ARTÍCULO

Effect of the heat treatment on the physicochemical characteristics of rubberwood: Results of thermal analysis and FTIR spectroscopy

Olga A. Shapchenkova¹ https://orcid.org/0000-0002-1392-5171 Sergei R. Loskutov¹ https://orcid.org/0000-0002-3779-8752 Antonina A. Aniskina¹ https://orcid.org/0000-0002-2696-0267 Suthon Srivaro² https://orcid.org/0000-0001-8851-5858 Zoltán Börcsök³ https://orcid.org/0000-0002-7492-9889 Zoltán Pásztory³ https://orcid.org/0000-0001-9326-0650^{*}

¹V.N. Sukachev Institute of Forest Siberian Branch Russian Academy of Science. Federal Research Center. Krasnoyarsk, Russia.

²Walailak University. Center of Excellence in Wood and Biomaterials. Nakhon Si Thammarat, Thailand.

³University of Sopron. Faculty of Wood Engineering and Creative Industries. Sopron, Hungary

♠Corresponding author: pasztory.zoltan@uni-sopron.hu

Abstract:

Heat treatment is an environmentally friendly method used to improve properties of rubberwood. In this work, the changes in the chemical composition, thermal behavior and thermal degradation kinetics of heat-treated *Hevea brasiliensis* (rubber tree) were evaluated using thermogravimetry, differential scanning calorimetry, and Fourier transform infrared spectroscopy. The rubberwood samples were exposed to temperatures of 180 $^{\circ}$ C and 220 $^{\circ}$ C in air under atmospheric pressure for durations of 15 25 and 35 h. Thermal analysis revealed degradation of hemicelluloses, an increase in the relative proportions of cellulose and lignin in heat-treated rubberwood. The thermal decomposition of rubberwood heat-treated at 220 °C started at a higher temperature compared to untreated wood. A shift in the position of peaks on differential thermogravimetry and differential scanning calorimetry curves of heat-treated samples was observed, indicating changes in the structure of wood polymers. The temperature of heat treatment had a stronger effect on the chemical composition of rubberwood than duration. Significant changes in the chemical composition of rubberwood occurred after the treatment duration of 15 h at both 180 °C and 220 °C. The duration of 25 h and 35 h had no further substantial effect. The isoconversional method of Flynn-Wall-Ozawa was used to determine the kinetics of thermal degradation of untreated and heat-treated rubberwood. It is found that the average values of activation energy in the conversion degree range of 0,05 - 0,65 (the thermal degradation of polysaccharides) increased with increasing treatment temperature and duration. Fourier transform infrared spectra demonstrated alterations in wood polymers.

Keywords: FTIR spectroscopy, heat treatment, *Hevea brasiliensis,* rubberwood, thermal analysis

Received: 27.07.2023 Accepted: 01.11.2024

Introduction

Rubberwood is a tropical hardwood species distributed in South East Asia, Africa, and South America. The largest areas of rubberwood plantations are located in Thailand, Malaysia, and Indonesia. Rubberwood plantations are created for producing rubber latex, which is intensively used in different industries. After the trees have been tapped for 25 - 30 years, they are felled and new ones are planted. Rubberwood is the most valuable raw material in the South East Asia region for dried wood lumbers and wood products, such as structural wood and furniture (Killmann and Hong 2000, Eufrade Junior *et al.* 2015, Zhao *et al.* 2019, Chanpet *et al.* 2020).

The low strength, dimensional instability, and durability of rubberwood constrain its use (Ratnasingam and Ioras 2012, Umar *et al.* 2016). Heat treatment is environmentally friendly and one of the most effective pretreatment methods that provides desirable properties of wood such as biological durability, greater dimensional stability and change on the original color without using chemicals (Esteves *et al.* 2013, Kubovský *et al.* 2020). This method is becoming the treatment of choice when dealing with fast-growing plantation of wood species used extensively for making furniture, wood-based panels in Indonesia, Malaysia, Thailand (Ratnasingam and Ioras 2013). Heat treatment initiates a process of wood polymer degradation and possible crosslinking with degradation products, which significantly changes the initial structure and interaction of wood polymers (López-González *et al.* 2013, Sikora *et al.* 2018). The chemical changes are affected by many external conditions (temperature, duration, atmosphere, and others). The temperature is considered as a key factor (Esteves and Pereira 2008, Kubovský *et al.* 2020). The effect of thermal modification on wood properties has been comprehensively described by Esteves and Pereira (2008), Hill *et al.* 2021.

