analysis to a single stem position, the bottom-only approach isolates local radial differences that may be obscured in whole-tree averages.

SG also showed a highly significant reduction in Outer wood ($t(13) = -4.972$, $p = 0.00025$), with a mean difference of -0.018 and a CI from -0.026 to -0.010 .

In contrast, carbon content ($p = 0.304$) and hydrogen content ($p = 0.0669$) did not exhibit statistically significant radial differences, with their confidence intervals crossing zero, indicating uncertainty in the direction of the difference.

These results confirm that, even when vertical variation is eliminated, radial position remains an important determinant for GCV, ash content, and SG, whereas its effect on carbon and hydrogen content is less consistent.

4.3.2 Eco-block Comparison of Radial Differences

To investigate whether the radial effects observed in the bottom-only dataset vary between geographic eco-blocks, separate paired t-tests were conducted for the North and South eco-blocks on variables that exhibited significant effects for both Eco-blocks and Radial in the FEMs (i.e., GCV and Ash) (Table 4-12).

Analyses were conducted separately for the North and South eco-blocks to examine whether radial differences vary geographically. Mean differences are calculated as outer minus inner at the bottom stem section within each eco-block ($n = 7$ pairs per eco-block). Positive values indicate higher outer values, and negative values indicate higher inner values.

Variable	Eco- blocks	t value	df	p value	Mean diff	95% CI lower	95% CI upper	Sig.
GCV	North	6.175	6	0.000829	0.241	0.146	0.336	***
GCV	South	1.209	6	0.272	0.146	-0.149	0.440	
Ash	North	-2.528	6	0.0448	-0.031	-0.060	-0.001	*
Ash	South	-3.487	6	0.0130	-0.092	-0.157	-0.027	**

Table 4-12 Paired t-test Results for Bottom-only Samples (Inner vs Outer) for GCV and Ash

Note: Significance codes: *** $p < 0.001$, ** $p < 0.01$, * $p < 0.05$

For GCV, the North eco-block showed a highly significant radial difference ($t(6) = 6.175$, $p = 0.000829$), with outerwood having a higher mean value than innerwood by 0.241 MJ kg^{-1} (95% CI: 0.146 to 0.336). In the South eco-block, the same directional trend was observed (outerwood > innerwood; mean difference = 0.146 MJ kg^{-1}), but the difference was not statistically significant ($t(6) = 1.209$, $p = 0.272$), and the confidence interval (-0.149 to 0.440) crossed zero.

For ash content, both eco-blocks displayed significant radial differences, with outerwood containing less ash than innerwood. In the North eco-block, the difference was modest but significant ($t(6) = -2.528$, $p = 0.0448$), with a mean reduction of 0.031% (95% CI: -0.060 to -0.001). In the South eco-block, the radial difference was stronger ($t(6) = -3.487$, $p = 0.0130$), with outerwood containing on average 0.092% less ash than innerwood (95% CI: -0.157 to -0.027).

These results indicate that the strong overall radial effect on GCV observed in the combined analysis is primarily driven by the North eco-block, whereas for Ash, the radial pattern is consistent across both eco-blocks, with the South showing a greater magnitude of difference. Building on these findings, Section 4.4 explores the relationships between GCV and other measured wood properties through correlation and regression analyses, providing further insight into the drivers of variation in energy content.

4.4 Correlation and Regression Analysis for Calorific Value

The GCV of woody biomass is a key parameter determining its energy potential and is strongly influenced by the chemical elements and physical properties of the wood. Carbon content is widely recognized as a primary contributor to higher calorific values, while ash content generally reduces combustion efficiency. Hydrogen may also play a role in enhancing energy density although to a lesser extent. In addition, SG has been considered as an indirect indicator of fuel quality, as it relates to wood density and thus energy yield per unit volume.

To quantify the relationships between GCV and these wood properties, a correlation and regression analysis was performed using the MeanData dataset ($n = 52$ samples), derived from the averaged results of three replicates per sample. The analysis focused on four independent variables — specific gravity (SG), carbon (C), hydrogen (H), and ash content, with gross calorific value (GCV) as the dependent variable.

