

ANALYSING THE EFFECT OF THERMAL MODIFICATION ON THE CALORIFIC VALUES OF *EUCALYPTUS NITENS* WOOD

ANALIZA VPLIVA TERMIČNE MODIFIKACIJE NA KALORIČNO VREDNOST LESA *EUCALYPTUS NITENS*

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Abstract / Izvleček

Abstract: Gross and net calorific value of 13 samples of *Eucalyptus nitens* wood were determined at HAWK (Hochschule für Angewandte Wissenschaft und Kunst), Göttingen, Germany. Among 13 samples, 12 were thermally modified and one was unmodified. Calorific values of samples were determined by using a bomb calorimeter, and the wood components (cellulose, hemicellulose, lignin, and extractives) already analysed by Wentzel et al. (2019). After determination of the values, samples were statistically analysed by R studio to find the relations among the calorific value, temperature, and wood components. The gross calorific value and net calorific value of the untreated sample of *Eucalyptus nitens* were found to be 18.83 MJ/kg and 17.48 MJ/kg, and after thermal modification these increased up to 20.24 MJ/kg and 18.84 MJ/kg. Upon statistical analysis, the results for lignin showed a strong correlation with the temperature of thermal treatment and calorific value.

Keywords: *Eucalyptus nitens*, gross calorific value, net calorific value, thermal modification, cellulose, hemicellulose, lignin, extractives

Izvleček: Na 13 vzorcih lesa *Eucalyptus nitens* je bila izmerjena zgornja in spodnja kalorična vrednost. 12 vzorcev je bilo termično modificiranih, en vzorec pa je bil nemodificiran. Kalorične vrednosti vzorcev so bile določene z uporabo bombnega kalorimetra z upoštevanjem lesnih komponent (celuloza, hemiceluloza, lignin in ekstraktivi), ki so jih že določili Wentzel et al. (2019). S statističnim programom R studio smo statistično analizirali dobljene rezultate, da bi ugotovili povezavo med kalorično vrednostjo, temperaturo modifikacije in lesnimi komponentami. Ugotovljeno je bilo, da sta zgornja in spodnja kalorična vrednost neobdelanega lesa *Eucalyptus nitens* znašali 18,83 MJ/kg in 17,48 MJ/kg, po termični modifikaciji pa sta znašali 20,24 MJ/kg in 18,84 MJ/kg, kar pomeni, da termična modifikacija lesa povzroča višje kalorične vrednosti. Statistična analiza je prikazala tesno korelacijo med deležem lignina ter temperaturo in kalorično vrednostjo.

Ključne besede: *Eucalyptus nitens*, zgornja kalorična vrednost, spodnja kalorična vrednost, termična modifikacija, celuloza, hemiceluloza, lignin, ekstraktivi

1 UVOD

1 INTRODUCTION

Modification of wood through thermal heating is applied to enhance certain properties to make wood more suitable for various applications. Thermal modification is altering the chemical wood

structure, i.e., cellulose, hemicellulose, lignin, and extractives, which ultimately improves the durability as well as the dimensional stability (Todaro et al., 2015). Biological decay and instability under a changing moisture regime are seen as a major drawback of wood, compared to competing materials (Homan & Jorissen, 2004). Properties that have been found to get altered by thermal modification include shrinking and swelling properties (Bak & Nemeth, 2012), losses in wood mass and strength, lower equilibrium moisture contents, a higher mechanical stiffness and modulus of elasticity (Kol et al., 2015) and improved durability (Rapp, 2001). Likewise, the calorific value of wood might also be altered after thermal treatments (Todaro et al., 2015).

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The energy content of wood, also known as the calorific or heating value, is the amount of heat released during wood combustion. It is the energy units released when a unit of fuel undergoes complete combustion in presence of oxygen (Telmo & Lousada, 2011a). The calorific value of wood can be expressed as the higher heating value (gross calorific value), and the low heating value (net calorific value). The gross calorific value of a wood sample is referred to as the specified energy ignition of woody biofuel per unit mass, burned in the presence of oxygen in a bomb calorimeter under clear and definite conditions, and expressed in joules. The net calorific value refers to the value when the wood biofuel per unit mass is burned in the presence of oxygen in a bomb calorimeter under definite conditions, with the water remaining in the reaction as water vapour (ISO 18125). A higher heating value has water in a condensed state, but for a lower heating value the water remains gaseous (Acar et al., 2012). A lower heating value rather than a higher heating value is obtained when the moisture in a biofuel is reduced and the water vapour that forms during hydrogen ignition is excluded (Acar et al., 2012). The chemical nature of wood determines the calorific value, which is directly linked to the species, and to the between and within-variability of individual trees (Dhamodaran et al., 1989).

Wood is widely used as an energy source by people living in developing countries, who together account for some 77% of the world population (Trossero, 2002). Increasing demand for wood for energy purposes calls for the more efficient utilization of wood. Thermal modification has a vital role in using limited wood resources more efficiently. Previous studies depict the direct relation between thermal modification and calorific values in wood of several species (Todaro et al., 2015; Calonego et al., 2016). The calorific value of wood is dependent on the wood's chemical constituents (cellulose, hemicellulose, lignin and extractives) (Telmo & Lousada, 2011b; Ngangyo-Heya et al., 2016; White, 2007), which are affected by changes in temperature (Todaro et al., 2013; Yildiz et al., 2006).

This article aims to analyse the calorific value of thermally modified *Eucalyptus nitens* wood, analysing several chemical constituents of wood,

finding the correlation between different wood constituents and heating values, and establishing the relationship between calorific values and wood components through linear modelling. *Eucalyptus nitens* is selected for this study because of its widespread nature and the fact that it is also a very widely used plantation species.

