

OIL-HEAT TREATMENT OF RUBBERWOOD FOR OPTIMUM CHANGES IN CHEMICAL CONSTITUENTS AND DECAY RESISTANCE

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UMAR I, ZAIDON A, LEE SH & HALIS R. 2016. Oil-heat treatment of rubberwood for optimum changes in chemical constituents and decay resistance. Effects of oil-heat treatment on chemical constituents and decay resistance of rubberwood (*Hevea brasiliensis*) were investigated in this work. Oil-heat treatment with palm oil as heating medium was carried out by immersing rubberwood samples (300 mm longitudinally \times 20 mm radially \times 20 mm tangentially) in hot oil bath. Wood samples were immersed in the palm oil at temperatures and time periods ranging from 172 to 228 °C and 95 to 265 min respectively. Cellulose, hemicellulose and lignin contents and weight loss of samples by the fungus *Pycnoporus sanguineus* were evaluated. Four linear and one quadratic models were developed using response surface methodology. High adjusted r^2 values were obtained and the adequacy of the models was confirmed. Cellulose and hemicellulose reduced in treated samples. Such reductions became greater with increasing temperature and exposure time. However, lignin content of samples increased with increasing temperature of treatment and extended time. Decay resistance of treated samples against *P. sanguineus* improved with increased treatment temperature and time. The enhancement in decay resistance was highly related to chemical constituents in the treated sample.

Keywords: Central composite design, *Hevea brasiliensis*, palm oil, *Pycnoporus sanguineus*, response surface methodology

INTRODUCTION

Rubberwood is a versatile timber and environmentally friendly material with low price and high export value as well as market potential. It is an important source of raw material for a wide range of applications in wood industry. However, owing to its low strength, dimensional instability and low durability, use of rubberwood is restricted to interior applications only. Improvement in stability, durability and strength properties of rubberwood can be achieved by heat treatment which has long been recognised as the effective method to enhance stability of wood (H'ng et al. 2012) as well as decay resistance against termites and other biological deterioration agents (Lee et al. 2013).

Heat treatment can reduce swelling of wood by 50 to 80% (Burmester 1973, Giebler 1983). However, improvement in dimensional stability by heat treatment is always accompanied by reduction in mechanical properties. Degradation

of hemicellulose is a major factor for the loss of mechanical strength (Boonstra & Tjeerdsma 2005). When wood is heated, hemicelluloses begin to degrade, resulting in the production of methanol, acetic acid and various volatile heterocyclic compounds such as less hygroscopic furans and γ -valerolactone (Stamm 1964, Hill 2006).

Vegetable oil heated to high temperature has been used by several researchers to treat wood (Sailer et al. 2000, Wang & Cooper 2005, Welzbacher & Rapp 2005, Manalo & Acda 2009). Vegetable oils such as palm, linseed, rapeseed, coconut, soybean and sunflower oils are non-toxic and inexpensive. Moreover, these oils are good heat transfer media and have high boiling point which is suitable for heat treatment of wood. Oil-heat treatment improves wood properties by a combination of changes in chemical properties, exposure to high

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temperature and oil uptake. Under the same treatment parameters, wood treated using oils had better properties and decay resistance than wood dried using oven in the presence of oxygen. The oxidative process during heat treatment of wood will reduce the strength of samples faster under aerobic conditions compared with anaerobic conditions (Hill 2006). Therefore, oils are good heating medium for heat treatment as they are able to transfer heat to the wood more readily and equally. Moreover, they are able to prevent oxygen from reaching the wood during treatment and lead to only slight reduction in strength (Dubey et al. 2011). Oil absorption during treatment forms a protective layer on the wood surface, leading to enhancement in dimensional stability of the treated wood (Tomak et al. 2011).

Heat treatment of wood using hot oils can reduce moisture from 30 to 52%, suggesting a reduction in hygroscopicity. At the same time, the equilibrium moisture content of the wood treated at 220 °C for 4 hours was reduced by about 50% (Wang & Cooper 2005).