Previous studies have shown that Fourier transform infrared spectroscopy and thermal analysis can be used to evaluate characteristics of heat-treated wood (Gao *et al.* 2006, González-Peña *et al.* 2009, Korošec *et al.* 2009, Korošec *et al.* 2017, Özgenç *et al.* 2017, Lin *et al.* 2018, Lopes *et al.*

2018, Kubovský *et al.* 2020). The results contribute to the recognition of the mechanisms of thermal degradation of wood and can provide insights into the applications of heat-treated wood for exterior and interior uses. The kinetic parameters of wood thermal degradation are useful for understanding the thermal degradation process and providing information for treatment design (Poletto *et al.* 2012). The Flynn-Wall-Ozawa (FWO), Friedman and Kissinger methods are widely applied to determine the kinetic parameters. There have been several studies of heat-treated rubberwood using thermal analysis and Fourier transform infrared (FTIR) spectroscopy (Devi *et al.* 2004, Srinivas and Pandey 2012, Zhang *et al.* 2019, Li *et al.* 2020a). However, little information has been provided on the parameters and kinetics of its thermal degradation.

The aim of this work was to evaluate changes in the chemical composition, thermal behavior and thermal degradation kinetics of rubberwood subjected to heat treatment at different temperatures and durations, using thermogravimetry (TG), differential scanning calorimetry (DSC) and the fourth derivative of the FTIR spectrum.

Material and methods

Rubber tree (*Hevea brasiliensis* (Willd. ex A.Juss.) Müll. Arg.) derived from the region of Nakhon Shi Tamarat in Thailand. Samples were dried to air dry conditions and stored for three months. However, before heat treatment over hundred degrees Celsius the samples had to be dried close to net zero moisture content to avoid undesirable cracks and damages. The samples of rubberwood 17 by 17 cm were treated in a chamber at 180 $^{\circ}$ C and 220 $^{\circ}$ C in an air atmosphere under atmospheric pressure for durations of 15 h 25 h and 35 h. For determining density EN 1097-3:1999 (1999) standard was used, however numbers of the samples were six for every temperature and treatment duration, and the results were averaged. Density was determined in net zero moisture conditions before treatment and right after thermal treatment.

Then samples of rubberwood were carefully sawed with a fine-tooth metal saw to obtain powder. The powdered samples were used for thermal analysis and FTIR spectroscopy.

Thermogravimetry (TG 209F1, Netzsch, Germany) was carried out in an air atmosphere with a gas flow of 20 mL/min from 25 °C to 700 °C, in a corundum crucible (Al_2O_3) at heating rates of 10 °C/min 20 °C/min and 40 °C/min. Differential scanning calorimetry (DSC 204 F1, Netzsch, Germany) was performed in an air atmosphere with a gas flow of 40 mL/min from 25 \degree C to 590 °C and a heating rate 10 °C/min, in an aluminum crucible with pierced lid. The data were analyzed using NETZSCH Proteus software. In this work, we discuss the results of thermal analysis (TG, DSC) in a temperature range of 150 °C - 600 °C where thermal degradation of the main wood polymers takes place.

FTIR spectra were obtained by VERTEX 80V IR Fourier Spectrometer (Bruker Optics Germany) in a spectral range of 8000 cm⁻¹ - 350 cm⁻¹ at a spectral resolution of 0,2 cm⁻¹, with a wavenumber repeatability of ± 0.05 cm⁻¹. The samples were prepared by mixing powdered samples with ~100 mg KBr and then compressing them to form a thin tablet.

The thermogravimetric data were used to determine the kinetic parameters through the isoconversional method of Flynn-Wall-Ozawa. The activation energy calculated according to the FWO method is called the apparent activation energy because it is the sum of the activation energies of the chemical reactions and physical processes that occur simultaneously during thermal degradation of wood. Baroni *et al.* (2016) demonstrated that the kinetic parameters calculated using the FWO model were in a satisfactory agreement with experimental data on wood decomposition.

The energy of activation (*Еа*) was calculated according to an Equation 1 (Mamleev *et al.* 2004):

$$
\ln(\beta) \approx \ln(\frac{AE_a}{RF(\alpha)}) - 5,3305 - 1,052\frac{E_a}{RT}
$$
 (1)

Where α is the degree of conversion: $\alpha = \frac{m_0}{n_0}$ *f m m m m* $\alpha = \frac{m_0 - m}{m - m_f}$, m0 is the initial sample mass in the TG

experiment, m is the actual sample mass at temperature T, mf is the final sample mass after thermal decomposition, β is the heating rate, R is the gas constant, A is the pre-exponential factor, F(a) is the function of the mathematical representation of FWO kinetic model. The activation energy (Еа) is calculated from the straight-line slope of $\ln(\beta)$ versus 1/T.

T-test was used to estimate whether TG and DSC parameters for heat-treated and untreated rubberwood were significantly different. The differences were considered significant at p<0,05. Statistical analysis of data was performed using the STATISTICA 10 program (StatSoft Inc, Tulsa, OK, USA).