4.4.1 Pearson Correlation Analysis

Pearson correlation analysis was conducted to evaluate the bivariate linear relationships between GCV and four wood property variables: SG, C, H, and Ash.

Pair	r (Pearson)	p-value	95% CI (Lower)	95% CI (Upper)
GCV ~ SG	-0.403	0.003*	-0.609	-0.146
GCV ~ C	0.206	0.143	-0.071	0.453
GCV ~ H	0.141	0.318	-0.137	0.399
GCV ~ Ash	-0.178	0.206	-0.430	0.100

Table 4-13 Pearson correlation coefficients (r), p-values, and 95% confidence intervals for the Relationships between GCV and SG, C, H, Ash (n = 52)

A significant negative correlation was found between GCV and SG ($r = -0.403$, $p = 0.003$), indicating that samples with higher SG tended to have lower calorific values. Carbon ($r = 0.206$, $p = 0.143$) and hydrogen ($r = 0.141$, $p = 0.318$) showed weak positive correlations with GCV, whereas ash content exhibited a weak negative correlation ($r = -0.178$, $p = 0.206$). However, these latter relationships were not statistically significant ($p > 0.05$).

The negative relationship between SG and GCV may reflect the influence of wood density on combustion efficiency, as denser samples may contain a higher proportion of structural compounds with lower energy yield per unit mass. The directions of the correlations for C, H, and ash are consistent with combustion theory, where carbon contributes positively and ash negatively to energy content, but the lack of statistical significance suggests that these effects may be moderated by other wood properties or spatial variability.

These correlation results were further examined through univariate regression models in Section 4.4.2 to quantify the individual effects of each wood property on GCV and to visualize their trends. This approach allows the identification of the most influential variable(s) and provides a direct basis for discussing how spatial variations in wood properties, as analyzed in Sections 4.2 and 4.3, may contribute to differences in energy content.

4.4.2 Univariate Regression Modeling

To further evaluate the individual effects of each wood property on calorific values, univariate linear regression models were fitted with GCV as the dependent variable and each predictor, SG, C, H, and Ash entered separately. This analysis complements the correlation results by quantifying the magnitude and direction of each relationship, while also providing visual representation of the fitted trends. Scatterplots with regression lines and model equations were produced to facilitate interpretation and to highlight the most influential variable(s).