Weight loss of wood due to fungal attack is related to its chemical composition. Thus, chemical composition can be used to predict decay resistance of treated wood against fungi. Improvement in resistance to fungal decay by oil–heat treatment has been reported to be caused by the increase in hydrophobicity, generation of toxic compounds and degradation of hemicelluloses in the treated wood (Weiland & Guyonnet 2003). The objective of this study was to evaluate the changes in chemical constituents of palm oil–heat-treated rubberwood. The changes in the chemical constituents after treatment were then correlated with decay resistance of the rubberwood. Optimisation model for heat treatment conditions using central composite design with response surface methodology was also developed in the present study.

MATERIALS AND METHODS

Response surface methodology and central composite design

In the present study, central composite design using response surface methodology was used to determine the effects of treatment

variables of rubberwood treated with hot palm oil on chemical constituents and decay resistance. Two independent variables, namely, treatment temperature and treatment time were selected and the response variables were holocellulose, cellulose, hemicellulose and lignin contents as well as decay resistance against *Pycnoporus sanguineus*.

The central composite design was applied using Design Expert Software (State Ease, Design Expert 9). A 13-run central composite design using response surface methodology was developed. Table 1 shows the range and the levels of the variables investigated in this study. Each of the independent variables was studied at five different levels. Experimental conditions of coded and actual values developed using response surface methodology with central composite design are shown in Table 2.

Sample preparation and heat treatment schedule

Rubberwood samples (20 years old) were prepared by cutting them into the size of 300 mm longitudinally × 20 mm radially × 20 mm tangentially and air drying to about 15% moisture content. Samples were conditioned at $65 \pm 2\%$ relative humidity and temperature of 20 ± 2 °C for 4 weeks until constant weight was reached. The defect-free samples were divided into 14 groups (13 runs + 1 untreated), each containing 10 samples, for treatment at various temperatures and durations.

The heat treatment was carried out in a metal tank three-quarters filled with palm oil as heating medium. The boiling point of the palm oil used in this study was 320 °C, which was higher than the temperature required for the treatment of wood in this study (172 to 228 °C). Conditioned rubberwood specimens were treated with hot bath of palm oil at different temperatures and exposure times according to the response surface methodology models. The palm oil was heated in the metal tank to the required temperatures as stated in Table 2 before the rubberwood samples were immersed into it. After the respective required immersion times (Table 2), the samples were taken out from the tank. Residual oil on the rubberwood surface was wiped off using cloth to avoid absorption by the wood. The samples were left in a conditioning

Table 1 Actual and coded values tabulation

Factor	Actual and coded values				
	- α	-1	0	1	α
Temperature (°C)	172	180	200	220	228
Time (min)	95	120	180	240	265

Table 2 Experimental conditions using central composite design

Coded factor		Actual factor	
Temperature	Time	Temperature (°C)	Time (min)
- α	0	172	180
-1	-1	180	120
-1	1	180	240
0	- α	200	95
0	0	200	180
0	0	200	180
0	0	200	180
0	0	200	180
0	0	200	180
0	0	200	180
0	α	200	265
1	-1	220	120
1	1	220	240
α	0	228	180

room at 25 °C with relative humidity of 65% and their weights were checked daily until constant consecutive weights were achieved.

Evaluation of chemical composition in treated rubberwood sample

Determination of holocellulose, cellulose and lignin contents of the samples was conducted in accordance to TAPPI standards, namely, T9m-54 (TAPPI 1998), T203 os-74 (TAPPI 1994) and T222 om-02 (TAPPI 2002) respectively. Hemicelluloses was determined by subtracting the α -cellulose from the holocellulose contents. All percentages of chemical constituents were averages of three replicates to the nearest of $\pm 0.1\%$. Prior to the chemical analysis, samples having dimension of 20 mm \times 20 mm \times 20 mm were cut from the oil–heat-treated rubberwood for preparation of sawdust. The wood specimens were ground to a sieve size of 40–25 mesh. Polar and water soluble extractives were removed using hot water followed by mixture of ethanol

and acetone at a ratio of 1:2. After removal of extractives, the sawdust was air dried until constant weight was reached.

Evaluation of decay resistance of treated sample

The oil–heat-treated rubberwood was tested in the laboratory for decay resistance against white rot fungus, *P. sanguineus*, following ASTM (2005). The result of the treatment was determined by the weight loss (%) caused by the fungal decay. Eight test blocks of size 18 mm \times 18 mm \times 10 mm were prepared from each group of treated and untreated specimens. The blocks were stabilised in a conditioning room at 25 \pm 2 °C and 65 \pm 5% relative humidity until they reached constant weights.