Results and discussion

Density

Thermal treatment significantly affected the density of the rubberwood samples. See the data in Table 1.

Table 1: Density change of treated and untreated rubberwood samples

* average density value of six sample

The rise of temperature from 180 °C to 220 °C considerable increase the mass loss what is in harmony with former research in other wood species (Pásztory 2017). Interesting that there is not much difference between 25 h and 35 h in 220 °C treatment. It seems most of degradable component decomposed in this temperature and the longer treatment causes only slight mass loss.

Thermal analysis (TG, DSC)

Thermal degradation of wood in TG and DSC measurements occurs as a result of the breakdown of its individual components (Kačík *et al.* 2017). Hemicelluloses, cellulose, and lignin degrade at different temperature ranges. Hemicelluloses decompose in a lower temperature range (225 - 325) °C than cellulose (305 - 375) °C (Shen *et al.* 2009). Lignin starts to decompose slowly at low temperatures of 200 $\mathrm{°C}$ - 275 $\mathrm{°C}$ but the main process occurs around 400 $\mathrm{°C}$ (Brebu and Vasile 2010). The intervals of the thermal degradation of wood components partly overlap.

The thermogravimetric (TG) and differential thermogravimetric (DTG) curves of untreated and heat-treated rubberwood are presented in Figure 1. The TG curve shows the mass loss and the DTG curve represents the mass loss rate. As can be seen from Figure 1, the shape of DTG curves and position of DTG peaks for the heat-treated samples differ from untreated wood. According to DTG peaks, the thermal degradation of rubberwood samples can be divided into three stages of mass loss: at (180 - 200) °C - (300 - 303) °C and (300 - 303) °C -380 °C, and at 380 °C - 500 °C, which related to the thermal decomposition of hemicelluloses, cellulose and lignin, respectively. In an oxidizing atmosphere, the first two stages are characterized by the release of volatile substances and their ignition, which leads to the formation of char. The third stage is associated with the combustion (oxidation) of char. Lignin is the main contributor in this stage as it is the main responsible for char formation (López-González *et al.* 2013, Kačík *et al.* 2017). The mass loss occurring at each stage of the thermal decomposition of untreated rubberwood is consistent with the literature data on the chemical composition of rubberwood: 57,7 - 77,8 % holocellulose, $38,5 - 41,6$ % α -cellulose, and $16,6 - 17,8$ % Klason lignin (Simatupang *et al.* 1994, Zaki *et al.* 2012, Severo *et al.* 2016).

Figure 1: TG and DTG curves of rubberwood in an air atmosphere at heating rate 10 °C/min. (line 1): untreated; (line 2): heat treated at 180 °C; (line 3): heat treated at 220 °C duration: (a) 15 h; (b) 25 h; (c) 35 h.

The first DTG peak at 295 °C on the DTG curve of untreated wood assigned to the breakdown of amorphous polysaccharides (mainly hemicelluloses) became visible as a shoulder or disappeared after heat treatment (Figure 1). It indicates the loss of hemicelluloses in the heat-treated samples.

During heat treatment in a temperature range from 170 °C to 230 °C hemicelluloses are the most affected compounds of wood (Korošec *et al.* 2017). Their decomposition occurs through deacetylation and dehydration reactions. Acetic acid released acts as a catalyst for depolymerization, which further increases the decomposition of polysaccharides (Esteves and Pereira 2008).

The thermal decomposition of rubberwood heat-treated at 220 °C started at a higher temperature compared to the untreated wood. The heat-treated rubberwood exhibited significantly lower mass loss of hemicelluloses compared to untreated wood (Table 2). It can be clearly seen that the decomposition of hemicelluloses increased with increasing treatment temperature 180 °C and 220 °C. The similar results of TG measurements were obtained by Korošec *et al.* (2009) for thermally treated spruce wood. The heat treatment temperature had a stronger effect than the duration of the heat treatment. A significant decrease in the relative proportion of hemicelluloses in the heattreated samples was observed after duration of 15 h at both temperatures. The extended time of 25 h and 35 h resulted in a slight decrease of hemicelluloses mass loss (< 1 %) indicating a diminishing trend of their further degradation during heat treatment. The differences in mass loss of hemicelluloses between all heat-treated samples and untreated rubberwood were statistically significant. González-Peña *et al.* (2009) also observed that a sample mass loss due to the decomposition of wood hemicelluloses was more affected by temperature than by processing time.

Table 2: Stages of rubberwood thermal degradation at a heating rate 10 °C/ min in an air atmosphere (mean \pm standard deviation).