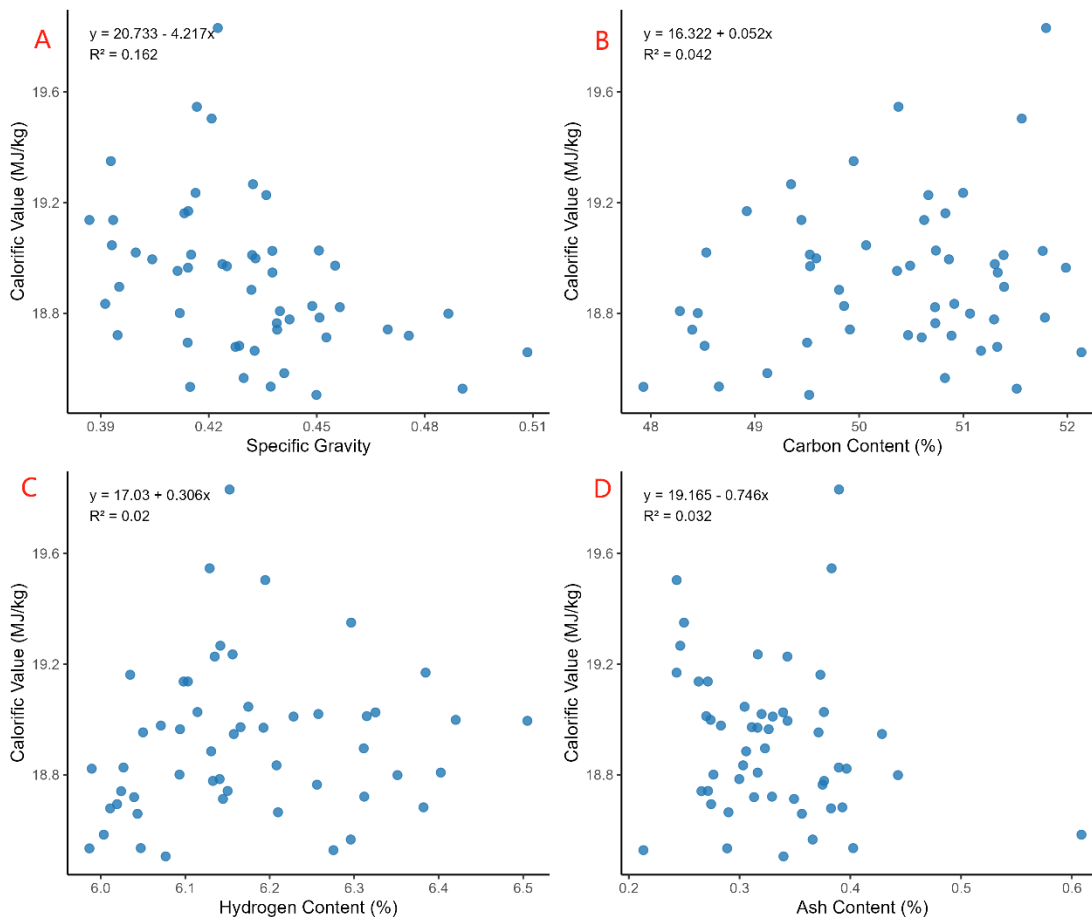


Figure 4.8 Scatterplots showing bivariate relationships between GCV and (A) SG, (B) carbon content, (C) hydrogen content, and (D) ash content.

Note:

Each panel reports the least-squares regression equation and coefficient of determination (R^2), based on the mean values of three replicates for each sample ($n = 52$). Among the four relationships, only the negative correlation between specific gravity and calorific value (panel A) was statistically significant ($p < 0.01$), while the others were non-significant ($p > 0.05$).

Predictor Variable	Regression Equation	R ²	p-value	Significance
SG	$y = 20.733 - 4.217x$	0.162	0.003	**
C (%)	$y = 16.322 + 0.052x$	0.042	0.143	
H (%)	$y = 17.030 + 0.306x$	0.020	0.318	
Ash (%)	$y = 19.165 - 0.746x$	0.032	0.206	

Table 4-14 Regression Statistics for Univariate Models of GCV against SG, C, H, and Ash

Note:

- 1) Significance levels: $p < 0.05$ (*), $p < 0.01$ (**)
- 2) Regression equations are based on univariate linear models with GCV as the dependent variable (n = 52).

The univariate regression analyses revealed that among the four wood properties tested, only SG showed a statistically significant relationship with GCV ($p < 0.01$), exhibiting a negative slope (Figure 4.6A). This indicates that samples with higher SG tended to have lower GCV. Carbon content (Figure 4.6B) and hydrogen content (Figure 4.6C) were positively associated with GCV, whereas ash content (Figure 4.6D) was negatively associated; however, these trends were weak and non-significant ($p > 0.05$). The coefficients of determination (R^2) were generally low (< 0.20), suggesting that single variables explained only a small proportion of the variation in GCV. These results are consistent with the correlation analysis in Section 4.4.1, where SG was the only variable exhibiting a significant correlation with GCV.

The regression statistics for all univariate models are summarized in Table 4-14, providing the regression equations, R^2 , and significance levels. These values complement the visual interpretation of the scatterplots, enabling direct comparison of the strength and direction of each relationship. Consistent with the graphical trends, SG exhibited the highest explanatory power ($R^2 = 0.162$) and was the only significant predictor of GCV ($p < 0.01$). The remaining variables showed low R^2 values (< 0.05) and non-significant p-values, reinforcing the conclusion that their individual contributions to GCV are minimal.

Given that only one predictor exhibited a significant univariate relationship with GCV and that the others showed weak, non-significant trends, multiple linear regression (MLR) analysis was not pursued. This decision was made to maintain focus on the most relevant variable and to avoid overfitting models with limited explanatory power.

Although some correlations appeared statistically significant, the effect sizes were small and the explanatory power of regression models remained weak. Therefore, these relationships should be interpreted as symbolic tendencies rather than meaningful predictive drivers of calorific value.