Culture bottles were prepared following ASTM D2017-05 (ASTM 2005). Each culture bottle was filled with 150 g sieved soil and 70 mL distilled water. For fungus inoculation, feeder strip using rubberwood (34 mm long \times 28 mm

wide × 3 mm thick) was placed on the soil of each culture bottle and incubated between 25 and 27 °C for approximately 3 weeks. When the feeder strips were covered by mycelium and ready to receive test blocks, test blocks were placed with their cross-section surfaces centred in contact with the mycelium-covered feeder strips. The bottles containing test blocks were incubated for 12 weeks. After incubation, the test blocks were weighed and left on trays or rack in a conditioning room until constant weights were reached. Each block was weighed again and the weight loss of the test block was calculated using the equation below:

$$\text{Weight loss (\%)} = ((W_a - W_b)/W_a) \times 100 \quad (1)$$

where W_a = conditioned weight of the test block before exposure to fungus (g) and W_b = conditioned weight of the test block after exposure to fungus (g).

RESULTS AND DISCUSSION

Regression and adequacy of the models

Table 1 presents the actual and predicted values of chemical constituents and mass loss of oil–heat-treated rubberwood under 13 different treatment conditions through the response surface methodology analysis. From the experimental results, response surface methodology models for chemical constituents and weight loss by *P. sanguineus* of the oil–heat-treated rubberwood were subsequently developed. The linear and quadratic equations determined for the chemical constituents and weight loss by *P. sanguineus* of the treated rubberwood were as follows:

$$\text{Holocellulose} = 64.19 - 3.74\text{Temp} - 1.00\text{Time} \quad (2)$$

$$\text{Hemicellulose} = 25.85 - 1.65\text{Temp} - 0.38\text{Time} \quad (3)$$

$$\text{Cellulose} = 38.35 - 2.10\text{Temp} - 0.62\text{Time} \quad (4)$$

$$\text{Lignin} = 30.76 + 3.76\text{Temp} + 0.78\text{Time} \quad (5)$$

$$\begin{aligned} \text{Weight loss by } P. \text{ sanguineus} = \\ 12.302 - 4.253\text{Temp} - 1.598\text{Time} + \\ 0.545\text{Temp} \times \text{Time} + 1.136\text{Temp}^2 + \\ 0.036\text{Time}^2 \end{aligned} \quad (6)$$

where Temp = treatment temperature (°C) and Time = treatment time (min).

Step-by-step investigation was used to develop accurate response surface methodology models, which resulted in establishing new linear models for actual factors. As a result, four new multiple linear equations (7–10) and one quadratic equation (11) were obtained. The final equations in terms of actual factors:

$$\text{Holocellulose} = 104.63 - 0.19\text{Temp} - 0.017\text{Time} \quad (7)$$

$$\text{Hemicellulose} = 43.46 - 0.08\text{Temp} - 6.42\text{Time} \quad (8)$$

$$\text{Cellulose} = 61.17 - 0.105\text{Temp} - 0.103\text{Time} \quad (9)$$

$$\text{Lignin} = -10.20 + 0.19\text{Temp} + 0.013\text{Time} \quad (10)$$

$$\begin{aligned} \text{Weight loss by } P. \text{ sanguineus} = \\ 189.96 - 1.43\text{Temp} - 0.12\text{Time} + \\ 0.00045 \text{Temp} \times \text{Time} + 0.0028\text{Temp}^2 + \\ 1.013\text{Time}^2 \end{aligned} \quad (11)$$

Adequacy of the model for chemical constituents of rubberwood was approximated by the lack-of-fit test and the value was 0.452 for holocellulose, 0.727 for cellulose, 0.332 for hemicellulose and 0.344 for lignin. Insignificant values of lack-of-fit (0.3–0.8) of the linear models reflected that the model was statistically apt for further investigation. Meanwhile, a value of 0.680 was obtained by the lack-of-fit test of the model for weight loss of rubberwood due to decay by *P. sanguineus* and the insignificant value in quadratic model reflected that the model was statistically apt for further investigation.