The second peak on the DTG curve attributed to the decomposition of cellulose for samples heattreated at 220 °C shifted to a lower temperature range due to decomposition of hemicelluloses and probably amorphous regions of cellulose. The differences in the second peak temperature were statistically significant between heat-treated at 220 °C for 15, 25, 35 h and untreated rubberwood. Amorphous cellulose starts to decompose when the treatment temperature reaches 180 °C. The crystalline cellulose is more resistant to heat treatment (Korošec *et al.* 2017). TG results showed a statistically significant increase in mass loss associated with the second peak after the heat treatment at both temperatures (Table 2). We believe that the higher relative proportion of cellulose was observed due to decomposition of hemicelluloses and, as a result, a change in the ratio of major wood components in the heat-treated samples. Our results are consistent with observations of Kačík *et al.* (2017) for heat-treated silver fir wood. With longer treatment duration at both temperatures, the mass loss slightly decrease because cellulose was more affected.

The third DTG peak in the temperature range of $380 \degree C - 500 \degree C$ mainly related to thermoxidation of lignin shifted to a higher temperature range for the heat-treated samples, except for rubberwood heat-treated at 180 °C for 35 h. This may be due to the effect of hemicelluloses decomposition and some alterations in lignin. Lignin starts to degrade in the beginning of the heat treatment but at a lower rate than polysaccharides (Esteves and Pereira 2008). The differences in third peak temperature were statistically significant between heat-treated and untreated rubberwood, except for the heat treatment at 180 \degree C for 15 h. The mass loss associated with lignin degradation increased after heat treatment at 180 °C and 220 °C, indicating a higher proportion of lignin. These changes in mass loss of lignin were statistically significant for all heat-treated samples. The samples heat-treated at 220 °C exhibited much greater mass loss than samples heat-treated at 180 °C. An increase in lignin content after heat treatment is attributable to decomposition of polysaccharides and condensation reactions between lignin and polysaccharide breakdown products (Hill *et al.* 2021). The results of thermogravimetry are consistent with the findings that the relative proportion of lignin increases in heat-treated wood (Brito *et al.* 2008, Ates *et al.* 2009, Severo *et al.* 2016, Lopes *et al.* 2018, Cui and Matsumura 2019). No statistically significant differences were found in the residual mass, corresponding to the presence of inorganic salts, between heat-treated and untreated wood.

In an air atmosphere, the heat flow curves (DSC curves) for all samples showed two main exothermic peaks in the temperature region 150 \degree C - 520 \degree C related to the thermal degradation of polysaccharide complex and lignin, respectively (Figure 2). The intensity of the first peak decreased and the intensity of the second peak increased after heat treatment at 220 °C for 25 h and 35 h. Both exothermic peaks on the DSC curves of rubberwood treated at 220 °C shifted to a higher temperature region compared to untreated rubberwood. This indicates a stronger effect of high temperature on wood polymers. These results were statistically significant. The values of exothermic effect for the samples heat treated at 180 °C for 35 h and at 220 °C for 25 h and 35 h were higher compared to untreated wood (Figure 3), but these differences were not statistically significant.

Figure 2: DSC profiles of rubberwood in an air atmosphere at a heating rate of 10 °C/min. (line 1): untreated; (line 2): heat treated at 180 °C; (line 3): heat treated at 220 °C duration: (a) $15 h$; (b) $25 h$; (c) $-35 h$.

Figure 3: Exothermic effect of rubberwood thermal decomposition in an air atmosphere at a heating rate of 10 °C/min obtained by DSC (mean \pm standard deviation).

Kinetic analysis

The kinetics of wood thermal degradation can be summarized by three reactions corresponding to decomposition of the main wood components: the most reactive hemicelluloses, cellulose, and lignin. Figure 4 shows the dependence of activation energy (E_a) on conversion degree between 0,05 and 0,95. In the temperature range of the thermal decomposition of polysaccharide complex (hemicelluloses, cellulose) at $0.05 < \alpha < 0.65$ the average value of E_a increased with the heat treatment temperature and duration (Figure 5a). With increasing temperature and duration of heat treatment, the proportion of hemicelluloses in the polysaccharide complex decreases but the degree of cellulose ordering increases due to dehydration and removal of firmly bound moisture from the interfibrillar space. This probably leads to a corresponding increase in *Ea*. During the thermal decomposition of wood in the conversion degree range of 0,05 - 0,65, the dependence $E_a = f(\alpha)$ for the heat-treated samples was characterized by two activation energy maxima, which indicate the two-stage process of the thermal decomposition of polysaccharide complex (Figure 4). No significant differences in E_a values were observed at the stage of lignin degradation (0,60 < α)

 (0.95) (Figure 5b) the average values of E_a in both cases were close - 337,4 kJ/mol \pm 82,3 kJ/mol (the heat treatment at 180 °C) and 334,9 kJ/mol \pm 65,4 kJ/mol (the heat treatment at 220 °C). As it can be seen from Figure 4 and Figure 5, the changes in lignin caused by the heat treatment are stochastic apparently due to the specific structure of lignin.