4.5 Intra-Tree Variation in Typical Trees

To illustrate the spatial variation patterns within individual trees, two representative specimens were selected for detailed intra-tree analysis: Tree N-17 from the North eco-block and Tree S-2 from the South eco-block. These trees were chosen based on their complete vertical and radial sampling structure (top, middle, and bottom sections; inner and outer radial positions) and contrasting magnitudes of variation in GCV. Tree S-2 exhibited the largest vertical range in GCV among the complete-sample trees (0.820 MJ kg^{-1}), while Tree N-17 showed a moderate but clear vertical trend (0.533 MJ kg^{-1}). The aim of this section is to qualitatively compare the vertical (sectional) and radial (inner–outer) patterns of key wood properties in these two trees, highlighting individual-specific deviations from the general trends reported in Sections 4.2 and 4.3

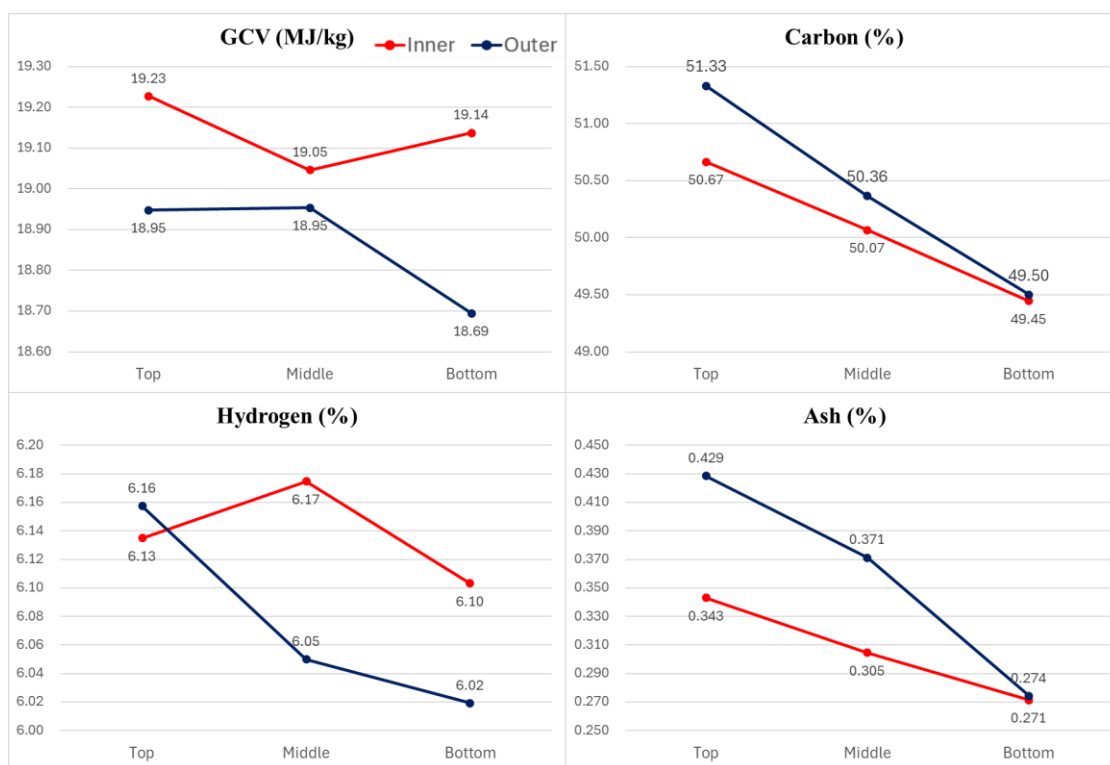


Figure 4.9 Vertical (sectional) and Radial (inner–outer) Variation in GCV, carbon, hydrogen, and ash content for Tree N-17 (North eco-block).

Note: Inner wood generally showed higher GCV, while carbon and ash contents decreased from top to bottom; hydrogen content exhibited minimal variation.

