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CORRELAÇÃO ENTRE A COMPOSIÇÃO QUÍMICA DA MADEIRA E O AUMENTO DO PODER CALORÍFICO ATRAVÉS DO TRATAMENTO TÉRMICO

CORRELATION BETWEEN THE CHEMICAL COMPOSITION OF WOOD AND THE INCREASING OF ITS CALORIFIC VALUE THROUGH HEAT TREATMENT

CORRELACIÓN ENTRE LA COMPOSICIÓN QUÍMICA DE LA MADERA Y EL AUMENTO DE SU PODER CALORÍFICO MEDIANTE TRATAMIENTO TÉRMICO

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RESUMO

Introdução: A maior importância da biomassa reside no seu poder calorífico superior, quando considerada para produção de energia. O poder calorífico é significativamente afetado pelas alterações na composição química da madeira que ocorrem durante o tratamento térmico.

Objetivo: Compreender a influência do tratamento térmico no poder calorífico dos constituintes químicos de duas madeiras de folhosas: Sapelli e Castanheiro e duas madeiras de resinosas: pinheiro silvestre e pinheiro siberiano.

Métodos: O poder calorífico foi determinado por um calorímetro Parr – modelo 6400. O teor de extrativos foi determinado por extração sucessiva de Soxhlet utilizando cerca de 3 g de cada amostra e 150 ml de diclorometano, etanol e água como solventes. O teor de extrativos foi determinado de acordo com o método TAPPI 204, e a lenhina insolúvel pelo método Klason Tappi T 222 om-02. Para a determinação da holocelulose foi utilizado o método do clorito ácido.

Resultados: O poder calorífico das madeiras não tratadas variou entre 18,98 MJ/kg para o castanheiro e 20,35 MJ/kg para o pinheiro siberiano. O tratamento térmico resultou num aumento do poder calorífico para a maioria das amostras de madeira em estudo.

Conclusão: O aumento do poder calorífico observado durante o tratamento térmico em madeiras de folhosas e resinosas deve-se principalmente ao aumento do teor de lignina, embora os extrativos de diclorometano também desempenhem um papel importante.

Palavras-chave: tratamento térmico; composição química; poder calorífico

ABSTRACT

Introduction: The greatest importance of biomass lies in its Higher Heating Value (HHV), when considered for energy production. The calorific value is significantly affected by the changes in the chemical composition of the wood that occur during heat treatment.

Objective: To understand the effect of heat treatment on the calorific value of the chemical constituents of two hardwoods: Sapelli and chestnut, and two softwoods: Scots pine and Siberian pine.

Methods: The calorific value was determined by a Parr calorimeter – model 6400. The content of extractives was determined by successive Soxhlet extraction using about 3 g of each sample and 150 ml of dichloromethane, ethanol, and water as solvents. The extractives content was determined in accordance with TAPPI 204, and insoluble lignin by the Klason method Tappi T 222 om-02. For the determination of holocellulose, the acid chlorite method was used.

Results: The calorific value of untreated wood ranged from 18.98 MJ/kg for chestnut to 20.35 MJ/kg for Siberian pine. Heat treatment resulted in an increase in the calorific value for most of the wood samples studied.

Conclusion: The rise in HHV observed during heat treatment in softwoods and hardwoods is mainly due to the increase in lignin content, although dichloromethane extractives also play an important role.

Keywords: heat treatment; chemical composition; calorific value

RESUMEN

Introducción: La mayor importancia de la biomasa radica en su mayor poder calorífico, cuando se considera para la producción de energía. El poder calorífico se ve significativamente afectado por los cambios en la composición química de la madera que se producen durante el tratamiento térmico.

Objetivo: Comprender la influencia del tratamiento térmico en el poder calorífico de los componentes químicos de dos maderas de hoja ancha: sapelli y castaño, y dos maderas de coníferas: pino silvestre y pino siberiano.