2 MATERIALS AND METHODS

2 MATERIAL IN METODE

2.1 SAMPLE PREPARATION AND THERMAL MODIFICATION

2.1 PRIPRAVA VZORCEV IN TERMIČNA MODIFIKACIJA

Wood samples of *Eucalyptus nitens* (H. Deane & Maiden) were thermally modified at different temperatures in an earlier study, performed by Wentzel et al. (2019). Samples originated from a *Eucalyptus* plantation in the Región del Bío-Bío, Chile, with the plantation trees being 19 years old when sampled. Samples were sized 20*50*650 mm³ (radial*tangential*longitudinal) and the average wood density was 663 kg/m³. Samples were stored in a climate room having 20 °C / 65% RH, with the samples showing a moisture content of 12% ($\pm 0.85\%$). The samples were then dried in the simple kiln to avoid deformations and defects.

Modification was carried out in both an open and closed system. In the open system the temperature was increased at a rate of 12 °C per hour until 100 °C was reached inside the vessel. Afterwards, the pre-drying process was continued at heating rate of 2 °C per hour, until 130 °C was reached. The temperature was again raised at the rate of 12 °C per hour until the temperature required for the modification was reached, and the temperature was then kept constant for 3 hours and data on any modifications at that temperature was recorded. The temperatures for the open system of modification were 160 °C, 180 °C, 200 °C, 220 °C and 230 °C. For the closed system of modification, the WTT process by Willems (2009) was carried out. The modification temperatures used in the closed system of modification were 150 °C, 160 °C and 170 °C, with the relative humidity of 30% and 100% for each temperature.

2.2 DETERMINATION OF WOOD COMPONENTS

2.2 DOLOČANJE LESNIH KOMPONENT

Extractives, cellulose, hemicellulose and lignin contents were determined by Wentzel et al. (2019), who applied the wood and pulp test method T 204 cm-07 (TAPPI, 1997) to achieve this. Measurement of cellulose content was done by separation of lignin by sodium chloride from holocellulose, followed by using sodium hydroxide solution for separation of cellulose from the hemicellulose (Wentzel et al., 2019).

2.3 DETERMINATION OF GROSS AND NET CALORIFIC VALUE

2.3 DOLOČITEV ZGORNJE IN SPODNJE KALORIČNE VREDNOSTI

Determination of calorific value was done in the laboratory of HAWK, Göttingen. Thirteen wood samples modified at different temperatures were used for the determination of their calorific values. The fine dust particles of the different samples were subjected to a mechanical press to convert them into pellets that weighed less than 50 mg. Calorimeter C 7000 from the company IKA was used to obtain the energy liberated during the combustion of wood particles. One sample was put in a bomb

calorimeter three times for the calculation of the calorific value. A bomb calorimeter was used since it is easy to operate at high efficiency.

2.3.1 Calculation Procedure

2.3.1 Postopek izračuna

The procedure and calculations for the gross calorific value were done based on ISO 18125. Calculations for the gross calorific value and the net calorific value were performed using software and the following equation:

$$Q_{p,net,d} = Q_{v,gr,d} - 212.2 \times w(H)_d - 0.8 \times [w(O)_d + w(N)_d]$$

Where,

$Q_{p,net,d}$ is the net calorific value.

$Q_{v,gr,d}$ is the gross calorific value.

$w(H)_d$ is the amount of hydrogen content in percent.

$w(O)_d$ is the amount of oxygen content in percent.

$w(N)_d$ is the amount of nitrogen content in percent.

2.4 STATISTICAL ANALYSIS

2.4 STATISTIČNA ANALIZA

Microsoft Excel was used to obtain various graphs. R statistics were used to find the relation

Table 1. Wood components and calorific values at different modification temperatures

Preglednica 1. Spodnje kalorične vrednosti (NCV), zgornje kalorične vrednosti (GCV) ter kemijska sestava lesa pri različnih temperaturah modifikacije; CS – zaprt sistem in OS – odprt sistem modifikacije.

Temperature [Celsius] and relative humidity [%]	NCV [MJ/kg]	GCV [MJ/kg]	Lignin** [%]	Extractives** [%]	Hemicellulose** [%]	Cellulose** [%]
Unmodified	17.48	18.83	22.5	4.7	27.4	48.3
150 and 30 (CS)	17.98	19.33	21.0	6.0	23.5	50.1
160 and 30 (CS)	17.7	19.05	23.1	7.6	17.6	51.3
170 and 30 (CS)	17.33	18.68	22.8	8.4	14.2	53.9
150 and 100 (CS)	17.19	18.54	25.4	12.7	5.9	55.7
160 and 100 (CS)	18.07	19.42	26.5	13.2	6.5	53.7
170 and 100 (CS)	18.73	20.08	31.8	10.1	10.3	49.7
160 (OS)	17.61	18.96	20.8	6.8	18.8	52.2
180 (OS)	17.62	18.97	23.5	9.0	18.7	48.6
200 (OS)	18.05	19.39	23.7	12.3	10.4	52.5
210 (OS)	18.89	20.24	27.4	12.7	10.8	49.3
220 (OS)	18.44	19.79	28.6	9.1	11.8	50.2
230 (OS)	18.72	20.07	36.9	7.4	12.2	45.8

GCV = Gross calorific value

NCV = Net calorific value

**Wentzel et al. 2019

CS = Closed system modification

OS = Open system modification

between different chemical components and calorific values. Simple linear regression analysis was applied for the estimation of the heating value. Linear regression was also used to build the model and predict the effects of the chemical components on the heating value.