Figure 4.9 illustrates vertical (sectional) and radial (inner–outer) variation in GCV, carbon, hydrogen, and ash content for Tree N-17. For GCV, the inner radial position showed a slight decline from the top ($19.23 \text{ MJ}\cdot\text{kg}^{-1}$) to the middle section ($19.05 \text{ MJ}\cdot\text{kg}^{-1}$), followed by a modest increase at the bottom ($19.14 \text{ MJ}\cdot\text{kg}^{-1}$). In contrast, the outer radial position remained stable between the top and middle sections ($18.95 \text{ MJ}\cdot\text{kg}^{-1}$) before decreasing to $18.69 \text{ MJ}\cdot\text{kg}^{-1}$ at the bottom. Carbon content decreased progressively from top to bottom in both radial positions, with outer wood consistently exhibiting slightly higher values than inner wood. Hydrogen content exhibited minimal vertical variation, ranging from 6.13–6.17% in inner wood and 6.05–6.16% in outer wood. Ash content declined vertically in both radial positions, with outer wood consistently showing higher ash levels than inner wood.

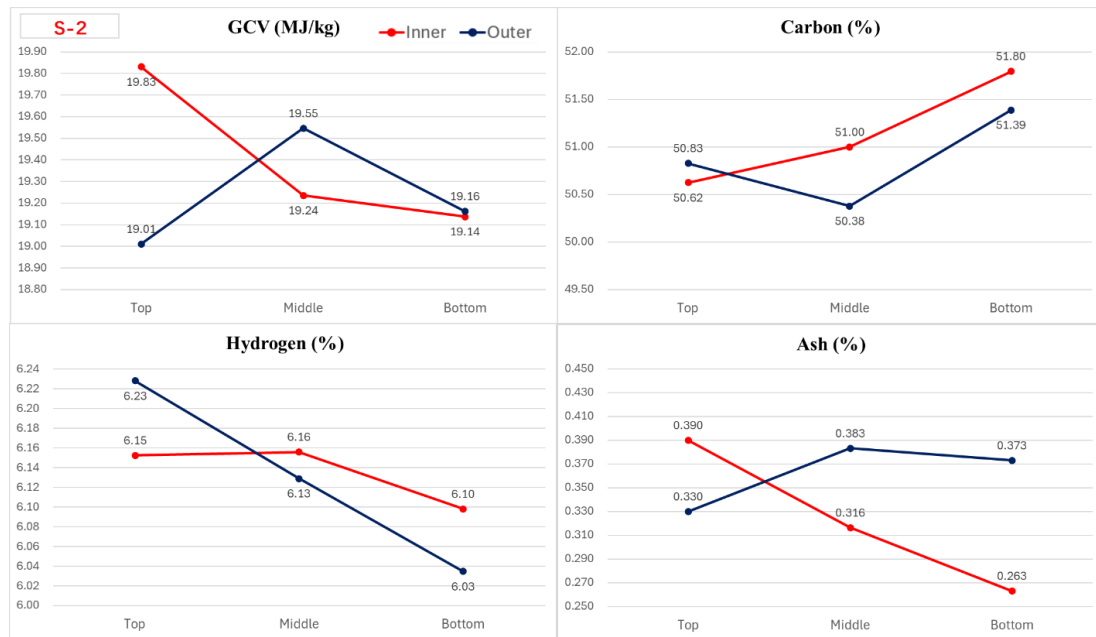


Figure 4.10 Vertical (sectional) and Radial (inner–outer) Variation in GCV, carbon, hydrogen, and ash content for Tree S-2 (South eco-block).

Note: Inner wood exhibited a marked decline in heat content from top to bottom, while outer wood peaked in the middle section. Carbon content increased vertically in both radial positions, with a larger change in inner wood. Ash content displayed an outer > inner pattern, while hydrogen content decreased steadily from top to bottom in both radial positions.

Figure 4.10 illustrates the corresponding variation in Tree S-2. In contrast to Tree N-17, GCV in the inner radial position decreased sharply from the top ($19.83 \text{ MJ}\cdot\text{kg}^{-1}$) to the bottom ($19.14 \text{ MJ}\cdot\text{kg}^{-1}$), whereas the outer radial position peaked at the middle section ($19.55 \text{ MJ}\cdot\text{kg}^{-1}$) before declining toward the base. Carbon content increased from top to bottom in both radial positions, with the innerwood showing a larger magnitude of change (50.62% to 51.80%) compared with outerwood (50.83% to 51.39%). Hydrogen content decreased steadily in both radial positions, with slightly higher values in outerwood at the top section. Ash content in the inner radial position declined sharply from top to bottom, while outer wood peaked in the middle section before decreasing toward the base.