Figure 4: The dependence of activation energy on conversion degree determined by FWO method for rubberwood heat-treated at 180 °C and 220 °C for 15 h 25 h and 35 h.

Figure 5: (a) The dependence of the average activation energy of the thermal decomposition of polysaccharide complex and (b) lignin on treatment duration.

FTIR spectroscopy

Analysis of the FTIR spectra of wood is normally represented in the "fingerprint" region (1800 $cm⁻¹$ and 600 $cm⁻¹$) in which specific and common bands appear assigned to hemicelluloses, cellulose, and lignin. Figure 6 shows the FTIR spectra of the heat-treated and untreated rubberwood samples. The resolution of spectra can be enhanced by derivative FTIR spectroscopy. We used the fourth derivatives of the FTIR spectra to identify peaks (Figure 7). The negative values of the 4th derivatives are taken to be zero, since the maxima of the derivatives correspond (by wavenumber value) to the maxima of the original FTIR spectra. The intensities of absorption bands were obtained from the original FTIR spectra.

Figure 6: FTIR spectra of rubberwood samples treated at 180 °C at 220 °C during 25 h as an example.

Figure 7: The fourth derivatives of FTIR spectra of heat-treated and untreated rubberwood as an example.

The absorption bands between 1750 cm^{-1} and 1700 cm^{-1} are attributed to C=O stretch in unconjugated ketones and in ester groups (frequently of polysaccharide origin); conjugated aldehydes and carboxylic acids (Esteves *et al.* 2013, Pozo *et al.* 2016). FTIR results showed that the intensities of the absorption bands at 1735 cm^{-1} and 1720 cm^{-1} decreased at heat treatment 180 °С for 15 h compared to untreated wood, which might be due to the breaking of acetyl groups in hemicelluloses (Kotilainen *et al.* 2000, Esteves *et al.* 2013, Kubovský *et al.* 2020). The absorption band at 1735 cm⁻¹ shifted to lower wavenumbers for rubberwood heat-treated at 220 °C. The intensities of the bands at 1735 cm^{-1} and 1720 cm^{-1} increased with increasing treatment severity. This may be due to an increase in carbonyl or carboxyl groups in polysaccharides or lignin as a result of oxidation (Kotilainen *et al.* 2000, Esteves *et al.* 2013). Li *et al.* (2020b) reported that the thermal oxidation reaction among main components of rubberwood become more intense as the heat treatment temperature increases. An increase in the intensity of the bands around 1730 cm⁻¹ after thermal modification of wood was observed by other authors (Esteves *et al.* 2013, Özgenç *et al.* 2017, Sikora *et al.* 2018).

The absorption bands at 1595 cm^{-1} for aromatic skeletal vibrations plus C=O stretching and 1502 cm-1 for aromatic skeletal vibration are considered as characteristic for lignin (Pozo *et al.* 2016). The absorption band at 1502 cm^{-1} shifted to smaller wavenumbers for heat-treated samples. Compared to untreated wood, the intensities of the bands at 1595 cm^{-1} and 1502 cm^{-1} decreased after heat treatment at 180 °С for 15 and 25 h due to lignin degradation reactions. With increasing severity of the heat treatment, the intensity of these bands increased. We believe this may be due to several reasons: 1) oxidation of some reactive sites in lignin resulting in formation of carbonyl groups (Kotilainen *et al.* 2000, Li *et al.* 2020a), 2) a substantially higher content of lignin (Pandey and Nagveni 2007), 3) condensation from the cleavage of β-O-4 linkages and the breaking of aliphatic side chains of lignin (Lin *et al.* 2018, Sikora *et al.* 2018). Kubovský *et al.* (2020) reported

that the predominance of lignin degradation occurred at lower temperatures of the heat treatment; higher temperatures caused mainly condensation reactions.

The absorption bands at 1164 cm^{-1} and 1061 cm^{-1} are characteristic for polysaccharides. The band at 1164 cm⁻¹ is assigned to C-O-C asymmetric stretch vibrations and the band at 1061 cm⁻¹ is attributed C−O stretching vibrations (Pozo *et al.* 2016). The absorption band at 1164 cm-1 shifted to smaller wavenumbers for rubberwood heat-treat at 220 °С. The intensity of these bands decreased for heat treatment at 180 °С for 15 h and increased with severity of treatment. These results are consistent with observations of González-Peña *et al.* (2009) and Özgenç *et al.* (2017) who reported an increase in the intensities of the bands at $1155 \text{ cm}^{-1} - 1159 \text{ cm}^{-1}$ and 1057 cm^{-1} for thermally-modified wood. The authors suggested that the higher intensity of these bands might be associated with an increase in the content of crystalline cellulose as well as with condensation reactions. Increased absorption band at 1061 cm^{-1} can also indicate the formation of aliphatic alcohols. Kubovský *et al.* (2020) observed a slight increase in the height of the band at 1161 cm-1 for the holocellulose complex isolated from heat-treated samples, which indicates dehydration reactions with the formation of covalent intermolecular bonds, i.e., cross-links, by ether bonds and gradual degradation of polysaccharides.