3 RESULTS

3 REZULTATI

3.1 EFFECT OF THERMAL MODIFICATION

3.1 UČINEK TERMIČNE MODIFIKACIJE

The calorific values and wood components (cellulose, hemicellulose, lignin, and extractives) of unmodified and thermally modified wood

samples of *Eucalyptus nitens* are presented in Table 1. The results show that the gross and net calorific values increased with thermal modification. The maximum values were observed when the samples were treated at 170 °C with a high relative humidity. Similarly, with an increase in temperature there was increase in lignin and extractive contents and decrease in cellulose and hemicellulose. In the open system of modification, as illustrated by Figure 2, the maximum rise in calorific value was seen between 210 °C and 230 °C. Overall, in both systems of modification an increase in the heating value was observed with the increase in temperature for *Eucalyptus nitens*.

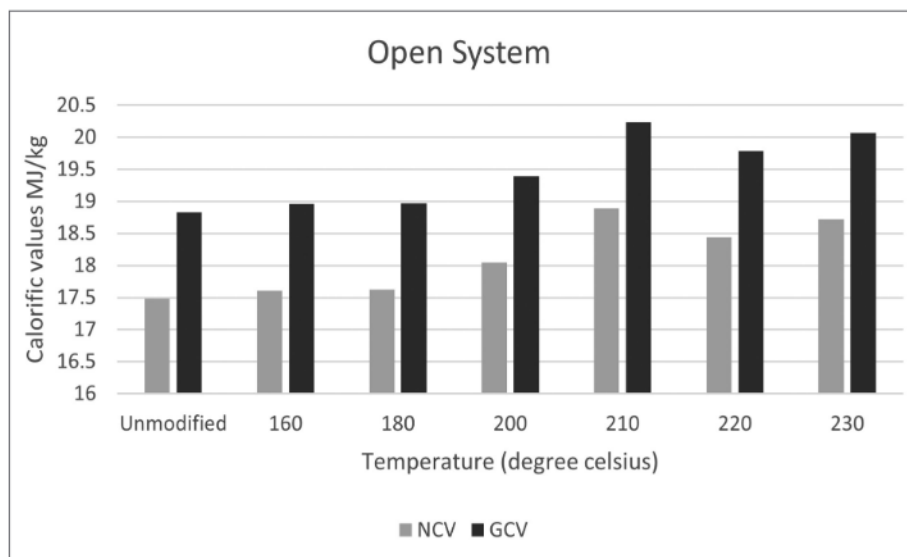


Figure 1. Open system of modification: Net (NCV) and gross (GCV) calorific values of untreated wood and wood modified at different temperature regimes
Slika 1. Odprt sistem modifikacije: Spodnje (NCV) in zgornje kalorične vrednosti (GCV) netretiranega lesa in lesa, modificiranega pri različnih temperaturnih režimih

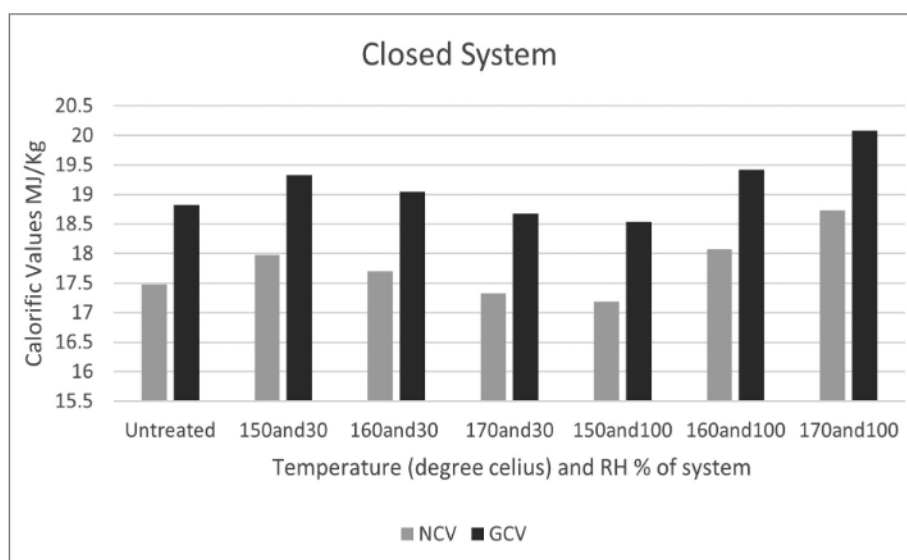


Figure 2. Closed system of modification: Net (NCV) and gross (GCV) calorific values of untreated wood and wood modified at different temperature regimes
Slika 2. Zaprt sistem modifikacije: Spodnje (NCV) in zgornje kalorične vrednosti (GCV) netretiranega lesa in lesa, modificiranega pri različnih temperaturnih režimih

3.2 STATISTICAL ANALYSIS

3.2 STATISTIČNA ANALIZA

3.2.1 Temperature of both modifications and calorific values

3.2.1 Temperatura modifikacije in kalorična vrednost

The relation between calorific value and temperature is illustrated in Figure 3. GCV (MJ/kg) and NCV (MJ/kg) were found to be positively correlated with temperature (°C), as seen in figures a and b.

3.2.2 Temperature and wood components

3.2.2 Temperatura in lesne komponente

Changes in wood constituents upon treating with different temperatures are depicted by Figure 4. Cellulose and hemicellulose were found to be negatively correlated with temperature (Figure 4 a and c) whereas lignin was positively correlated and extractives increased slightly with temperature (Figure 4 b and d). From the statistical analysis, the effects of temperature on cellulose and lignin were significant (shown in a and b), with p-values of 0.0268 and 0.0226 at a 5% level of significance.

3.2.3 Calorific value and wood components

3.2.3 Kalorična vrednost in osnovne sestavine lesa

The statistical relationship between calorific values (GCV and NCV) and wood components (cellulose, hemicellulose, lignin, and extractives) is elucidated by Figure 5. The calorific value was found to be negatively correlated with cellulose (Figure 5 a and b) and hemicellulose (Figure 5 c and d). However, the correlation was high in case of cellulose, with a coefficient of -0.695. There was a positive correlation of calorific value with lignin (Figure 5 e and f) and extractives (Figure 5 g and h). Calorific value was found to be positively and highly correlated with lignin, with a coefficient of 0.716 (lignin vs GCV) and 0.715 (lignin vs NCV).