A direct comparison of the two representative trees reveals distinct contrasts in the magnitude and direction of intra-tree variability. Tree S-2 exhibited greater vertical changes in heat and carbon content than Tree N-17, particularly in the inner radial position. By contrast, radial differences in ash content were consistent across trees, with outer wood generally exceeding inner wood, while hydrogen content showed minimal radial variation. These findings indicate that, although the general patterns identified in Sections 4.2 and 4.3 are evident at the population level, notable deviations can occur at the individual-tree level, likely due to localized growth conditions, resource allocation patterns, and inherent physiological differences. Such results highlight the importance of accounting for individual-tree variability when evaluating biomass quality and developing representative sampling strategies for fuel property assessment.

4.6 Discussion

The dataset comprised trees collected from two contrasting biogeographic eco-blocks (North and South), allowing a comparison of eco-blocks differences in wood properties. Within each tree, samples were further stratified by vertical position along the stem (Top, Middle, Bottom) and radial position from bark to pith (Outer vs. Inner). A combination of fixed-effects linear models and mixed-effects models was employed to capture both population-level trends and tree-level variability, supplemented by bottom-only paired comparisons and regression analyses. The findings therefore represent the variability patterns of this specific population of black spruce and should be interpreted within the ecological context of Labrador.

Distinct spatial patterns were observed in the chemical elements and calorific value of black spruce wood. Carbon content declined from the top to the bottom sections of the stem and was consistently higher in the outer wood, reflecting increased lignification and the greater presence of latewood. Calorific value exhibited moderate vertical variation, with only slight changes along the stem, but showed clearer radial differences, with inner wood generally presenting higher energy values. Hydrogen content remained largely uniform across both vertical and radial dimensions, indicating relative chemical stability. In contrast, ash content decreased from the upper to the lower stem but was consistently elevated in the outer portion, likely due to higher deposition of inorganic constituents near the cambium. These results are consistent with previous descriptions of radial and vertical variation in wood properties, which highlight the influence of age-related tissue development and the transition from juvenile to mature zones in determining chemical and energetic characteristics (Niemz et al., 2023; Rowell, 2005).

The relationships between chemical elements and calorific value further emphasize the role of intrinsic wood properties in determining energy potential. Carbon content was positively associated with gross calorific value, supporting the notion that carbon-rich tissues contribute more effectively to combustion energy release (Demirbas, 2002). Conversely, ash content exerted a strong negative influence on calorific value, as inorganic residues do not contribute to energy production and can even reduce combustion efficiency through slagging and fouling. Hydrogen content, despite its theoretical role in enhancing energy density, showed little variability and therefore limited predictive value in this study. These findings highlight the importance of considering both organic and inorganic fractions of biomass when evaluating fuel quality. From an applied perspective, such insights are directly relevant to the optimization of biomass energy systems, where the selection of feedstocks with high carbon and low ash contents can significantly improve conversion efficiency and sustainability (McKendry, 2002).

Despite providing new insights into spatial variability in black spruce, this study has several limitations that should be acknowledged. The analysis was restricted to a single species from Newfoundland and Labrador, and therefore the results may not be directly generalizable to other eco-blocks or coniferous species. In addition, the regression models used to evaluate the relationship between chemical elements and calorific value exhibited limited explanatory power, indicating that key drivers of energy potential may lie beyond basic elemental composition and could include anatomical structure, mineral inclusions, or other environmental influences. Future research should expand to incorporate a broader range of species, larger sample sizes, and direct combustion performance testing, as suggested in comprehensive assessments of biomass combustion properties (Jenkins et al.,

1998). Such efforts would improve the robustness and applicability of biomass fuel quality evaluations across diverse forest ecosystems.