Métodos: El poder calorífico se determinó mediante un calorímetro Parr – modelo 6400. El contenido extractivo se determinó mediante extracciones Soxhlet sucesivas utilizando aproximadamente 3 g de cada muestra y 150 ml de diclorometano, etanol y agua como solventes. El contenido de extractivos se determinó según el método TAPPI 204 y de lignina insoluble mediante el método Klason Tappi T 222 om-02. Para la determinación de la holocelulosa se utilizó el método del clorito ácido.

Resultados: El poder calorífico de las maderas sin tratar osciló entre 18,98 MJ/kg para el castaño y 20,35 MJ/kg para el pino siberiano. El tratamiento térmico dio lugar a un aumento del poder calorífico en la mayoría de las muestras de madera analizadas.

Conclusión: El aumento de poder calorífico observado durante el tratamiento térmico en maderas duras y blandas se debe principalmente al aumento del contenido de lignina, aunque los extractivos de diclorometano también juegan un papel importante.

Palabras clave: tratamiento térmico; composición química; valor calorífico

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INTRODUCTION

Biomass, particularly wood- and shrub-derived feedstocks that account for more than 80% of biomass used for energy, is an affordable and sustainable renewable alternative to fossil-based products for heat, power, fuels, materials, and chemicals, with Higher Heating Value (HHV) being one of its most important fuel properties (Menon and Rao, 2012). Biomass is characterized as lignocellulosic in nature, comprising both softwoods and hardwoods, commonly recognized as the standard biomass material. The chemical composition of biomass can be generally classified into two groups based on molecular sizes and structural functions: structural compounds (cellulose, hemicelluloses, and lignin), crucial for cell wall integrity, and nonstructural components (extractives and inorganic components), which can be eliminated without affecting the cell wall structure (Esteves et al, 2023).

There are several commercial thermal treatment processes, such as Thermowood ®, Plato ® Bois Perdure ®, or Rectification ®, which vary in their approach to heating and are typically conducted at relatively moderate temperatures (180-220°C). Nevertheless, these temperatures are sufficiently high to induce changes in the chemical composition of wood, specifically affecting extractives and structural compounds, resulting in a new material with improved properties (Domingos et al., 2020).

Hemicelluloses are commonly acknowledged as the initial components to undergo degradation during heat treatment due to their characteristics, such as low molecular weight, branched structure, and amorphous nature. Although cellulose is known to possess greater resistance in comparison to hemicelluloses, there is noticeable degradation of the amorphous cellulose, leading to an increase in crystalline cellulose (Domingos et al., 2020). The treatment's impact on lignin is evident, although its degradation proceeds at a slower rate when compared to carbohydrates, resulting in a higher percentage post-treatment. These chemical transformations induced by the treatment process are recognized for their ability to enhance the calorific value of heat-treated woods. The relationship between the chemical composition and the calorific value of wood primarily arises from the higher calorific value of lignin as opposed to cellulose. The lower HHV of cellulose is attributed to its high oxidation levels, which contrasts with lignin (Demirbas 2001; Moya and Tenório, 2013).

Extractives can significantly influence wood calorific value depending on their amount and composition, since less oxidized compounds such as lipids and terpenoid hydrocarbons generally yield more energy upon combustion than more oxidized phenolic compounds, with reported HHV values for extractives ranging from 32.3 to 37.2 MJ/kg (Howard, 1973; Chandler et al., 1983; Domingos et al., 2020; Senelwa and Sims, 1999).

HHV of lignin varies with lignin type and isolation method, ranging approximately from 22.2 to 28.5 MJ/kg depending on biomass source (Demirbas, 2017).

Cellulose exhibits distinct characteristics from hemicelluloses, and despite the several types of hemicelluloses present, their calorific values show minimal discrepancies attributed to their analogous chemical compositions. The heating value of cellulose remains consistent across various species, as indicated by multiple studies demonstrating similar values. For instance, reported values range closely from 17.22 MJ/kg (Goldberg et al., 2015) to 17.56 MJ/kg (Ioelovich, 2018).

There have been limited studies conducted on the impact of chemical composition on the calorific value of biomass, as evidenced by the bibliometric analysis (Esteves et al., 2023). However, multiple studies have indicated that the higher heating values (HHVs) of biomass materials are indicative of their chemical compositions, particularly the compositions of the macromolecular compounds that constitute the majority of biomass.

