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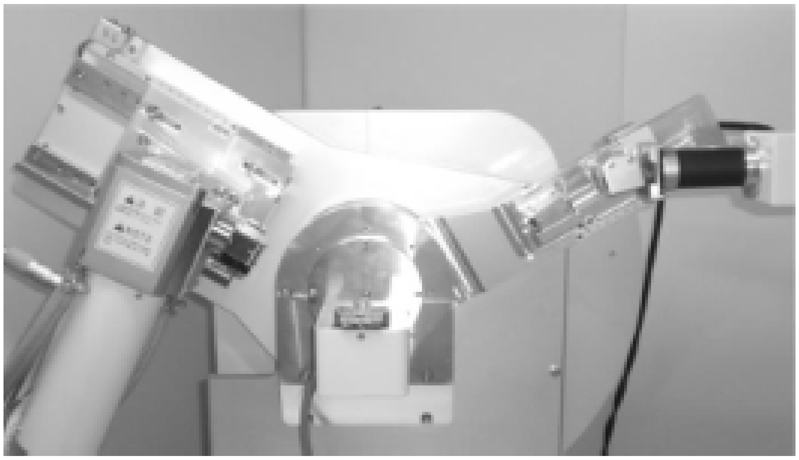

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The Characterization of Black-streaked Heartwood in Teak: Inter-tree Variation

Ganis Lukmandaru, Tatsuya Ashitani, and Koetsu Takahashi

Abstract

The objective of this study was to investigate the variation in the color and chemical characteristics of black-streaked heartwood of teak and explore the relationship of these chemical properties with the degree of blackening. The samples used were outer heartwood parts from 11 trees with black streaks both thin and thick and 7 trees with normal heartwoods for comparison. The colorimetric analysis in CIEL*a*b* system was used to determine the brightness values (L*) of black-streaked heartwood of teak ranging from 40~49 and a thick portion produced appreciably higher average values of extractive contents including n-hexane, ethyl acetate, and total extractive content as well as tectoquinone contents and pH values but lower squalene content compared to those in normal wood. The degree of blackening in the black-streaked heartwood was highly correlated to its extractive contents, especially the ethyl acetate soluble extractive content (r = −0.94) while moderate correlations were measured between the brightness index and tectoquinone content (negative) and squalene (positive). Moreover, no significant difference was found in the ash and individual inorganic elements contents between the group. The increase in pH values was observed to have corresponded with a decrease in brightness (r = -0.75). Therefore, the blackening was assumed to be due to the polymerization of quinones in weakly acidic conditions.

Keywords: darkening wood, quinones, extractives, inorganic materials, pH values.

Introduction

The discolorations in timber and lumber are one of the most serious defects in numerous economically important species of wood from tropical regions. An example of this is teak which is widely used for furniture or parquet and observed to have black streak discolorations leading to considerable degradation and economic loss. These black-streaked trees are locally known as *doreng* in Indonesia with the streak generally in the form of an annual ring in the transversal section as shown in Figure 1. The cause of this phenomenon remains unknown but has been related to the edaphic factor by Suhaendi *et al*. (1998).

Wood color is generally ascribed to the composition and structure of the extractives (Hillis 1987). This is evident in a previous report by Lukmandaru *et al*. (2009) which compared the color, pH, extractive content and components, and inorganic materials between normal and black-streaked wood in a radial position using partially black-streaked heartwood in only one sample. The relationship between the darkening part and the chemical properties of wood has also been observed in other species with different results (Kubo and Ataka 1998; Minato and Morita 2005; Romagnoli *et al*. 2013). Therefore, this study clarified the color and chemical characteristics of the black streak portion using a larger number of trees having black streak from the inner towards the outer heartwood part. It also examined the relationship between chemical properties and the degree of blackening.