Conclusions

The effect of heat treatment on the chemical composition, thermal behavior and thermal degradation kinetics of heat-treated rubberwood was studied. Thermal analysis (TG, DSC) of heattreated rubberwood indicated a loss of hemicelluloses, an increase in the relative proportions of cellulose and lignin, and changes in the structure of wood polymers.

The treatment temperature had a greater effect on the chemical composition of rubberwood than treatment duration.

The FWO results showed that the activation energy in the conversion degree range of 0,05 - 0,65 increased with increasing temperature and duration of the heat treatment.

FTIR spectra showed changes in the characteristic absorption bands of polysaccharides and lignin, but the interpretation of FTIR results is difficult because of the appearance of functional groups that coincide with the characteristic bands of wood polymers, due to different reactions occurring simultaneously during heat treatment.

Authorship contributions

O. A. S.: Investigation, methodology, visualization, writing. S. R. L.: Conceptualization. A. A. A.: Data curation. S. S.: Resource provide the appropriate. Z. B.: Investigation perform thermal treatments.

Z. P.: Project administration funding acquisition, finalizing text, revision.

Acknowledgements

The current study was performed in accordance with the Cooperation agreement on academic and research between V.N. Sukachev Institute of Forest SB RAS, Federal Research Centre "Krasnoyarsk Science Centre SB RAS" and University of Sopron.

References:

Ates, S.; Akyildiz, M.H.; Ozdemir, H. 2009. Effects of heat treatment on calabrian pine (*Pinus brutia* Ten.) wood. *BioResources* 4(3): 1032-1043. http://dx.doi.org/10.15376/biores.4.3.1032- 1043

Baroni, É.G.; Tannous, K.; Rueda-Ordόñez, Y.J.; Tinoco-Navarro, L.K. 2016. The applicability of isoconversional models in estimating the kinetic parameters of biomass pyrolysis. *Journal of Thermal Analysis and Calorimetry* 123: 909-917. http://dx.doi.org/10.1007/s10973-015-4707-9

Brebu, M.; Vasile, C. 2010. Thermal degradation of lignin - a review. *Cellulose Chemistry and Technology* 44(9): 353-363. https://www.cellulosechemtechnol.ro/pdf/CCT9(2010)/P.353- 363.pdf

Brito, J.O.; Silva, F.G.; Leão, M.M.; Almeida, G. 2008. Chemical composition changes in *Eucalyptus* and *Pinus* submitted to heat treatment. *Bioresource Technology* 99(18): 8545-8548. https://doi.org/10.1016/j.biortech.2008.03.069

Chanpet, M.; Rakmak, N.; Matan, N.; Siripatana, C. 2020. Effect of air velocity,

temperature, and relative humidity on drying kinetics of rubberwood. *Heliyon* 6(10). e05151. https://doi.org/10.1016/j.heliyon.2020.e05151

Cui, X.; Matsumura, J. 2019. Wood surface changes of heat-treated *Cunninghamia lanceolate* following natural weathering. *Forests* 10(9). e791. https://doi.org/10.3390/f10090791

Devi, R.R.; Maji, T.K.; Banerjee, A.N. 2004. Studies on dimensional stability and thermal properties of rubber wood chemically modified with styrene and glycidyl methacrylate. *Journal of Applied Polymer Science* 93: 1938-1945. https://doi.org/10.1002/app.20657

EN. 1097-3:1999. (1999). Tests for mechanical and physical properties of aggregates determination of loose bulk density and voids, https://www.en-standard.eu/une-en-1097-3-1999 tests-for-mechanical-and-physical-properties-of-aggregates-part-3-determination-of-loose-bulkdensity-and-

voids/?srsltid=AfmBOop7unz5ou_c1hhwSj3TWoxRL4ehIVYZGDsU8v1x7gls2LPTw3uI **Esteves, B.; Pereira, H. 2008.** Wood modification by heat treatment: a review. *BioResources* 4: 370-404. http://dx.doi.org/10.15376/biores.4.1.370-404

Esteves, B.; Velez, Marques, A.; Domingos, I.; Pereira, H. 2013. Chemical changes of heat treated pine and eucalypt wood monitored by FTIR. *Maderas. Ciencia y Tecnología* 15(2): 245- 258. http://dx.doi.org/10.4067/S0718-221X2013005000020