The objective of this research was to examine the correlation between the chemical composition of wood and the enhancement of its calorific value through thermal modification. A comprehensive analysis was conducted on two types of softwoods (Scots pine and Siberian pine) and two types of hardwoods (Sapelli and Chestnut)

1. METHODS

1.1 Sample

Samples of four different wood species were obtained from a local mill in Turkey in the region of Duzce city. The species were Sapelli (*Entandrophragma cylindricum* Sprague), Chestnut *(Castanea sativa Mill.*), Scots pine (*Pinus sylvestris* L.), and Siberian pine (*Pinus sibirica* Du Tour). These samples were heat-treated by the ThermoWood ® method, using a kiln belonging to a private commercial Novawood Factory in Gerede – Bolu. These woods were chosen since they are commonly available commercially. Thermowood treatment was carried out using a controlled thermal modification process in the absence of oxygen to prevent combustion. Wood specimens were subjected to a maximum temperature of 212 °C in a closed chamber under a low-oxygen atmosphere, using steam. The treatment process consisted of three main phases: (i) initial drying and heating, during which the temperature was gradually increased to 212 °C over approximately 2–3 h (corresponding to a heating rate of about 2–5 $°C \cdot min^{-1}$) to reduce moisture content to near zero; (ii) thermal modification at 212 °C for 1 and 2 h; and (iii) a cooling and conditioning phase, in which the material was gradually cooled over 4–6 h and reconditioned to a target moisture content.

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1.2 Data collection instruments

The HHV was determined using a Parr calorimeter – model 6400 (Parr Instrument Company, USA). Three replicates for each wood sample were made, and results are reported as mean values with standard deviations. Prior to analysis, approximately 0.5 g of each sample was ground, oven dried at 105°C until constant mass, and afterwards pressed to form a small pellet, which was inserted into the heat pump. Combustion was carried out in an oxygen atmosphere at high pressure. Since it is not possible to determine directly the amount of heat released in the combustion, the temperature rise in the water contained in the calorimetric container surrounding the sample was measured. Knowing the temperature rise and the calorific capacity (C) of water (amount of heat required to heat the water 1°C), the HHV of the material was obtained. The calorimeter was calibrated using benzoic acid as a standard reference material. Corrections for ignition wire combustion and acid formation were applied according to the manufacturer's instructions.

Prior to chemical analysis, all samples were ground in a Retsch SMI mill and sifted with a sieve Retsch AS200 for 20 min at a speed of 50 rpm. The 40-60 mesh fraction was used.

The extractive content was measured through successive Soxhlet extractions, utilizing approximately 3 g of each sample, starting with 150 mL of dichloromethane (DCM) followed by ethanol and water as solvents. The extraction durations were 6 hours for DCM and 16 hours for both ethanol and water. The extractive content was determined in relation to the dry wood in accordance with TAPPI T 204 "Solvent Extractives of Wood and Pulp."(TAPPI, 2007). Insoluble lignin was determined by the Klason method Tappi T 222 om-02 (Tappi, 2002) with some changes. A total of 350 mg of ground samples was placed in a beaker, and 3 mL of 72% chilled sulfuric acid was added to each. The beakers were then placed in a 30 °C thermal bath for one hour, with the mixture stirred using a glass rod every 10 minutes. Afterward, 84 mL of distilled water was added to each sample, which was then transferred to 100 mL thermal glass bottles. These bottles were placed in an autoclave containing water at the bottom and heated for one hour at 120 °C. The bottles of the autoclave were removed and cooled with ice. The mixture was filtered with N°4 crucibles. The percentage of insoluble lignin was determined in relation to dry wood.

The determination of Holocellulose was done according to the chlorite method (Wise et al 1946), and α-cellulose was determined following Tappi T 429 cm-10 (2010) as described by (Domingos et al., 2020), and the hemicellulose was obtained by difference. Three replicates for each wood sample were made.