Materials and Method

Sample Preparation

The trees used in this study were collected from the Perhutani plantation, Randublatung, Central Java which is a with black calcareous soil and characterized by the frequent occurrence of black-streaked trees. The trees were between 25~45-years old, straight-stemmed, and sound with 5 cm discs obtained at different heights from the butt end of the trunks. Furthermore, wood powder at 40~60 mesh of the discolored trees was obtained from the outer heartwood part (0.5 cm from sapwood heartwood border in cardinal directions) for color and chemical analysis. Different black-streaked disks were collected using visual inspection and the brightness (L*) value was measured by spectrophotometer after which they were classified into thick with L* < 45 having six individuals and thin with L* = 45 to 50 containing five individuals. In addition, seven disks were obtained from different trees with normal heartwood in the same sites with L*>50. The sample conditions are, therefore, described in Table 1.

Figure 1. Black-streaked heartwood of a teak tree (cross section)

Color Properties

The color of the specimens was measured with an NF777 spectrophotometer (Nippon Denshoku Ind. Co Ltd) having a sensor head of 6 mm in diameter and using illuminant D65, 10° viewing angle. The CIE color data (L*, a*, b*) were obtained in triplicate where L* is for lightness representing the position on the black-white axis (L= 0 for black, L= 100 for white), a* = green-red coordinate and b* = blue-yellow coordinate. The color saturation (C) was calculated using $C = \sqrt{[(a^*)^2 + (b^*)^2]}$ while the tonality angle (hue) was determined according to H = arctang (b*/a*).

Chemical Analyses

The extractive content was determined using 2 g wood meal based on oven dry weight in a Soxhlet apparatus and extracted using a 6-h sequence of *n*-hexane, ethyl acetate (EtOAc), and methanol (MeOH). The solvents were evaporated in vacuo after which they were dried and weighed to determine the *n*-hexane, EtOAc, and MeOH based on an oven-dry wood meal (m/m) and the Total Extractive Content (TEC) value, which was obtained by summing all the values for each of the contents. Meanwhile, the solubility in cold- and hot-water (ASTM D-1110-1984) was determined separately.

The contents of the main extractive components in the ethanol-benzene extracts were measured using Hitachi G-3500 GC and Shimadzu QP-5000 GC-MS with the detector being FID, the column was 30 m NB-1 bonded capillary, column temperature was 120~300°C (programing 4°C min^{-1}), detector and injector temperature at 250°C and held at 300°C for 15 min, while the carrier gas was helium after which one μL of the solution at 100 mg mL^{-1} concentration was injected manually into the gas chromatograph. Moreover, for the quantification of individual substances, calibrations were made using known amounts of standard tectoquinone (2-methyl anthraquinone) while compounds were identified by comparing their mass spectra with data from previous studies (Perry *et al*. 1991; Lemos *et al*. 1999) and the injection of standards. GC-MS (JEOL XS mass spectrometry at 70 eV) was used for gas chromatographic separations.

The ash content was measured according to the ASTM D-1102-1984 standard method. Moreover, the wood powder samples at 0.2 g were prepared for elemental analysis using a nitric acid-perchloric acid (5:3, v/v) solution using a digestion procedure. The amount of silica was also determined by filtering the solution while the contents of some inorganic materials such as calcium (Ca), magnesium (Mg), potassium (K), iron (Fe), and phosphorous (P) were measured through atomic absorption spectrophotometry (Hitachi Z-5000) and flame-photometry. Furthermore, 1 g per part of the wood powder was submerged overnight in 20 mL distilled water and the pH of the filtrate was measured with a pH meter (Horiba). Three measurements were made for each part.

Statistical Analysis

Data were tested to confirm a normal data distribution (Kolomogorv-Smirnov test). The effects of grouping (brightness level) were calculated by analysis of variance (One-way ANOVA) GLM procedures. The effects were taken into account only when significant at the 95% level using Type III Sums of Squares. The relationships between the brightness index and other independent characteristics were studied with Pearson's or Spearman's correlation analysis. All statistics were calculated with SPSS 10.0 software.