Coefficient of multiple regressions (r^2) was used to evaluate the fit of the model while the adequacy of the model was confirmed by the adjusted r^2 . The values of r^2 ranged between 0.914 and 0.984 in the linear models while a

value of 0.959 was obtained for the quadratic model. These values indicated very high fitness of the models. Adequacy of the linear models was further confirmed by adjusted r^2 and the values were between 0.897 and 0.981. On the other hand, the quadratic model proved adequate with an adjusted r^2 value of 0.884. High adjusted r^2 values obtained in all models suggested that the relation between the responses and the variables could be determined with high accuracy using the developed models.

Effects of oil–heat treatment on chemical constituents of the samples

The effects of variables on the response of chemical constituents of the samples are shown in Figures 1–5. Holocellulose content decreased with increasing treatment time and temperature (Figure 1). Figure 1 shows that significant reduction in holocellulose was observed when rubberwood was treated at high temperature in hot palm oil. The holocellulose content of treated wood ranged from 58.9 to 69.4% compared with 70.6% of untreated wood. The lowest holocellulose content was observed when the rubberwood was treated at 228 °C for 180 min. At high temperatures (>180 °C), due to degradation of cellulose and depolymerisation of hemicellulose during heating, the holocellulose content reduced. Holocellulose content of heat-treated Scots pine samples decreased from 79.7 to 63.3% at 180 °C (Boonstra & Tjeerdsma 2005). The reduction was probably due to degradation of cellulose and hemicellulose. Holocellulose contents of beech and pine have also been reported to decrease after heat treatment (Inari et al. 2007). Holocellulose content starts to reduce when the temperature of treatment is over 140 °C (Hill 2006).

Cellulose content decreased with increasing treatment time and temperature (Figure 2). Cellulose content of samples treated at 200 °C for 95 min reduced to 39.1% compared with untreated wood (42.4%) (Figure 2). The cellulose content continued to reduce as the treatment temperature and time increased. The lowest cellulose content of 35.6% was recorded when the wood was treated at 220 °C for 240 min.

Figure 3 shows that the hemicellulose content of treated rubberwood also decreased

with increasing time and temperature. Untreated rubberwood had 28.2% hemicellulose and this value reduced to 22.8% when the wood was treated at 228 °C for 180 min. However, the reduction was not as high as the loss of the cellulose content. Treatment at 180 °C was not efficient for depolymerisation of hemicelluloses but the efficiency increased when the temperature was above 185 °C (Boonstra & Tjeerdsma 2005).

Lignin content increased with increasing treatment time and temperature (Figure 4). Lignin content increased from 23.7% initially to a value of 34.8% when it was treated in hot palm oil. Increment in lignin content after oil–heat treatment was caused by degradation of cellulose and hemicellulose in the wood (Kamdem et al. 2002). Degradation of chemical contents takes place in the sequence of hemicellulose, cellulose and lignin (Kamdem et al. 2002). Lignin is the most thermally stable constituent in wood and it will increase simultaneously with the decrease in holocellulose. When wood is heated, there will be some loss in polysaccharides (i.e cellulose and hemicellulose) which results in increment of lignin content (Sandermann & Augustin 1964). Therefore, lignin content increased simultaneously with the decrease in holocellulose and this finding was in agreement with the result reported by Sandermann and Augustin (1964). In the present study, lignin content increased from 24.6 to 35.7% as temperature rose from 172 °C to 228 °C.

Effects of oil–heat treatment on the decay resistance against *P. sanguineus*

Weight loss of samples decreased with increasing treatment temperature and time (Figure 5). Materials treated at higher temperature (above 150 °C) and longer treatment time generally result in better rot and mold resistance (Sundqvist 2004). Minimum mass loss of 8.23% was attained at 228 °C and 180 min. Treatment temperature was more crucial in the enhancement of decay resistance of treated samples compared with treatment time. Lower mass loss was observed in the samples treated using higher temperature but lower exposure time. For example, sample treated at 220 °C for 240 min had a mass loss of 8.65%. This value was higher than the sample treated at 228 °C for 180 min which had a mass