The statistical treatment of the data consisted of the determination of Standard deviations.

2. RESULTS AND DISCUSSION

Table 1 shows the average and the standard deviation of HHV for four different species of wood, two softwoods and two hardwoods, before and after being heat treated for 1 h and 2 h. In this study, the HHV of untreated softwoods ranged from 19.60 MJ/kg to 20.35 MJ/kg, and for hardwoods from 18.98 to 19.30 MJ/kg, therefore confirming that softwoods generally have higher HHV as stated in other studies (Telmo and Lousada, 2011; Domingos et al., 2020; García et al., 2012). Softwoods generally have higher heating values than hardwoods due to their higher lignin and resin content. According to Harker et al. (1982), who compiled information from the literature on 402 wood species, calorific values for hardwoods were found to be between 15.6 and 23.7 MJ/kg, while for softwoods, they ranged between 18.6 and 28.5 MJ/kg. On the contrary, in the Phyllis database (2002), the values reported for softwoods ranged from 18.40 to 20.52 MJ/Kg and for hardwoods from 17.38 to 23.05 MJ/Kg. Telmo and Lousada (2011) tested several softwoods, European and tropical hardwoods used for pellets, and stated that the higher calorific values for softwoods ranged from 19.66 to 20.36 MJ/Kg, and for European hardwoods, varied between 17.63 and 19.13 MJ/Kg. Tropical hardwood, however, generally presented higher HHV, ranging from 19.05 to 20.81 MJ/Kg, which can be due to the higher amount of extractives. Additionally, studies made by Ioelovich (2018), where he determined the Higher Heating Values of lignins from various types of wood and herbaceous substances through a method involving sulfur extraction, revealed that softwoods exhibited higher HHVs compared to hardwoods and herbaceous plants. The HHV for spruce was recorded at 26.73 MJ/kg, whereas pine displayed a value of 27.00 MJ/kg. However, the HHV for poplar, a hardwood, was lower at 25.45 MJ/kg, aligning more closely with the HHVs of herbaceous materials like bagasse (25.21 MJ/kg), switchgrass (25.27 MJ/kg), straw (25.16 MJ/kg), and corn stalks (25.20 MJ/kg).

When comparing the amount of lignin between the softwoods and hardwoods, it is clear that both softwoods have higher lignin content, which can be the main reason for the higher heating values. Similarly, the higher HHV of Siberian pine can be due to the higher amount of lignin (26.6%) compared to Scots pine (25.8%), but also to the higher amount of lipophilic extractives (4.4%) compared to (0.5%) (Table 2). Nevertheless, according to Telmo and Lousada (2011), the higher HHV of softwoods is more related to the presence of extractives (resin content) than to lignin.

Table 1 - High Heating Value of untreated and heat-treated woods at 1-2h with standard deviations in brackets

HHV(MJ/kg)	Sapelli	Standard deviation	Chestnut	Standard deviation	Scots pine	Standard deviation	Siberian pine	Standard deviation
Initial	19.304	(0.058)	18.979	(0.084)	19.601	(0.067)	20.346	(0.003)
Heat treated (1h)	19.744	(0.109)	19.888	(0.044)	20.584	(0.098)	20.203	(0.063)
Heat treated (2h)	19.877	(0.105)	20.030	(0.182)	20.867	(0.120)	20.357	(0.098)

Heat treatment resulted in an increase in HHV for almost all wood specimens under examination. The increase was more pronounced in Chestnut wood, rising from 18.98 MJ/kg to 20.03 MJ/kg, while the smallest was observed for Siberian wood, showing a modest rise from 20.35 MJ/kg to 20.36 MJ/kg, and even a decrease for the 1h treatment As mentioned before, untreated wood HHV is lower than for heat-treated wood, which is clear in Table 1. It is widely recognized that thermal treatments such as ThermoWood® lead to a rise in the lignin and extractive contents, due to the accelerated degradation rate of polysaccharides. The increase in HHV can be linked to the increase in lignin content in contrast to carbohydrates, given that lignin is acknowledged to possess a higher HHV compared to carbohydrates. This apparent increase in lignin is due to the faster degradation of polysaccharides, leading to a percentage increase in lignin.