Results and Discussion

Color Properties

The brightness measurement in Table 1 shows the samples were simply divided into three groups of normal, thick, and thin black-streaked woods. The brightness values

(L*) of black-streaked heartwood were classified in the range 40~49 while the lowest value for normal heartwood was 51. Previous studies on the teak grown in India (Bhat *et al*. 2005) and Togo (Kokutse *et al*. 2006) were recorded to have brightness index ranged between 48 and 58 while Moya and Berrocal (2010) reported 46 to 76 for heartwood from teak trees growing in Costa Rica. Even though different color equipment was used as well as the effect of other factors such as genetics, edaphic, tree age, and others on the color properties, the ranges showed the possibility of finding black streak in each locality. As expected, the black streak areas provided significantly lower average values in yellowness (b*), hue, and chroma as shown in Table 1 while no significant differences were observed between the thick and thin samples using Duncan test. Moreover, the redness values (a*) in the black-streaked samples were found to be higher than in normal wood but Duncan test showed the difference is not statistically significant.

Table 1. Description of the sample conditions and colour properties in teak heartwood of black-streak and normal.

Samples	Tree Ring Number	Disc Diameter	Color properties				
			L*	a*	b*	Hue	Chrome
Thick black streaked							
No tree 1	35	33.0	40.50	7.30	21.10	70.96	22.67
2	29	23.8	41.40	6.80	20.50	71.78	21.61
3	29	24.0	42.00	7.10	21.70	71.94	22.80
4	28	24.7	43.00	6.80	21.20	72.12	22.30
5	37	27.0	44.80	7.90	23.00	71.10	24.36
6	37	31.8	44.99	7.20	22.30	72.07	23.47
		Average	42.78 a	7.18	21.63 d	71.66 f	22.86 h
		Std. dev.	1.82	0.40	0.90	0.50	0.95
Thin black streaked							
No tree 7	33	22.1	45.60	6.90	21.70	72.44	22.74
8	33	27.2	45.90	9.20	24.20	69.16	25.94
9	32	35.2	47.50	7.20	23.50	72.97	24.60
10	26	25.6	47.50	7.60	22.50	71.32	23.70
11	30	31.8	49.00	7.40	23.20	72.35	24.38
		Average	47.10 b	7.60	23.02 d	71.64 f	24.27 h
		Std. dev.	1.38	0.89	0.95	0.50	1.18
Normal							
No tree 12	44	27.3	51.30	8.10	24.10	71.46	25.46
13	27	33.5	52.10	7.80	25.10	72.82	26.23
14	37	39.5	51.70	7.80	24.70	72.57	25.89
15	31	32.0	57.70	5.50	26.20	78.25	26.79
16	32	26.0	58.60	5.00	25.20	78.68	25.66
17	30	23.5	57.30	7.90	28.20	74.39	29.27
18	30	25.5	61.30	4.60	27.90	80.41	27.58
		Average	55.71 c	6.67	25.91 e	75.51 g	26.69 i
		Std. dev.	3.97	1.55	1.59	3.53	1.34

Remarks: Std. dev. = standard deviation; the same letters on the same column are not statistically different at $P < 0.05$ by Duncan's test.

Extractive Content

Darker heartwood is generally assumed to contain more extractives but the values obtained are presented in Table 2. The average extractive contents through successive extraction showed *n*-hexane, EtOAc, and TEC levels were clearly different between thick black-streaked and normal wood groups while slight differences were found between the normal and discolored portion in cold-water and hot-water extractive contents. These results indicate black-streaked heartwood has higher apolar compounds than the normal tissues while only n-hexane and total extractive contents were observed to have varied significantly between its thick and thin samples using analysis of variance. Meanwhile, the Duncan test showed that only the total extractive content followed the tendency of the brightness index and it seems reasonable to assume the increases in its value by 14~19% were due to the production of darkened heartwood. This is, however, more pronounced in the EtOAc extractive content levels which streaks and normal heartwood areas ranged from 4.38 to 7.42% and 0.75 to 3.86%, respectively.