Eufrade Junior, H.J.; Ohto, J.M.; da Silva, L.L.; Palma, H.A.L.; Ballarin, A.W. 2015. Potential of rubberwood (*Hevea brasiliensis*) for structural use after the period of latex extraction: a case study in Brazil. *Journal of Wood Science* 61: 384-390. https://doi.org/10.1007/s10086-015-1478-7

Gao, M.; Sun, C.Y.; Wang, C.X. 2006. Thermal degradation of wood treated with flame retardants. *Journal of Thermal Analysis and Calorimetry* 85(3): 765-769. https://doi.org/10.1007/s10973-005-7225-3

González-Peña, M.M.; Curling, S.F.; Hale, M.D.C. 2009. On the effect of heat on the chemical composition and dimensions of thermally-modified wood. *Polymer Degradation and Stability* 94(12): 2184-2193. https://doi.org/10.1016/j.polymdegradstab.2009.09.003

Hill, C.; Altgen, M.; Rautkari, L. 2021. Thermal modification of wood-a review: chemical changes and hygroscopicity. *Journal of Materials Science* 56: 6581-6614. https://doi.org/10.1007/s10853-020-05722-z

Kačík; F.; Luptáková, J.; Šmíra, P.; Eštoková, A.; Kačíková, D.; Nasswettrová, A.; Bubeníková, T. 2017. Thermal analysis of heat-treated silver fir wood and larval frass*. Journal of Thermal Analysis and Calorimetry* 130: 755-762. http://doi.org/10.1007/s10973-017-6463-5 **Killmann, W.; Hong, L.T. 2000.** Rubberwood - the success of an agricultural by-product. *Unasylva* 51: 66-72. https://www.researchgate.net/publication/283167477_Rubberwood_-

_The_success_of_an_agricultural_by-product

Korošec, R.C.; Lavrič, B.; Rep, G.; Pohleven, F.; Bukovec, P. 2009. Thermogravimetry as a possible tool for determining modification degree of thermally treated Norway spruce wood. *Journal of Thermal Analysis and Calorimetry* 98: 189-95. http://dx.doi.org/10.1007/s10973-009- 0374-z

Korošec, R.C.; Renko, S.; Rep, G.; Bukovec, P. 2017. Determination of the thermal modification degree of beech wood using thermogravimetry. *Journal of Thermal Analysis and Calorimetry* 130: 1383-1390. http://dx.doi.org/10.1007/s10973-017-6446-6

Kotilainen, R.; Toivannen, T.; Alén R. 2000. FTIR monitoring of chemical changes in softwood during heating. *Journal of Wood Chemistry and Technology* 20(3): 307-320. https://doi.org/10.1080/02773810009349638

Wood Science 66(1). e50. http://dx.doi.org/10.1186/s10086-020-01897-w

Kubovský, I.; Kačíková, D.; Kačík, F. 2020. Structural changes of oak wood main components caused by thermal modification. *Polymers* 12(2): e485. https://doi.org/10.3390/polym12020485 **Li, T.; Li, G.; Li, J.; Li, X.; Lu, Q.; Li, M. 2020b**. Characterization of the effluents condensated by volatile organic compounds during heat-treated rubberwood process. *Journal of*

Li, X.; Li, T.; Li, G.; Li, M.; Lu, Q.; Qin, S.; Li, J. 2020a. Effects of UV light irradiation on color changes in thermally modified rubber wood based on FTIR. *BioResources* 15(3): 5179- 5197. http://dx.doi.org/10.15376/biores.15.3.5179-5197

Lin, B.J.; Colin, B.; Chen, W.H.; Pétrissans, A.; Rousset, P.; Pétrissans, M. 2018. Thermal degradation and compositional changes of wood treated in a semi-industrial scale reactor in vacuum. *Journal of Analytical and Applied Pyrolysis* 130: 8-18. https://doi.org/10.1016/j.jaap.2018.02.005

Lopes, J. de O.; Garcia, R.A.; Souza, N.D. 2018. Infrared spectroscopy of the surface of thermally-modified teak juvenile wood. *Maderas. Ciencia y Tecnología* 20(4): 737-746. http://dx.doi.org/10.4067/S0718-221X2018005041901

López-González, D.; Fernandez-Lopez, M.; Valverde, J.L.; Sanchez-Silva, L. 2013. Thermogravimetric-mass spectrometric analysis on combustion of lignocellulosic biomass. *Bioresource Technology* 143: 562-574. https://doi.org/10.1016/j.biortech.2013.06.052

Mamleev, V.; Dourbigot, S., Le Bras, M.; Lefebvre, J. 2004. Three model-free methods for calculation of activation energy in TG. *Journal of Thermal Analysis and Calorimetry* 78(3). e1009. http://dx.doi.org/10.1007/s10973-005-0467-0