3.2.4 Linear relationship

3.2.4 Linearno razmerje

The effects of temperature, lignin and cellulose were found to be significantly related to the calorific value of wood. Therefore, multiple regression analysis was carried out which includes these three as independent variables and energy content as a dependent variable. The results of the multiple regression analysis are shown in Table 3.

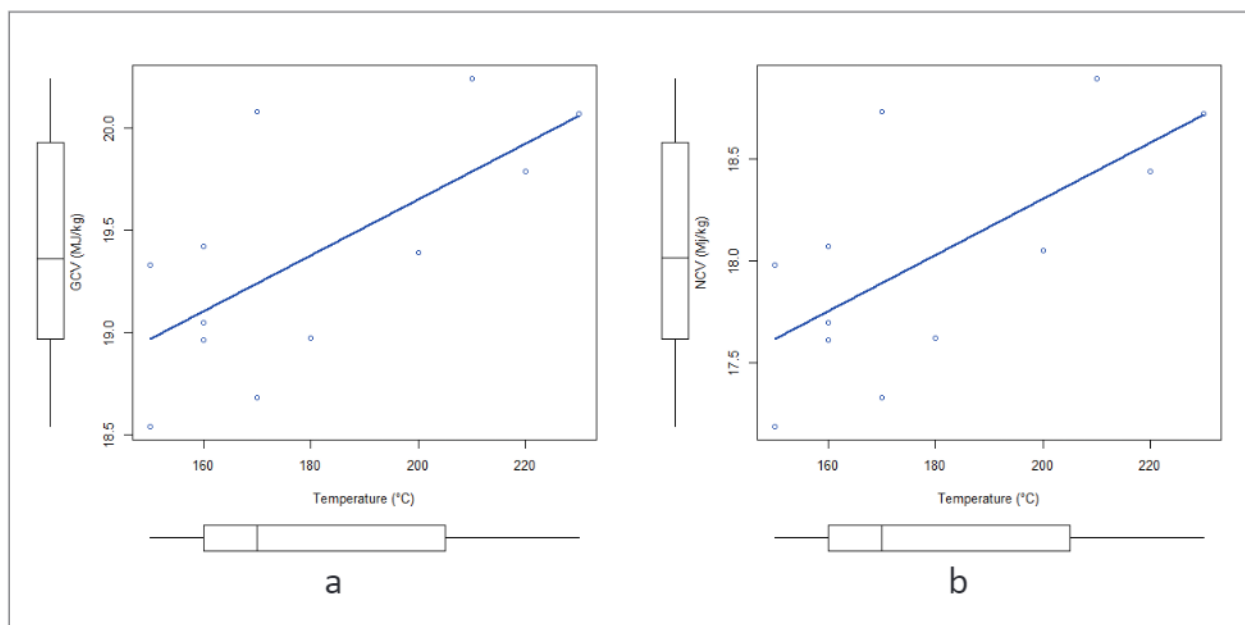


Figure 3. Relationship between temperature and calorific value; a (Temperature vs GCV) and b (Temperature vs NCV)

Slika 3. Razmerje med temperaturo in kalorično vrednostjo; a (temperatura v primerjavi z GCV) in b (temperatura v primerjavi z NCV)