The GC analysis of ethanol-benzene extract for both black-streaked and normal heartwood is shown in Figure 2. The major components identified were lapachol, tectoquinone, squalene, tectol, and desoxylapachol or its isomer (Lukmandaru and Takahashi 2009) and their quantification is summarized in Table 3. ANOVA, however, showed significant differences exist only in tectoquinone and squalene contents among the groups. The tectoquinone content was observed to have varied from 0.72 to 4.20% in thick black streaks part and 0.29 to 2.54% in normal part but a contrasting result was recorded for squalene with the value found to be significantly lower in the discolored part which was 0.26 to 2.88% compared to the normal heartwood at 0.26 to 1.24%. Meanwhile, the tectoquinone contents recorded in previous studies were reported to have varied from 0.3 to 2% while squalene was 1 to 2% in teak wood (Sandermann and Simatupang 1966; Windeisen *et al* 2003; Lukmandaru and Takahashi 2009).

The desoxylapachol concentration was found to be lower in discolored areas than normal heartwood but the ANOVA showed the difference between the groups is not statistically significant. A similar tendency was also measured in an unknown compound (UN1) which showed a comparatively higher concentration in the black-streaked region while another unknown component, UN2, was not detected in the black-streaked area but in three individuals containing normal heartwood. The results also showed no considerable differences between the groups based on the amounts of other constituents due to wide variations by examining their standard deviations.

The higher extractives and tectoquinone contents as well as the lower squalene content found in the black streak parts have been reported in a previous study (Lukmandaru *et al*. 2009). The phenolic compounds of wood are commonly closely related to coloration (Moya *et al*. 2012; Romagnoli *et al*. 2013; Paques *et al*. 2013) but some phenolics have already been identified in teak while those in the wood color of this species are unknown. Meanwhile, the discolorations in living trees are initiated predominantly through wounds, dying branches, and roots (Shigo 1976). Moreover, the role of tectoquinone in natural durability of teak has been recognized in several reports (Rudman *et al.* 1958; Sandermann and Simatupang 1966; Haupt *et al*. 2003) and even though a direct bioassay test was not attempted and the mechanism of resistance associated with the discolored tissue was not determined in this study; the blackening processes was suggested to be related to some protective functions against biological origin. This may have much in common with *Diospyros kaki* where the black portion is more resistant than the adjacent normal heartwood (Noda *et al.* 2002).