Özgenç, Ö.; Durmaz, S.; Boyaci, I.H.; Eksi-Kocak, H. 2017. Determination of chemical changes in heat-treated wood using ATR-FTIR and FT Raman spectrometry. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 17. e395. http://doi.org/10.1016/j.saa.2016.08.026

Pandey, K.K.; Nagveni, H.C. 2007. Rapid characterisation of brown and white rot degraded chir pine and rubberwood by FTIR spectroscopy. *Holz als Roh- und Werkstoff* 65: 477-481. https://doi.org/10.1007/s00107-007-0181-9

Pásztory, Z.; Horváth, N.; Börcsök, Z. 2017. Effect of heat treatment duration on the thermal conductivity of spruce and poplar wood. *European Journal of Wood and Wood Products* 75: 843-845. https://doi.org/10.1007/s00107-017-1170-2

Poletto, M.; Zattera, A.J.; Santana, R.M.C. 2012. Thermal decomposition of wood: Kinetics and degradation mechanisms. *Bioresource Technology* 126: 7-12. http://dx.doi.org/10.1016/j.biortech.2012.08.133

Pozo, C.; Díaz-Visurraga, J.; Contreras, D.; Freer, J.; Rodríguez, J. 2016. Characterization of temporal biodegradation of radiata pine by *Gloeophyllum trabeum* through principal component analysis-based two-dimensional correlation. *Journal of the Chilean Chemical Society* 61(2): 2878-2883. http://dx.doi.org/10.4067/S0717-97072016000200006

Ratnasingam, J.; Ioras, F. 2012. Effect of heat treatment on the machining and other properties of rubberwood. *European Journal of Wood and Wood Products* 70: 759-761. https://doi.org/10.1007/s00107-011-0587-2

Ratnasingam, J.; Ioras, F. 2013. Load-bearing characteristics of heat-treated rubberwood furniture components and joints. *European Journal of Wood and Wood Products* 71: 287-289. http://dx.doi.org/10.1007/s00107-013-0662-y

Severo, E.T.D.; Calonego, F.W.; Sansígolo, C.A.; Bond, B. 2016. Changes in the chemical composition and decay resistance of thermally-modified *Hevea brasiliensis* wood. *PLoS ONE* 11(3). e0151353 https://doi.org/10.1371/journal.pone.0151353

Shen, D.K.; Gua, S.; Luo, K.H.; Bridgwater, A.V.; Fang, M.X. 2009. Kinetic study on thermal decomposition of woods in oxidative environment. *Fuel* 88(6): 1024-1030. http://dx.doi.org/10.1016/j.fuel.2008.10.034

Sikora, A.; Kačík, F.; Gaff, M.; Vondrová, V.; Bubeníková, T.; Kubovský, I. 2018. Impact of thermal modification on color and chemical changes of spruce and oak wood. *Journal of Wood Science* 64: 406-416. https://doi.org/10.1007/s10086-018-1721-0

Simatupang, M.H.; Schmitt, U.; Kasim A. 1994. Wood extractives of rubberwood (*Hevea brasiliensis*) and their influences on the setting of the inorganic binder in gypsum-bonded particleboards. *Journal of Tropical Forest Science* 6(3): 269-285. https://www.jstor.org/stable/43582437

Srinivas, K.; Pandey, K.K. 2012. Photodegradation of thermally modified wood. *Journal of Photochemistry and Photobiology B: Biology* 117: 140-145. https://doi.org/10.1016/j.jphotobiol.2012.09.013

Umar, I.; Zaidon, A.; Lee, S.H.; Halis, R. 2016. Oil-heat treatment of rubberwood for optimum changes in chemical constituents and decay resistance. *Journal of Tropical Forest Science* 28(1): 88-96. https://www.jstor.org/stable/43748082

Zaki, J.A.; Muhammed, S.; Shafie, A.; Daud, W.R.W. 2012. Chemical properties of juvenile latex timber clone rubberwood trees. *Malaysian J Anal Sci* 16(3):228-234.

http://mjas.analis.com.my/wp-content/uploads/2018/11/Junaiza.pdf

Zhang, N.; Xu, M.; Cai, L. 2019. Improvement of mechanical, humidity resistance and thermal properties of heat-treated rubber wood by impregnation of SiO₂ precursor. *Scientific Reports* 9. e982. https://doi.org/10.1038/s41598-018-37363-3

Zhao, B.; Yu, Z.; Zhang, Y.; Qi, C. 2019. Physical and mechanical properties of rubberwood (*Hevea brasiliensis*) dyed with *Lasiodiplodia theobromae*. *Journal of Wood Science* 65(1). e63. https://doi.org/10.1186/s10086-019-1843-z