Table 2 – Chemical composition of untreated and heat-treated woods for 1h and 2h

		Dicloromethane (%)	Ethanol (%)	Water (%)	Total (%)	Lignin (%)	Holocellulose (%)
Sapelli	0h	0.57	6.51	3.80	10.88	24.31	64.81
	1h	0.72	3.52	2.84	7.08	30.53	62.38
	2h	0.73	4.67	4.27	9.67	32.16	58.16
Chestnut	0h	0.32	2.88	3.79	6.99	24.61	68.39
	1h	1.71	5.91	4.64	12.26	30.99	56.74
	2h	1.61	6.91	3.70	12.22	30.09	57.69
Scots pine	0h	0.52	1.11	1.13	2.76	24.20	73.04
	1h	1.82	3.26	2.88	7.96	31.02	61.01
	2h	0.87	3.97	3.13	7.97	35.43	56.60
Siberian pine	0h	4.42	1.00	0.99	6.41	26.33	67.26
	1h	2.69	2.41	1.52	6.62	33.30	60.08
	2h	2.35	2.25	1.70	6.3	34.25	59.45

There were no considerable differences between the wood samples treated for 1 and 2 hours. Nevertheless, as indicated by Domingos et al. (2016), who investigated the HHV of *Eucalyptus globulus* and *Pinus pinaster* woods subjected to heat-treatment for 2 to 24h at temperatures ranging from 170 °C to 190 °C, there was a noticeable increase in HHV following heat treatment. The increase in HHV was more pronounced at higher treatment temperatures and with prolonged treatment durations. Consequently, an increase is expected between the 1-hour and 2-hour duration of the treatment. This discrepancy could potentially be attributed to the utilization of an industrial apparatus during the treatment process, preventing the opening of the autoclave halfway through the cycle. Consequently, the specimens subjected to 1-hour treatment at 212 °C belonged to a distinct batch in comparison to those exposed to 2-hour treatment at the same temperature.

A linear regression was made to show the relationship between Klason lignin and HHV regardless of whether the wood was untreated or heat-treated. The correlation coefficient $R^2 = 0.54$ shows the positive linear relation between HHV and Klason lignin. It should be noted that species-specific linear regressions were not performed due to the limited number of data points available per species (untreated, 1 h, and 2 h conditions), which limits statistical robustness and the reliability of the coefficients of determination. Consequently, the correlations presented in this study should be interpreted as general trends across different wood species rather than as species-specific relationships. Looking at possible outliers, it can be seen that untreated Siberian pine has an HHV higher than would be expected by the linear regression, which can be due to the high amount of dichloromethane extractives in untreated wood, as stated before. Lipophilic extractives are the extractives that generally have higher HHV due to their low oxygen content compared to ethanol-soluble and water-soluble compounds.