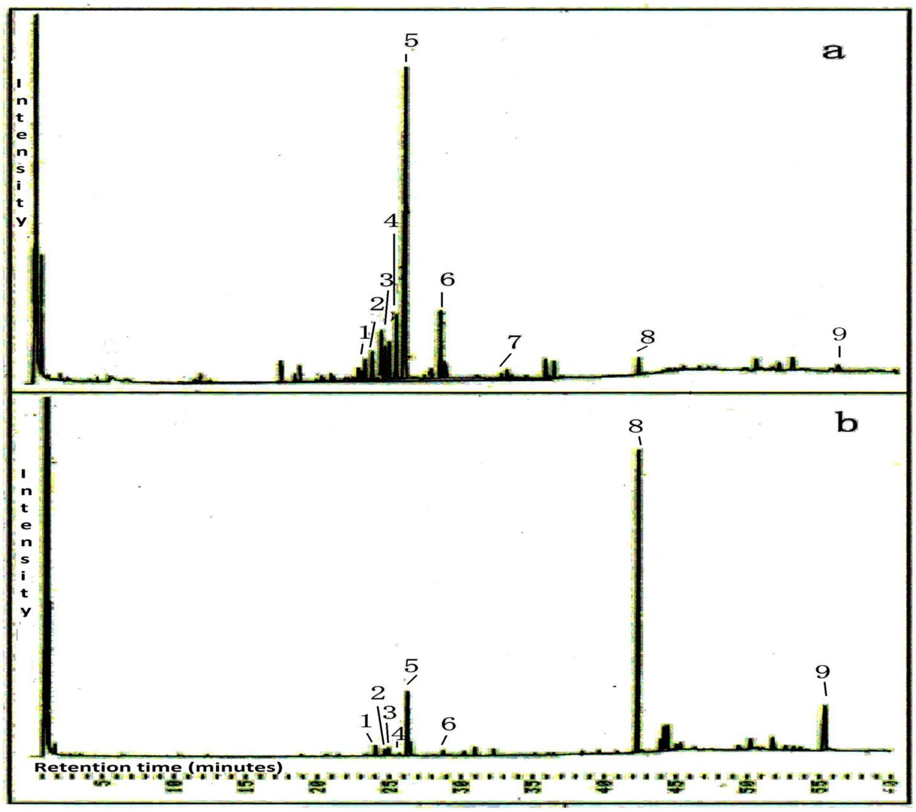

Figure 2. Gas chromatogram of ethanol-benzene extracts of a) black-streaked heartwood and b) normal heartwood of teak. Nine main components are detected: 1. desoxylapachol, 2. palmitic acid, 3. lapachol, 4. isodesoxylapachol, 5. tectoquinone, 6. Unknown compound (UN3), 7. 2-hydroxymethyl-anthraquinone, 8. squalene, 9. tectol.

Table 2. The extractive contents (% based on dry wood) in teak heartwood of black-streak and normal

Extract	Thick black streaked			Thin black streaked			Normal			F-ratio
	Min.	Max.	Average	Min.	Max.	Average	Min.	Max.	Average	
n-hexane	6.35	9.17	8.06 (1.19) b	5.50	6.92	6.33(0.62) a	3.88	6.37	5.15(0.95) a	14.60**
Ethyl acetate	4.38	7.42	5.99 (22) d	4.21	5.60	4.90(0.56) d	0.75	3.86	2.09(1.17) c	23.22**
Methanol	2.77	5.61	4.54 (0.95) fg	4.39	5.05	4.95(0.34) g	2.04	5.26	3.42(1.26) f	3.97*
Total extractive	17.11	19.68	18.61 (0.97) k	15.14	17.30	16.19(0.78) j	8.20	14.77	10.66(2.74) i	30.95**
Cold-water	1.19	2.21	1.91(0.38) x	1.62	3.58	2.76(0.75) y	1.33	3.16	2.11(0.64) xy	2.89*
Hot-water	3.60	5.18	4.41(0.56) lm	3.65	5.59	4.73(0.74) m	2.99	4.68	3.69(0.68) l	7.89**

Remarks: min. = minimum values, max. = maxium values, ** significant at 1 % level, * significant at 5 % level. Total extractive content is the sum n-hexane, ethyl acetate, and methanol extractive contents (successive extraction). Cold-water and hot-water solubles were extracted separately. Average of 6 trees (thick black streaked), 5 trees (thin black streaked), and 7 trees (normal) with the standard deviation in parentheses. The same letters on the same row are not statistically different at $P < 0.05$ by Duncan's test.

Table 3. The amount of major components (% based on dry wood) in the ethanol-benzene extracts in teak heartwood of black-streak and normal