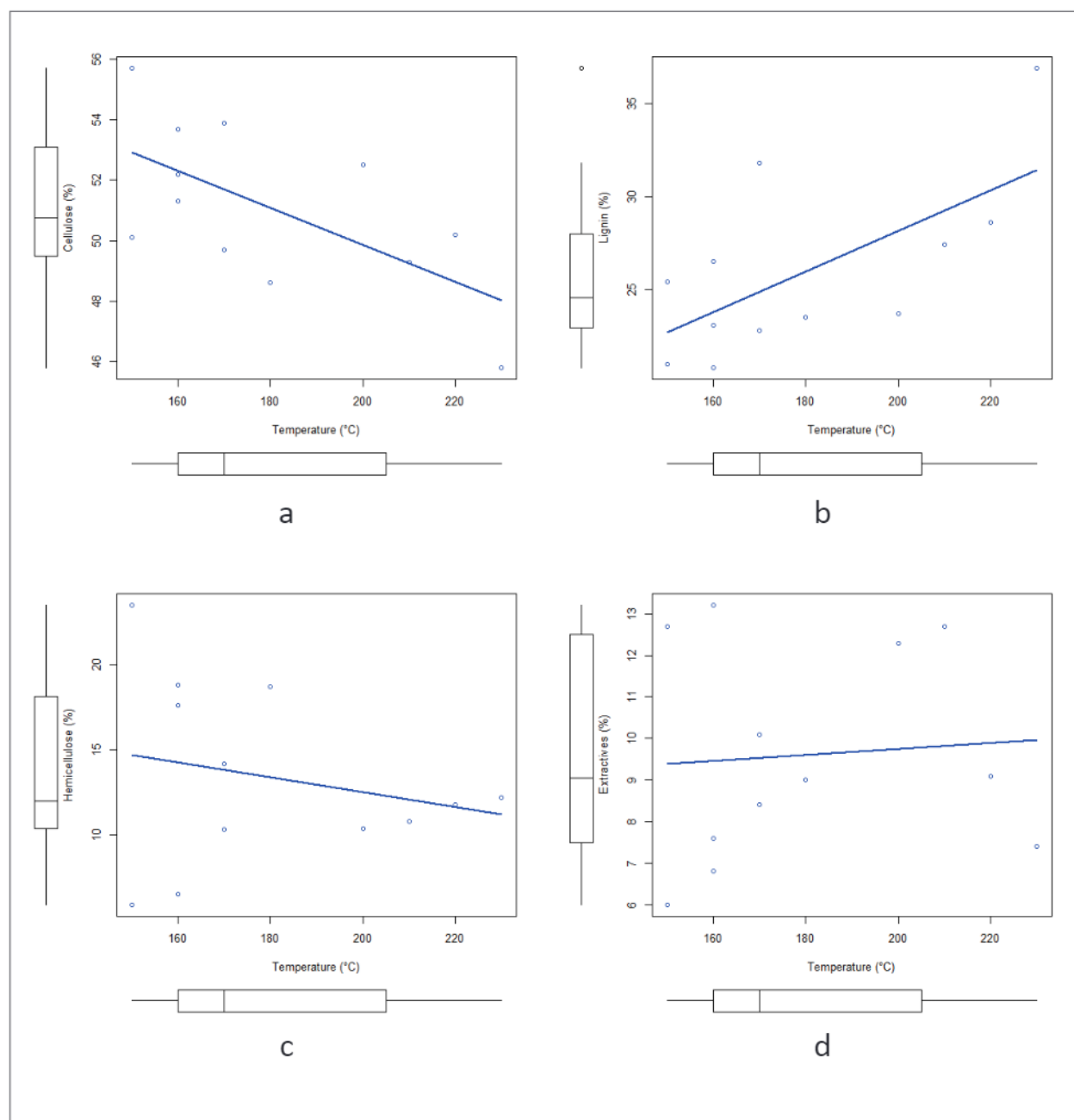


Figure 4. Percentages of wood components as affected by temperature: a (cellulose vs temperature), b (lignin vs temperature), c (hemicellulose vs temperature) and d (extractives vs temperature).

Slika 4. Deleži kemijskih komponent v odvisnosti od temperature: a (celuloze v odvisnosti od temperature), b (lignina v odvisnosti od temperature), c (hemiceluloze v odvisnosti od temperature) in d (ekstraktivov v odvisnosti od temperature).

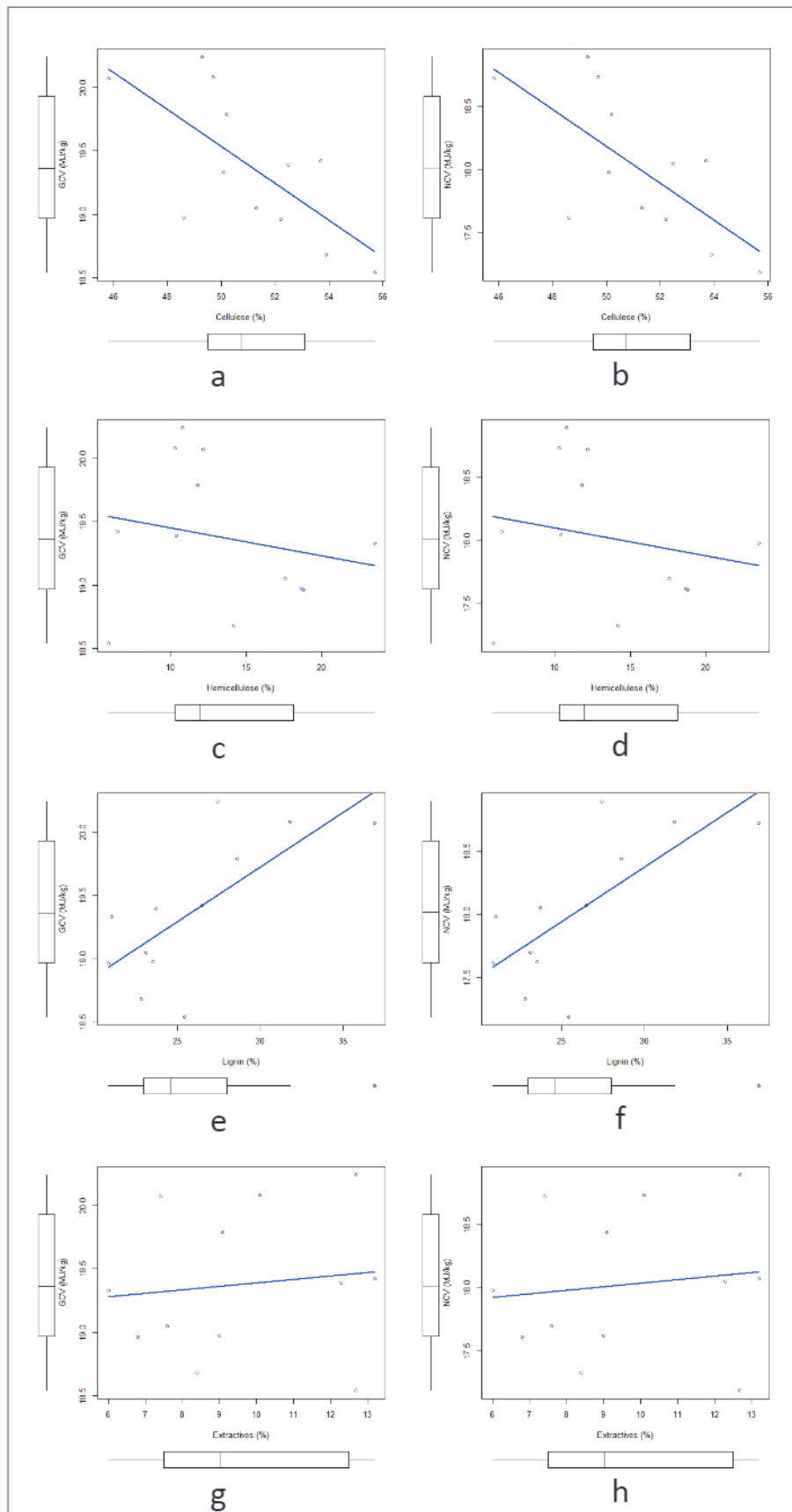


Figure 5. Relationship between calorific value and wood components: a (GCV vs cellulose), b (NCV vs cellulose), c (GCV vs hemicellulose), d (NCV vs hemicellulose), e (GCV vs lignin), f (NCV vs lignin), g (GCV vs extractives) and h (NCV vs extractives)