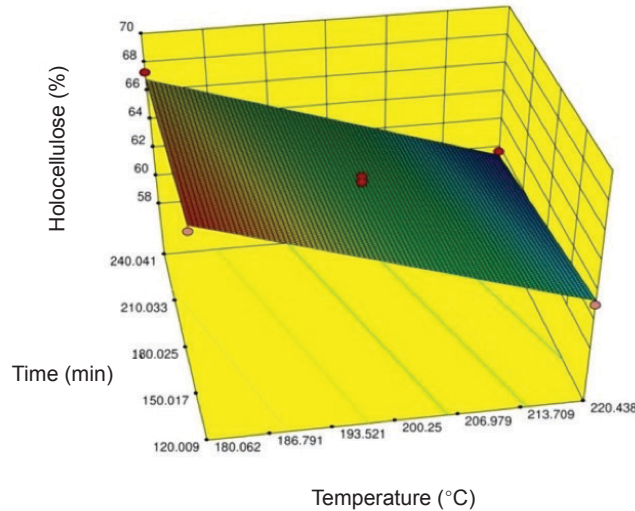


Figure 1 Three-dimensional surface plot of holocellulose as a function of time and temperature

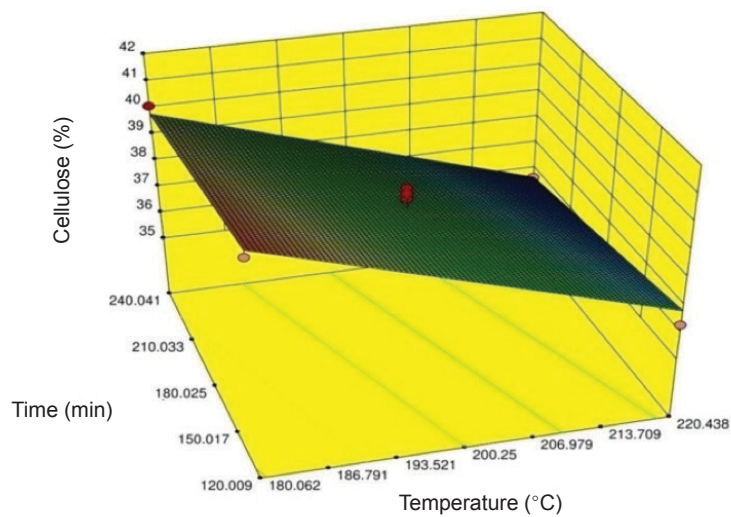


Figure 2 Three-dimensional surface plot of cellulose as a function of time and temperature

loss of 8.23%. These percentage loss indicated that by raising treatment temperature by 8 °C, treatment time can be shortened by 60 min in order to achieve comparable decay resistance (8.65 versus 8.23% of mass loss). The effect of exposure time was more prominent when compared with the same treatment temperature, as wood samples subjected to heat for longer duration showed better decay resistance.

Significant Pearson’s correlations were observed between weight loss and chemical

constituents at $p \leq 0.05$ (Table 3). Positive and high correlations were found for holocellulose ($r = 0.958$), cellulose ($r = 0.936$) and hemicellulose ($r = 0.909$), indicating that weight loss increased as chemical contents increased. Degradation of holocellulose, cellulose and hemicellulose during the oil–heat treatment resulted in reduced weight loss of treated wood against *P. sanguineus*. Release of acetic acid by degradation of hemicellulose might have limited the colonisation of fungus and consequently

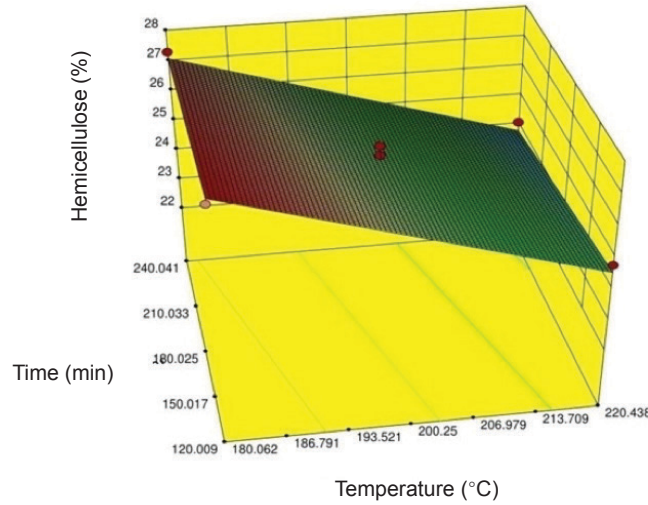


Figure 3 Three-dimensional surface plot of hemicellulose as a function of time and temperature