Components	Thick black streaked			Thin black streaked			Normal			F-ratio
	Min.	Max.	Average	Min.	Max.	Average	Min.	Max.	Average	
Desoxylapachol	0.10	0.35	0.21(0.11)	0.04	0.78	0.46(0.28)	0.15	2.38	0.79(0.86)	1.66
Palmitic acid	0.03	0.10	0.06(0.02)	0.03	0.14	0.08(0.04)	0.03	0.70	0.20(0.22)	1.85
Lapachol	0.00	0.15	0.05(0.05)	0.00	0.86	0.29(0.35)	0.00	0.48	0.24(0.16)	2.06
Isodesoxylapachol	0.58	2.24	1.20(0.58)	0.31	2.45	1.26(0.77)	0.10	3.54	1.11(1.22)	0.03
Unknown 1	0.00	1.13	0.06(0.04)	0.03	0.12	0.06(0.04)	0.00	0.09	0.03(0.03)	1.05
Tectoquinone	0.72	4.20	2.42(1.26) b	0.95	2.78	1.71(0.92) ab	0.27	2.54	0.94(0.93) a	3.20*
Unknown 2	0.00	0.00	0.0 (0.0)	0.00	0.00	0.0+0.0	0.00	0.60	0.10(0.22)	1.17
Unknown 3	0.04	0.20	0.12(0.05)	0.02	0.29	0.11(0.12)	0.02	0.19	0.12(0.05)	0.02
HMAQ	0.00	0.80	0.16(0.31)	0.00	0.18	0.05(0.08)	0.00	0.43	0.08(0.15)	0.41
Squalene	0.43	0.68	0.55(0.09)c	0.26	1.24	0.65(0.37) c	0.23	2.88	1.66(0.89) d	6.80**
Tectol	0.46	1.45	0.85(0.35)	0.20	1.20	0.64(0.38)	0.24	1.21	0.84(0.31)	0.68

Remarks: min. = minimum values, max. = maxium values, ** significant at 1 % level, * significant at 5 % level
HMAQ = 2-hydroxymethyl-anthraquinone. Average of 6 trees (thick black streaked), 5 trees (thin black streaked), and 7 trees (normal) with the standard deviation in parentheses. The same letters on the same row are not statistically different at $P < 0.05$ by Duncan's test.

Inorganic Contents and pH Value

Table 4 shows the amounts of inorganic materials as well as the pH value in the outer heartwood and the ash and silica levels of discolored parts are observed to be comparatively higher than in normal ones but ANOVA indicated no significant differences in the brightness level factor. Meanwhile, the values for Ca and K contents were observed to be significant as observed with the 2190 to 4760 ppm variation reported for Ca in the discolored portion compared to 1140 to 3090 ppm in normal part. This is in line with the report of the previous study (Lukmandaru *et al*. 2009) which showed Ca values to be slightly higher in the partially black-streaked heartwood compared to the adjacent normal ones. The Duncan test, however, reported no statistically significant difference between thick black-streaked and normal parts. The same pattern was also observed in K contents.

All the pH values were in the weakly acidic range, except for sample no. 8 with pH 7.07. A comparison of these values showed the discolored wood to have higher levels as observed with the 5.66 to 7.07 recorded for black streak portion while the normal heartwood ranged from 4.96 to 6.35. The ANOVA showed a significant brightness level factor and Duncan test also confirmed a significant difference between the black-streaked and normal heartwood parts.

Table 4. The amount of inorganic elements (% based on dry wood) and pH values in teak heartwood of black-streak and normal

	Thick black streaked			Thin black streaked			Normal			F-ratio
	Min.	Max.	Average	Min.	Max.	Average	Min.	Max.	Average	
Ash	1.40	2.90	2.11 (0.57)	1.80	3.09	2.39 (0.48)	0.85	3.05	1.64 (0.93)	1.65
Silica	7500	16000	10500 (3446)	7500	21000	11800 (5472)	500	12500	7500 (4387)	1.46
Potassium	330	1040	551 (264) a	480	1860	1336 (532) b	340	1680	758(517) a	4.30*
Magnesium	310	480	398 (60)	310	630	454 (116)	230	640	445 (174)	0.31
Calcium	2190	2840	2535 (241) c	2740	4760	3458 (819) d	1140	3090	2031(849) c	6.10*
Iron	37	118	67 (27)	42	60	55 (7)	32	75	56 (14)	0.72
Phosphorous	62	155	115 (40) ef	93	383	184 (117) e	24	180	77 (50) f	3.23*
pH values	5.66	6.97	6.39 (0.46) h	5.74	7.07	6.20 (0.50) h	4.96	6.35	5.39(0.48) g	7.89**

Remarks: min. = minimum values, max. = maxium values, ** significant at 1 % level, * significant at 5 % level. Average of 6 trees (thick black streaked), 5 trees (thin black streaked), and 7 trees (normal) with the standard deviation in parentheses. The same letters on the same row are not statistically different at $P < 0.05$ by Duncan's test.