Slika 5. Razmerje med kalorično vrednostjo in sestavinami lesa:

a (GCV v primerjavi s celulozo), b (NCV v primerjavi s celulozo), c (GCV v primerjavi s hemicelulozo), d (NCV v primerjavi s hemicelulozo), e (GCV v primerjavi z ligninom), f (NCV v primerjavi z ligninom), g (GCV v primerjavi z ekstraktivi) in h (NCV v primerjavi z ekstraktivi)

Table 2. Linear relationship between calorific value (dependent variable) and various independent variables

Preglednica 2. Linearna zveza med kalorično vrednostjo (odvisna spremenljivka) in različnimi neodvisnimi spremenljivkami

Relation	Model	Multiple R squared	Adjusted R squared	p-value
Calorific value and temperature (T)	GCV = 16.911+0.0137*T NCV = 15.557+0.0137*T	0.4575 0.4590	0.4033 0.4049	0.0157 0.0154
Calorific value and lignin (L)	GCV = 17.1418+0.0861*L NCV = 15.795+0.086*L	0.5128 0.5116	0.4641 0.4628	0.0088 0.0089
Calorific value and cellulose (C)	GCV = 26.8268-0.1458*C NCV = 25.4687-0.1457*C	0.4844 0.4832	0.4328 0.4315	0.0119 0.0121
Calorific value and hemicellulose (H)	GCV = 19.6692-0.02184*H NCV = 18.3213-0.0219*H	0.04204 0.04241	-0.0537 -0.0533	0.5226 0.5208

GCV: Gross calorific value; NCV: Net calorific value

Table 3. Multiple regression analysis

Preglednica 3. Analiza multiple regresije

Model	Multiple R squared	Adjusted R squared	P-value
GCV = 21.1194 +0.00419*T +0.04635*L - 0.07245*C	0.6569	0.5282	0.02903
NCV = 19.74042 +0.00427*T +0.046104*L - 0.072019*C	0.6561	0.5272	0.02927
GCV = 17.1101 +0.085762*L +0.004166*E	0.5131	0.4049	0.03920
NCV = 15.760314 +0.08536*L +0.004599*E	0.5121	0.4036	0.03960
GCV = 21.36830+0.06390*L-0.10565*C+0.03953*H+0.12669*E	0.7259	0.5692	0.03818
NCV = 20.16484+0.06259*L-0.10733*C+0.03821*H+0.12582*E	0.7254	0.5685	0.03839

T = Temperature, C = Cellulose, H = Hemicellulose, L = Lignin, E = Extractives

4 DISCUSSION

4 RAZPRAVA

Thermally modified samples of *Eucalyptus nitens* wood led to an increase in the calorific value of the wood in this experiment. As shown in Table 1, the gross calorific value and net calorific value recorded in the untreated samples of *Eucalyptus nitens* were found to be 18.83 MJ/kg and 17.48 MJ/kg, and after treatment the maximum values of 20.24 MJ/kg and 18.84 MJ/kg were recorded. The relationship between temperature and calorific value is also depicted by the high correlation between temperature and calorific value, as illustrat-

ed in Figure 3. When *Eucalyptus nitens* wood was thermally modified, there was an increase in both net and gross calorific values along with changes in lignin, holocellulose and extractive contents. These findings are similar to those found by Calonogo et al. (2016) for mature *Eucalyptus grandis* wood when treated at 180 °C. Previous studies suggest the change in calorific value is a result of changes in the wood components (Telmo & Lausada, 2011b; Demribas, 2001). Furthermore, this relationship between calorific value, temperature and wood components is also elucidated by the results of the statistical analyses (Figures 3, 4 and 5) and multiple

regression model (Tables 2 and 3).

The results of the experiment showed an increase in lignin content upon thermal treatment of *Eucalyptus nitens* wood, as shown in Figure 4b. This is also supported by the results of Esteves et al.'s (2008) experiment with *Eucalyptus globulus* wood, where the lignin content was found to be increased with autoclaving and oven drying of the sample. Previous studies suggest that the formation of insoluble by-products and humification results in an increase in lignin, which is the result of the hemicellulose degradation (Tjeerdsma et al., 1998; Wirkberg & Mannu, 2004; Esteves & Pereira, 2009).

The higher correlation between lignin and calorific value demonstrated by this experiment, as indicated by the higher correlation coefficient of 0.716, suggests a direct relationship between lignin and calorific values, as the increase in the former causes an increase in the latter. A similar correlation was found by an experiment by Demribas (2001) that examined 14 lignocellulosic materials, where a higher correlation coefficient of 0.874 was found between lignin and a high heating value. Previous studies note that the heating value is mostly defined by the lignin content, as compared to hemicellulose lignin has higher amounts of carbon and hydrogen, which are the main heat producing constituents in wood (Telmo & Lausada, 2011b; Demribas, 2001).