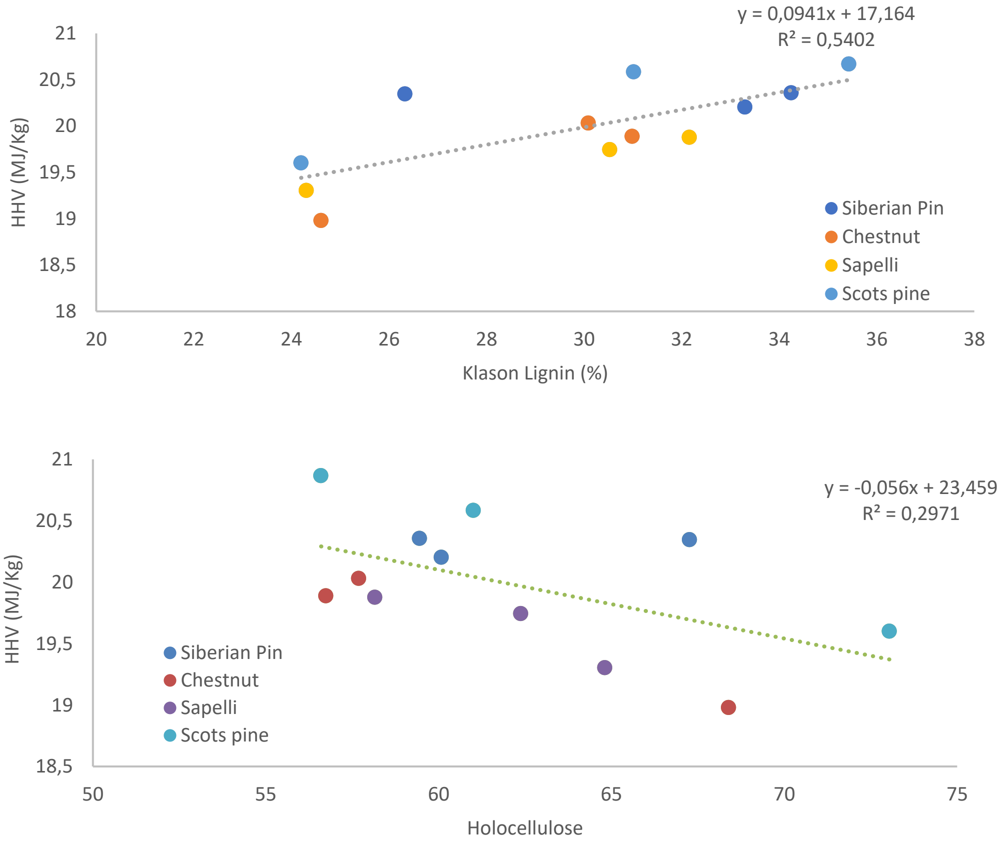

Figure 1 - Variation of HHV with: a) Klason Lignin; b) Holocellulose.

Comparable findings were reported by White (2007) for a mixture consisting of eight species, including four softwoods and four hardwoods. ($R^2 = 0.70$). A better linear correlation between the HHVs and lignin of nine extracted biomass samples was reported by Acar and Ayanoglu (2012), for which the determination coefficient was $R^2 = 0.93$. The higher determination coefficient achieved by these authors can be due to the removal of extractives, eliminating the influence of the existence of extractives with very different HHVs. Studies carried out by Ngangyo-Heya et al. (2016), for five timber species of the semi-arid land of Mexico, found a positive tendency between HHVs and lignin with a determination coefficient (R^2=0.44). Stronger correlations for the linear regressions between lignin content and HHV were reported by Domingos et al. (2016) for heat-treated pine and eucalypt woods, with R^2 values of 0.89 for pine and 0.90 for eucalypt wood.

Holocellulose values show a higher dispersion for untreated and heat-treated wood (Figure 1b). The linear regression between holocellulose content and HHV has an $R^2 = 0.30$. Although this value shows that there is no significant correlation between holocellulose content and HHV of wood, the results can indicate that there is a positive trend for lignin and a negative trend for the holocellulose. It has been stated that cellulose has relatively low heat content due to its high oxidation levels, while lignin, due to its low oxidation levels, has higher heat content (Kumar et al. 1992)

Figure 2 shows the variation of HHV with dichloromethane, ethanol, and water extractives. These nonstructural compounds are also important for the final HHVs of materials, depending on their compositions and amounts. Generally, heat-treated wood has a higher amount of extractives than untreated wood (Domingos et al., 2020).

For dichloromethane extractives, a positive relationship with HHV is observed, although it is relatively weak ($R^2 = 0.27$). This trend can be attributed to the inherently high HHV of these extractives, which may exceed 40 MJ/kg (Esteves et al., 2023). Overall, both extractive content and lignin content contribute to the HHV of the wood, and since there is an increase in lignin percentage, the deviations from the model can be due to the increase or decrease of lipophilic extractives. Nevertheless, the effect of lignin content seems to be more important since there is a weaker correlation between lipophilic extractives and HHV of wood than there is for lignin content. For ethanol extractives, no clear positive or negative trends could be found, $R^2 = 0.01$, while for water extractives, there seems to be a negative trend despite the low correlation between water extractives and HHV ($R^2 = 0.08$). This is to be expected since water extractives are most likely composed of sugars and other compounds with high oxygen content and therefore low HHV. Ethanol-soluble compounds produced during heat-treatment of wood are mainly monosaccharides and their dehydration products, as well as some phenolic compounds like syringaldehyde, syringic acid, and sinapaldehyde (Esteves et al. 2008).