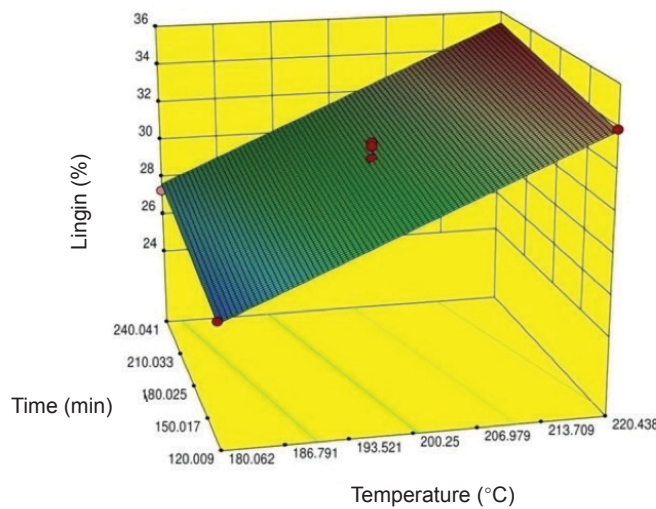


Figure 4 Three-dimensional surface plot of lignin as a function of time and temperature

improved decay resistance of treated samples (Weiland & Guyonnet 2003). Transformation of hemicelluloses from hydrophilic and easily digestible to hydrophobic molecules during heat treatment was also one of the possible factors that contributed to lower weight loss of treated samples. Negative but significant correlation was found between weight loss and lignin ($r = -0.963$) which indicated that weight loss increased with decreasing lignin content. Furfural produced during heat treatment reticulate with lignin and

become indigestible for rot fungi (Weiland & Guyonnet 2003).

CONCLUSIONS

Response surface methodology models were successfully developed with four multiple linear and one quadratic equations. High adjusted r^2 values (~ 0.90) proved the adequacy of the models. Degradation of cellulose and hemicellulose occurred at high treatment temperature and

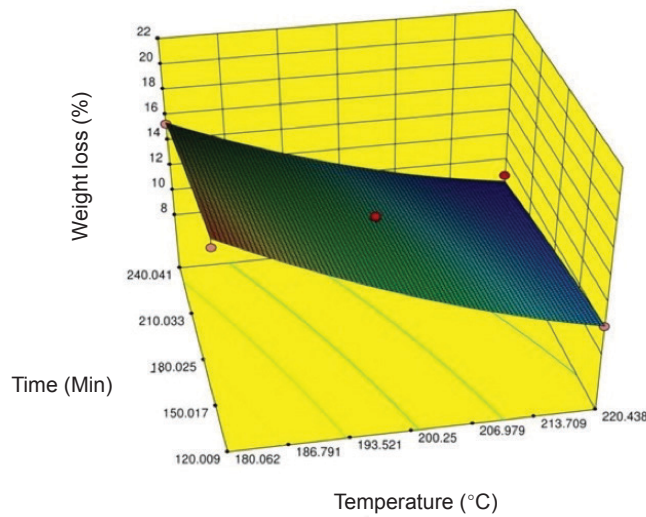


Figure 5 Three-dimensional surface plot of weight loss as a function of time and temperature

Table 3 Pearson’s correlation of weight loss with chemical constituents

		Holocellulose	Cellulose	Hemicellulose	Lignin
Weight loss (%)	Pearson’s	0.958**	0.936**	0.909**	-0.963**
	Significance	0.000	0.000	0.000	0.000

** = significant at $p \leq 0.05$

exposure time and their contents decreased with increasing temperature and time. However, lignin content of treated wood increased as the treatment severity increased. Decay resistance of treated wood against *P. sanguineus* improved after heat treatment with palm oil. This improvement was highly related to the reduction of hemicellulose and cellulose ($r = 0.936$ and 0.909 respectively).