From the statistical analysis, cellulose was found to be negatively correlated with temperature and calorific value, as demonstrated by Figures 4a, 5a and 5b. Cellulose is the most stable compound due to its crystalline nature (Esteves & Pereira, 2009). The crystallinity of cellulose was found to be less affected by temperature in previous studies (Bourgois et al., 1989; Yildiz et al., 2006). When thermal modification is carried out, cellulose undergoes some temporary effects of temperature on its unstructured region (Bhuiyan & Hirai, 2005; Wirkberg & Mannu, 2004). Hemicellulose was also found to be negatively correlated with temperature and calorific value in this study. Hemicellulose degrades first even at a relatively low temperature, and the most common temperature for wood modification ranges from 180 °C to 250 °C (Esteves & Pereira, 2009). When hemicellulose starts degrading, it forms acetic acid which acts as a catalyst for the formation of furfural, formaldehyde and other

aldehydes (Tjeerdsma et al., 1998). As a result, the percentage of the hemicellulose decreases even at low temperature treatment. The extractive contents in this experiment on *Eucalyptus nitens* were initially increased upon heating, but gradually started to degrade with a further increase in temperature beyond 220 °C. Similar results were reported by Esteves et al. (2008) for the extractives of *Eucalyptus globulus* upon heat treatment. Previous studies suggest that when wood is thermally treated the volatile substances vanish, but degradation of the cell walls leads to the creation of new compounds (Esteves & Pereira, 2009).

5 CONCLUSIONS

5 ZAKLUČKI

The calorific value of *Eucalyptus nitens* wood was found to be increased upon thermal modification. The experiments showed that lignin was significantly and highly correlated with temperature and calorific value. Statistical analyses and comparisons with the results of previous studies indicate that changes in temperature favour alteration in wood's chemical constituents and changes the calorific value. Based on the results obtained in the current work, it is concluded that wood with high lignin content can result in high energy content. As an increase in the calorific value was observed with thermal treatment, *Eucalyptus nitens* wood can be used efficiently for energy production after thermal modification.

6 SUMMARY

6 POVZETEK

Les se zaradi svoje kurilne oziroma kalorične vrednosti v mnogih delih sveta uporablja kot pomemben vir energije. Povečanje povpraševanja po lesu za energetske namene zahteva učinkovito uporabo lesa. Ugotovljeno je bilo, da se s termično modifikacijo lesa spreminja delež lesnih komponent, kar je ključnega pomena za povečanje njegove kalorične vrednosti. V HAWK, Hochschule für Angewandte Wissenschaft und Kunst, Göttingen, je bila izvedena analiza vpliva termičnih sprememb na kalorično vrednost lesa *Eucalyptus nitens*. Glavni cilj raziskave je bil določiti kalorično vrednost termično modificiranega lesa in ugotoviti razmerje med ka-

lorično vrednostjo in temperaturo modifikacije ter deleži lesnih sestavin. Za to študijo smo uporabili termično modificirane vzorce lesa *Eucalyptus nitens* pri različnih temperaturah, ki so jih pripravili Wentzel et al. (2019). Po navedbah avtorjev je les izviral iz nasada evkalipta v regiji Regio del Bío-Bío v Čilu, vzorci pa so bili odvzeti pri starosti nasada 19 let. Zgornje in spodnje kalorične vrednosti so bile določene z bombnim kalorimetrom. Po določitvi kaloričnih vrednosti vzorcev, modificiranih pri različnih temperaturah in znanih podatkih o deležih posameznih komponent lesa (celuloze, hemiceluloze, lignina in ekstraktivov), določenih v predhodni študiji (Wentzel et al., 2019), je bila opravljena tudi statistična analiza za ugotavljanje zveze med kaloričnimi vrednostmi, temperaturo modifikacije in deleži lesnih komponent. Z uporabo statističnega programa R-studio je bilo statistično analiziranih 12 modificiranih in en nemodificiran vzorec.

Ugotovljeno je bilo, da sta bruto in neto kalorična vrednost neobdelanega vzorca *Eucalyptus nitens* 18,83 MJ/kg in 17,48 MJ/kg, po obdelavi pa sta bili izmerjeni vrednosti 20,24 MJ/kg in 18,84 MJ/kg, kar je pokazalo povečanje kalorične vrednosti zaradi termične modifikacije. Statistična analiza zgornje kalorične vrednosti in temperature je pokazala visoko korelacijo s korelacijskim koeficientom 0,676. Vrednost p pri linearni regresiji je bila 0,0152. Podobno smo opazili visoko korelacijo med neto kurilno vrednostjo in temperaturo s korelacijskim koeficientom 0,677 in p -vrednostjo 0,015.

Rezultati korelacij med temperaturo modifikacije, deležem celuloze, hemiceluloze, lignina in ekstraktivov ter kalorične vrednosti so pokazali negativno korelacijo vsebnosti celuloze in hemiceluloze s temperaturo in pozitivno korelacijo vsebnosti lignina in ekstraktivnih snovi s temperaturo. Analiza korelacije kalorične vrednosti z osnovnimi lesnimi sestavinami je pokazala negativen vpliv deleža celuloze in hemiceluloze na kalorično vrednost in pozitiven učinek lignina in ekstraktivnih snovi. V obeh primerih je bil vpliv lignina večji. Količina lignina je v tesni zvezi s kalorično vrednostjo. Korelacijski koeficient med deležem lignina in zgornjo kalorično vrednostjo je znašal 0,716, s spodnjo pa 0,715, kar potrjuje tudi p -vrednost 0,0088 pri 5-odstotni stopnji zaupanja. Pomemben vpliv deleža lignina so podprle tudi raziskave drugih avtorjev. Esteves et al. (2008) so izvedli raziskavo na lesu *Eucalyptus*

globulus in ugotovili, da se delež lignina povečuje z avtoklaviranjem in sušenjem vzorca v peči. Predhodne študije so tudi pokazale, da nastajanje netopnih stranskih produktov in rezultati humifikacije povečajo delež lignina zaradi razgradnje hemiceluloze (Tjeerdsma et al., 1998; Wikberg & Mannu, 2004). Podobno je bila visoka korelacija lignina s kalorično vrednostjo prikazana tudi v poskusu, ki ga je opravil Demirbas (2001) na 14 lignoceluloznih materialih, kjer je bil ugotovljen višji korelacijski koeficient 0,874 med ligninom in temperaturo. Številne študije so pojasnile, da so višje temperature večinoma posledica višje vsebnosti lignina, saj ima lignin visok delež ogljika in vodika, kar prispeva k energetski vrednosti (Telmo & Lausada, 2011b; Demirbas, 2001).