The GCV of black spruce residues measured in this study (~19 MJ/kg) is consistent with the ranges reported for other tree species in Eastern Canada. As shown in Table 4-15, balsam fir exhibits values between 18.3 and 19.1 MJ/kg (Bouchard et al., 2013), which overlap with the lower bound of black spruce. Red maple and yellow birch present similar energy values ranging from 18.0 to 19.2 MJ/kg (Hosegood et al., 2011). In contrast, white pine demonstrated relatively higher values of 19.5 to 20.3 MJ/kg (Paré et al., 2011), slightly exceeding those of black spruce. This may be due to the existence of high resin amount in white pine. These comparisons suggest that black spruce from Labrador is well within the expected calorific range of regional conifers, making it a good candidate for bioenergy applications.

Wood Species	Gross Calorific Value (MJ/kg)	Reference
Balsam Fir (<i>Abies balsamea</i>)	18.3 – 19.1	(Bouchard et al., 2013)
Red Maple (<i>Acer rubrum</i>)	18.0 – 18.6	(Hosegood et al., 2011)
Yellow Birch (<i>Betula alleghaniensis</i>)	18.5 – 19.2	(Hosegood et al., 2011)
White Pine (<i>Pinus strobus</i>)	19.5 – 20.3	(Paré et al., 2011)

Table 4-15 Reported oven-dry GCV of selected Canadian tree species and wood fuels

5 Conclusions

5.1 Summary of Key Findings

This study investigated the spatial variability of gross calorific value, carbon, hydrogen, and ash content in black spruce (*Picea mariana*) sampled from Labrador, Canada. The following key findings were obtained:

- Sulfur (S) content was essentially absent in this population, with only ppm-level traces detected in two replicates from a single sample, indicating that Labrador black spruce contains negligible sulfur.
- Carbon amount (C) decreased by approximately 1.4% from the bottom to the top of the stem and was consistently ~0.5–1% higher in the outer wood, reflecting radial differentiation in tissue composition.
- Hydrogen content (H) was remarkably stable (6.09–6.19%) across both vertical and radial positions, suggesting limited variability and weak explanatory power for calorific value.
- Gross calorific value (GCV) remained relatively stable along the stem (19.0–19.2 MJ·kg⁻¹), but showed clear radial variation, with inner wood averaging ~0.3 MJ·kg⁻¹ higher than outer wood.
- Ash content showed strong spatial contrasts: vertically, it was ~13% higher in the top than the bottom sections; radially, it was consistently ~11% higher in the outer wood than the inner wood.

- Relationships with GCV confirmed that carbon was positively associated with energy potential, ash exerted a strong negative influence, and hydrogen played only a minor role.
- Regression models explained a limited share of GCV variation (adjusted $R^2 < 0.1$), implying that additional factors—such as anatomical structure, mineral inclusions, or growth conditions, contribute to biomass energy quality.

In summary, this work provides the first detailed characterization of calorific value and elemental composition in black spruce sampled from the two districts of Labrador: CC19005 and CC19011. The results show that inner wood generally provides higher fuel quality than outer wood, and that carbon and ash are the most decisive chemical determinants. These insights not only clarify the intrinsic energy potential of black spruce within these eco-blocks but also establish a foundation for predicting biomass fuel quality in other conifer species. Future research extending across broader species, ecological zones, and combustion performance tests will strengthen the generalizability of these findings and support more reliable biomass energy assessments.

5.2 Implications

The findings of this study provide important implications for both biomass energy applications and future research directions.

- From a practical perspective, the consistently higher ash content in outer wood highlights potential challenges such as slagging and fouling during combustion, while the slightly higher GCV in inner wood suggests that stem-core material may provide more stable and efficient fuel.
- From a methodological perspective, the study demonstrates the importance of applying mixed-effects models to account for tree-level variability, as eco-blocks differences proved to be tree-driven rather than site-driven.
- For biomass assessment, the results emphasize the need for spatially informed sampling strategies instead of bulk averages, particularly when feedstock classification is intended to guide industrial utilization.

Looking ahead, further work should broaden the scope beyond black spruce in Labrador. Comparative studies across species and ecological blocks, coupled with direct combustion performance testing, would help validate whether these compositional patterns translate into operational outcomes. Integrating anatomical variables such as lignin content, extractives, and specific gravity profiles could improve predictive models for calorific value. Moreover, developing rapid assessment tools calibrated with chemical and calorimetric data could enable faster and more reliable screening of biomass fuel quality.

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