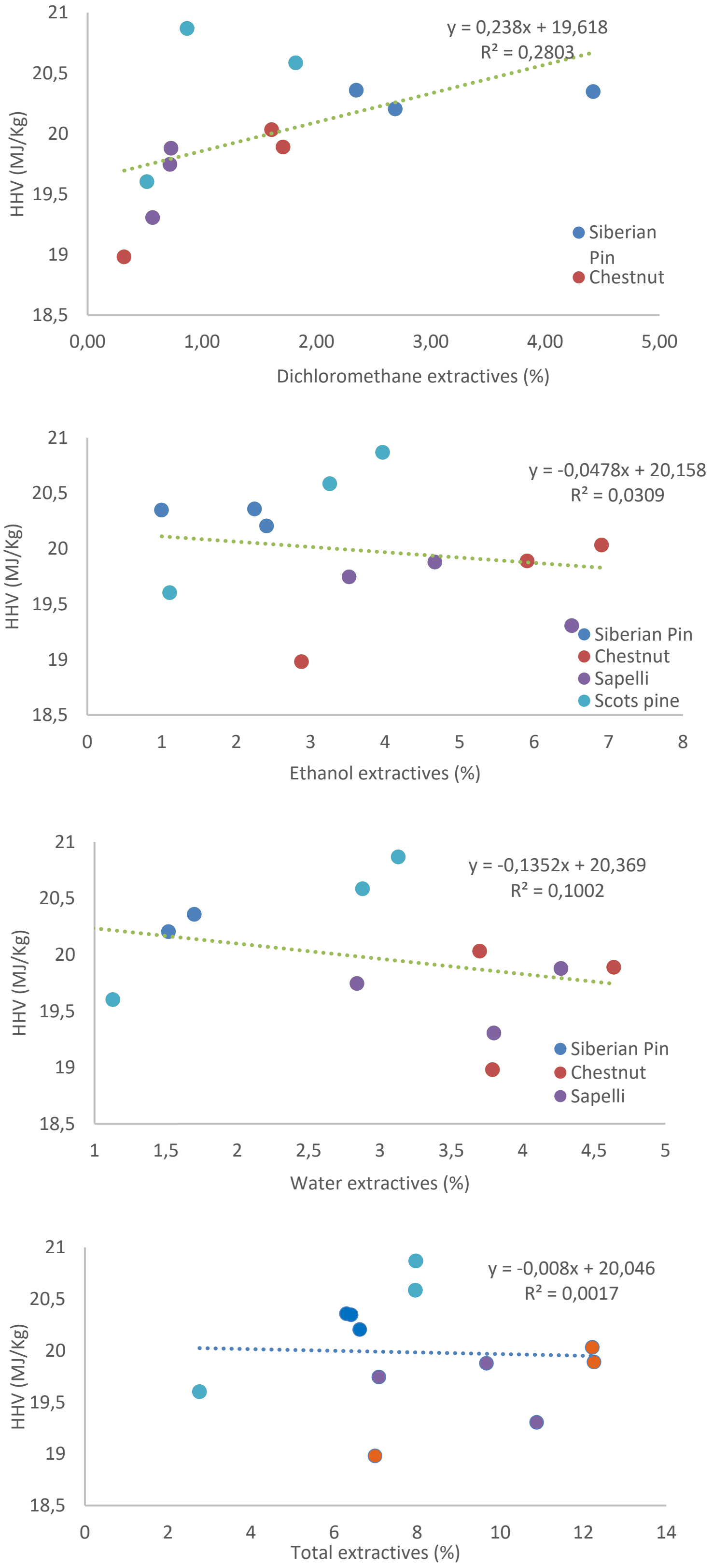

Figure 2- Variation of HHV with extractives of untreated and heat-treated woods: (a) Dichloromethane extractives; (b) ethanol extractives; (c) water extractives; (d) Total extractives