Iz rezultatov statistične analize in primerjave rezultatov s predhodnimi študijami je mogoče sklepati, da termična modifikacija ugodno vpliva na spremembe deležev osnovnih kemičnih sestavin lesa in s tem na kalorično vrednost. Na podlagi rezultatov lahko ugotovimo, da ima les z visoko vsebnostjo lignina večjo kalorično vrednost. Ker je bilo med termično modifikacijo opaženo povečanje kalorične vrednosti, lahko les *Eucalyptus nitens* po toplotni modifikaciji učinkovito uporabimo tudi za energetske namene.

REFERENCES

VIRI

- Acar, S., Ayanoglu, A., & Demirbas, A. (2012). Determination of higher heating values (HHVs) of biomass fuels. *Energy Education Science and Technology Part A: Energy science and Research* 28(2), 749-758.
- Bak, M., & Nemeth, R. (2012). Modification of wood by oil heat treatment. *International Scientific Development & Ecological Footprint*.
- Bhuiyan, T. R., & Hirai, N. (2005). Study of crystalline behavior of heat-treated wood cellulose during treatments in water. *Journal of Wood Science*, 51(1), 42-47.
- Bourgeois, J., Bartholin, M. C., & Guyonnet, R. (1989). Thermal treatment of wood: analysis of the obtained product. *Wood Science and Technology*, 23(4), 303-310.
- Calonego, F. W., Severo, E. T. D., Sansígolo, C. A., de Rezende, M. A., Bruder, E. M., & Costa, V. E. (2016). Calorific Value and Chemical Properties in Juvenile and Mature Wood of Thermally-Modified *Eucalyptus Grandis*. *Wood Industry/Drvna Industrija*, 67(3), 207-214.
- Demirbaş, A. (2001). Relationships between lignin contents and

Nepal, S., Wimmer, R., & Zelinski, V.: Analysing the effect of thermal modification on the calorific values of *Eucalyptus nitens* wood

- heating values of biomass. *Energy conversion and management*, 42(2), 183-188.
- Dhamodaran, T. K., Gnanaharan, R., & Thulasidas, P. K. (1989). Calorific value variation in coconut stem wood. *Wood Science and Technology*, 23(1), 21-26.
- Esteves, B., & Pereira, H. (2009). Wood modification by heat treatment: A review. *BioResources*, 4(1), 370-404.
- Esteves, B., Graca, J., & Pereira, H. (2008). Extractive composition and summative chemical analysis of thermally treated eucalypt wood. *Holzforschung*, 62(3), 344-351.
- Homan, W. J., & Jorissen, A. J. (2004). Wood modification developments. *Heron*, 49(4), 360-369.
- ISO 18125 (2017) Solid biofuels – Determination of calorific value.
- Kol, H. Ş., Sefil, Y., & Keskin, S. A. (2015). Effect of heat treatment on the mechanical properties, and dimensional stability of fir wood. In 27th International Conference Research for the furniture industry (pp. 17-18).
- Ngangyo-Heya, M., Foroughbahch-Pournavab, R., Carrillo-Parra, A., Rutiaga-Quifones, J. G., Zelinski, V., & Pintor-Ibarra, L. F. (2016). Calorific value and chemical composition of five semi-arid Mexican tree species. *Forests*, 7(3), 58.
- Rapp, A. O. (2001). Review on heat treatments of wood. In Proceedings of special seminar, Antibes, France.
- TAPPI (1997). Solvent extractives of wood and pulp. Test method T 204 cm-07.
- Telmo, C., & Lousada, J. (2011a). Heating values of wood pellets from different species. *Biomass and bioenergy*, 35(7), 2634-2639.
- Telmo, C., & Lousada, J. (2011b). The explained variation by lignin and extractive contents on higher heating value of wood. *Biomass and bioenergy*, 35(5), 1663-1667.
- Tjeerdsmas, B. F., Boonstra, M., Pizzi, A., Tekely, P., & Militz, H. (1998). Characterisation of thermally modified wood: molecular reasons for wood performance improvement. *Holz als Roh-und Werkstoff*, 56(3), 149.
- Todaro, L., Dichicco, P., Moretti, N., & D'Auria, M. (2013). Effect of combined steam and heat treatments on extractives and lignin in sapwood and heartwood of Turkey oak (*Quercus cerris* L.) wood. *BioResources*, 8(2), 1718-1730.
- Todaro, L., Rita, A., Cetera, P., & D'Auria, M. (2015). Thermal treatment modifies the calorific value and ash content in some wood species. *Fuel*, 140, 1-3.
- Trossero, M. A. (2002). Wood energy: the way ahead. *Unasylva*, 53(4), 3-12.
- Wentzel, M., Fleckenstein, M., Hofmann, T., & Militz, H. (2019). Relation of chemical and mechanical properties of *Eucalyptus nitens* wood thermally modified in open and closed systems. *Wood Material Science & Engineering*, 14(3), 165-173.
- White, R. H. (2007). Effect of lignin content and extractives on the higher heating value of wood. *Wood and fiber science*, 19(4), 446-452.
- Wikberg, H., & Maunu, S. L. (2004). Characterisation of thermally modified hard-and softwoods by ¹³C CPMAS NMR. *Carbohydrate polymers*, 58(4), 461-466.
- Willems, W. (2009). A novel economic large-scale production technology for high-quality thermally modified wood. In Proceedings of the 4th European conference on wood modification, Stockholm, Sweden (pp. 31-35).
- Yildiz, S., Gezer, E. D., & Yildiz, U. C. (2006). Mechanical and chemical behavior of spruce wood modified by heat. *Building and environment*, 41(12), 1762-1766.