Relationship between the Brightness Degree and Chemical Properties

The correlation analysis in Table 5 confirmed there is a highly significant negative correlation between the brightness and extractive contents with the strong negative linear relationship measured using ethyl acetate soluble content (r=−0.94) or total extractive content (r = −0.92). The high correlation coefficient between EtOAc extractive content and brightness is particularly emphasized in the scatter diagram in Figure 3 and an increase in EtOAc soluble extractives were observed to have corresponded thoroughly with the degree of blackening. This is established with its value recorded to be four times in the darkest streak heartwood while the total extractive content was twice higher compared to normal heartwood. This, therefore, means EtOAc soluble extractives have considerable roles in the formation of the darkened parts. A previous study conducted on *Tabebuia serratifolia* wood showed large amounts of polyphenols were found in the black parts, together with other quinone compounds, but low in lapachol concentrations (Romagnoli *et al*. 2013). The EtOAc soluble extracts are, however, believed to contain polymeric quinones which cause wood darkening.

In the component levels, the tectoquinone content was found to be negatively correlated (r = −0.62**) with the brightness value while the squalene (r = 0.56**) and palmitic acid concentration (r = 0.49*) were positively correlated as shown in Figure 4. This means the teak is darker when it contains higher amounts of tectoquinone and lower amounts of squalene and palmitic acid. The reason for this relationship does not necessarily have to be related to the chemical nature of tectoquinone but a specific feature in the responsible compounds correlated with anthraquinones concentration. Moreover, lapachol and dehydro-α-lapachone from the naphthoquinone group were also detected in *Tabebuia serratifolia* wood extract to have contributed to the yellow and pink color of the wood (Romagnoli *et al*. 2013). The enzymatic oxidation of anthraquinones and naphthoquinones was also assumed to be the first step of darkening.

The cause of lower squalene production in the discolored wood and its relationship with the degree of blackening has not been ascertained. Squalene, a triterpene, as well as palmitic acid from fatty acid family are both not a coloring matter. The tectoquinone, however, might has an indirect role through the formation of polymeric compounds responsible for discoloration which further reduces the production of terpenes such as squalene. Furthermore, the higher content of UN1 with 25 mins retention time and the absence of UN2 with 27.2 min in the discolored parts is also possibly related to the blackening phenomenon.

Previous reports on other species showed inorganic elements in wood to be correlated with the blackening process in heartwood (Kubo and Ataka 1998; Minato and Morita 2005). Even though irons technically form a complex of dark color due to its reaction with phenolic compounds, no considerable difference was found in its content for both normal and black-streaked woods studied. Moreover, the Ca, K, and silica contents were observed to be higher in the black streak parts compared to the normal ones but there was no significant correlation between them and the brightness index level. This means the formation of blackened heartwood is not directly related to these metals and they are hardly involved in the degree of blackening.

pH value also has the ability to play a role in the discoloration of some wood species (Sandermann and Dietrichs 1959) such as *Cryptomeria japonica* (Takahashi 1996) and *Pycnanthus angolensis* (Starck *et al*. 1984) which were found to be discolored due to a comparatively huge gradient of pH. Meanwhile, the brightness and pH levels were moderately inversely related according to Pearson's correlation (r = - 0.75) while the relationships between the degree of blackening and pH values are illustrated in Figure 5. This, therefore, means it is possible to attribute teak wood discoloration from black to pH change even though the value is still in the weakly acidic range. Moreover, the degrees of correlation between pH values and Ca or K content were low (data not shown). Another alternative reason or the blackening phenomenon is attached to the polymerization of phenolic compounds contained in the heartwood under a more weakly acidic condition. It is, therefore, necessary to determine the cause of higher pH in the black streak regions and relate it with the blackening process.

