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).
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, 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

2.1 SAMPLE PREPARATION AND THERMAL MODIFICATION

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% (±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

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

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

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:

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

Where, 
\( Q_{p,\text{net},d} \) is the net calorific value. 
\( Q_{v,\text{gr},d} \) 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

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

| 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
CS = Closed system modification  OS = Open system modification

**Wentzel et al. 2019
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*.

![Open System](image1)

Figure 1. Open system of modification: Net (NCV) and gross (GCV) calorific values of untreated wood and wood modified at different temperature regimes

![Closed System](image2)

Figure 2. Closed system of modification: Net (NCV) and gross (GCV) calorific values of untreated wood and wood modified at different temperature regimes
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3.2 STATISTICAL ANALYSIS

3.2.1 Temperature of both modifications and calorific values

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

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

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

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)](image)

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

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 illustrated 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 Calonego 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 analysis.
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; Wikberg & 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 holocellulose 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 corelated 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 corelated 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 ZAKLJUČKI

The calorific value of *Eucalyptus nitens* wood was found to be increased upon thermal modification. The experiments showed that lignin was significantly and highly corelated 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 vrednost jo in temperaturo modifikacije ter deleži lesnih sestavin. Za to študio 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 nasade 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 izvorno ugotovljena, 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 vedika, 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.

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