The correlation between total extractives and HHV of wood is even weaker, showing that there is no correlation between the two variables. Some investigations, such as those conducted by Moya and Tenorio (2013), suggest that the lack of strong correlations between extractives and HHVs could be elucidated by the characteristics of the components and the respective quantities found in the timber. According to Senelwa and Sims (1999), certain extractives comprise terpenoid hydrocarbons and lipids, while others consist of phenolic compounds possessing higher levels of oxidation compared to the former substances. Given that combustion is an oxidation process, and the calorific value of an organic compound is linked to its oxidation degree or reduction state, organic compounds containing only carbon and hydrogen yield greater energy upon combustion in comparison to those involving oxygen. Several authors presented correlations with the amount of total extractives. For example, Ngangyo-Heya et al. (2016) studied five Mexican tree species. These authors obtained a weak correlation, R = 0.13, of increasing HHV with increasing amounts of total extractives. Better results were obtained by Ruiz-Aquino et al. (2019), who reported a positive correlation between HHVs and extractives (R^2 = 0.34) for five tree species from Mexico, which was considered to be due to the similarity of species and type of extractives (Domingos et al 2020). Esteves et al. (2008) studied the differences in extractives from untreated and heat-treated wood and concluded that a significant portion of the original volatile compounds is either emitted or undergoes degradation through heat processing, leading to the appearance of new extractives resulting from the breakdown of structural components such as hemicelluloses and amorphous cellulose, which are the primary substrates affected by the thermal treatment. A considerable proportion of these newfound extractives is observed in aqueous and ethanol extracts, where the degradation products of polysaccharides can be found. Furthermore, while the lignin is subject to degradation during the treatment process, its degradation kinetics are significantly slower in comparison to those of polysaccharides. These changes in the composition of extractives may also contribute to the poor correlation coefficients achieved in this work.

CONCLUSION

This study confirms that softwoods exhibit slightly higher heating values (HHV) than hardwoods, which is consistent with previous literature and is primarily attributed to their higher content of lignin and also lipophilic extractives. Heat treatment was shown to increase the HHV of most wood species, with the most pronounced improvement observed in chestnut, while Siberian pine exhibited only marginal changes. These increases are associated with the thermal degradation of polysaccharides and the relative enrichment of lignin and extractives, both of which possess higher calorific values than carbohydrates.

A moderate positive correlation between HHV and Klason lignin content (R^2 = 0.54) was observed, supporting the general trend that lignin contributes significantly to energy content due to its lower oxygen-to-carbon ratio. In contrast, holocellulose showed a weak and non-significant relationship with HHV (R^2 = 0.30), reinforcing the idea that polysaccharides contribute less to HHV. Extractives, particularly dichloromethane-soluble (lipophilic) compounds, demonstrated a positive but weak correlation with HHV, suggesting that their high calorific value can influence results. Ethanol- and water-soluble extractives showed negligible or negative relationships with HHV, likely due to their higher oxygen content. Comparing treatment durations, the differences between 1 h and 2 h were relatively small and inconsistent across species, indicating that extending treatment time from 1 h to 2 h did not systematically produce significantly greater improvements in HHV.

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AUTHORS' CONTRIBUTION

Conceptualization, I.D. and J.F.; data curation, M.F. and Y.D.; formal analysis, M.F. and U.A.; funding acquisition, I.D. and J.F.; investigation, I.D. and Y.D.; methodology, I.D. and B.E.; project administration, I.D., resources, I.D. and J.F.; software, M.F.; supervision, I.D., validation, J.F., U.A. and B.E.; visualization, I.D., M.F. and U.A.; writing – original draft, I.D. and B.E.; writing – review & editing, I.D., M.F., Y.D., J.F., U.A. and B.E.

CONFLICT OF INTEREST

The authors declare no conflict of interests.

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