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REFERENCES

ASTM. 2005. ASTM-D2017-05. *Standard Test Method of Accelerated Laboratory Test of Natural Decay Resistance of Woods*. ASTM International, West Conshohocken.

BOONSTRA MJ & TJEERDSMA B. 2005. Chemical analysis of heat treated softwoods. *Holz als Roh- und Werkstoff* 64: 204–211.

BURMESTER A. 1973. Effect of heat-pressure-treatments of semi-dry wood on its dimensional stability. *Holz als Roh- und Werkstoff* 31: 237–243.

DUBEY MK, PANG S & WALKER JCF. 2011. Effect of oil heating age on colour and dimensional stability of heat treated *Pinus radiata*. *European Journal of Wood and Wood Products* 69: 255–262.

GIEBELER E. 1983. Dimensional stabilization of wood by moisture-heat-pressure- treatment. *Holz als Roh- und Werkstoff* 41: 87–94.

H’NG PS, LEE SH & LUM WC. 2012. Effect of post heat treatment on dimensional stability of UF bonded particleboard. *Asian Journal of Applied Science* 5: 299–306.

HILL CAS. 2006. *Wood Modification: Chemical, Thermal and Other Processes*. John Wiley & Sons Ltd, Chichester.

INARI GN, PETRISSANS M & GERARDIN P. 2007. Chemical reactivity of heat-treated wood. *Wood Science and Technology* 41: 157–168.

KAMDEM DP, PIZZI A & JERMENNAUD A. 2002. Durability of heat-treated wood. *Holz als Roh- und Werkstoff* 60: 1–6.

- LEE SH, H'NG PS, PENG TL & LUM WC. 2013. Response of *Coptotermes curvignathus* (Isoptera: Rhinotermitidae) to formaldehyde catcher-treated particleboard. *Pakistan Journal of Biological Science* 16: 1415–1418.
- MANALO RD & ACDA MN. 2009. Effects of hot oil treatments on physical and mechanical properties of three species of Philippine bamboo. *Journal of Tropical Forest Science* 21: 19–24.
- SAILER M, RAPP AO, LEITHOFF H. 2000. *Improved Resistance of Scots Pine and Spruce by Application of an Oil-Heat Treatment*. IRG/WP 00-40162. International Research Group on Wood Preservation, Stockholm.
- SANDERMANN W & AUGUSTIN H. 1964. Chemical investigation on the thermal decomposition of wood. Part III: chemical investigation on the course of decomposition. *Holz als Roh- und Werkstoff* 22: 377–378.
- STAMM AJ. 1964. *Wood and Cellulose Science*. The Ronald Press Co, New York.
- SUNDQVIST B. 2004. Colour changes and acid formation in wood during heating. PhD thesis, Luleå University of Technology, Luleå.
- TAPPI. 1994. *Tappi Test Method T203 os-74—Alpha-, Beta-, and Gamma-Cellulose in Pulp*. TAPPI Press, Atlanta.
- TAPPI. 2002. *TAPPI Test Method T222 om-02—Acid-Insoluble Lignin in Wood And Pulp*. TAPPI Press, Atlanta.
- TAPPI. 1998. *TAPPI Test Method T9m-54—Holocellulose in wood*. TAPPI Press, Atlanta.
- TOMAK ED, HUGHES M, YILDIZ UC & VIITANEN H. 2011. The combined effects of boron and oil heat treatment on beech and Scots pine wood properties. Part 1: boron leaching, thermogravimetric analysis, and chemical composition. *Journal of Materials Science* 46: 598–607.
- WANG J & COOPER P. 2005. Effect of oil type, temperature and time on moisture properties of hot oil-treated wood. *Holz als Roh- und Werkstoff* 63: 417–422.
- WEILAND J & GUYONNET R. 2003. Study of chemical modifications and fungi degradation of heatily modified wood using DRIFT spectroscopy. *Holz als Roh- und Werkstoff* 61: 216–220.
- WELZBACHER CR & RAPP AO. 2005. *Durability of Different Heat Treated Materials From Industrial Processes in Ground Contact*. IRG/WP 05-40312. International Research Group on Wood Protection, Stockholm.