Table 5. Correlation coefficient (*r*) between L* brightness and chemical properties in heartwood of black-streak and normal

Chemical properties	L*	Inorganic contents	L*
Extractive contents		Ash	-0.39
n-hexane	-0.69**	Silica	-0.24
Ethyl acetate	-0.94**	Calcium	-0.39
Methanol	-0.40	Magnesium	0.14
Total extractive	-0.92**	Potassium	-0.06
Cold-water	-0.05	Iron	-0.19
Hot water	-0.55*	Phosphorous	-0.43
		pH values	-0.75**
Extractive component			
Desoxylapachol	0.38		
Palmitic acid	0.49*		
Lapachol	0.25		
Isodesoxylapachol	-0.19		
Unknown 1	-0.45		
Tectoquinone	-0.62**		
Unknown 2	0.64*		
Unknown 3	0.03		
2-hydroxymethyl-anthraquinone	-0.02		
Squalene	0.56**		
Tectol	-0.03		

Remarks: ** significant at 1 % level, * significant at 5 % level

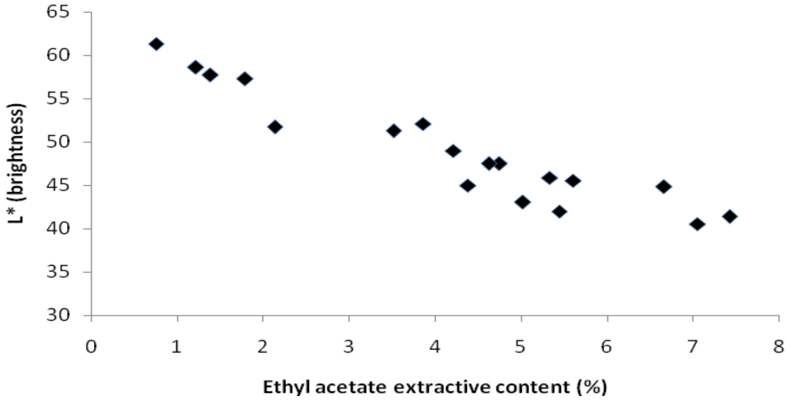

Figure 3. Relation between ethyl acetate extractive content and L* (brightness) in teak heartwood of black-streak and normal.

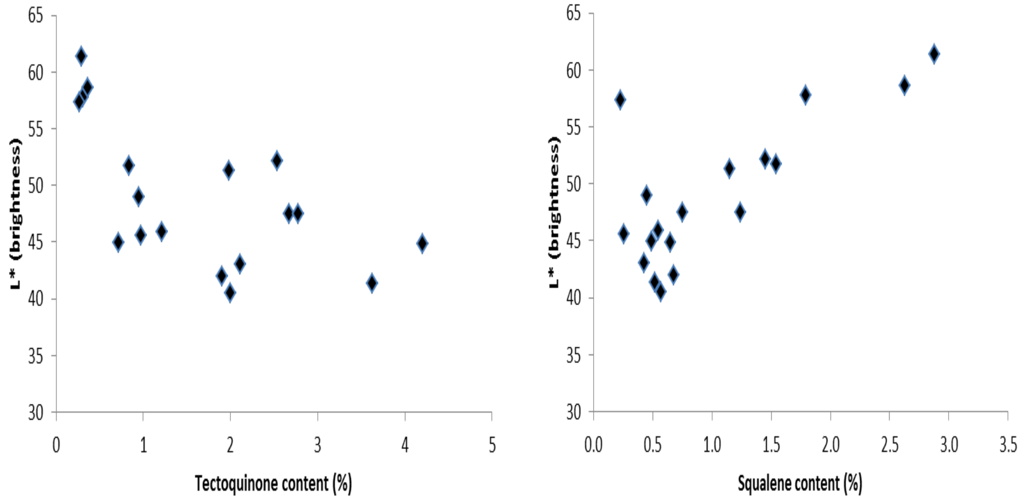

Figure 4. Relation between ethyl acetate extractive content and L* (brightness) in teak heartwood of black-streak and normal.

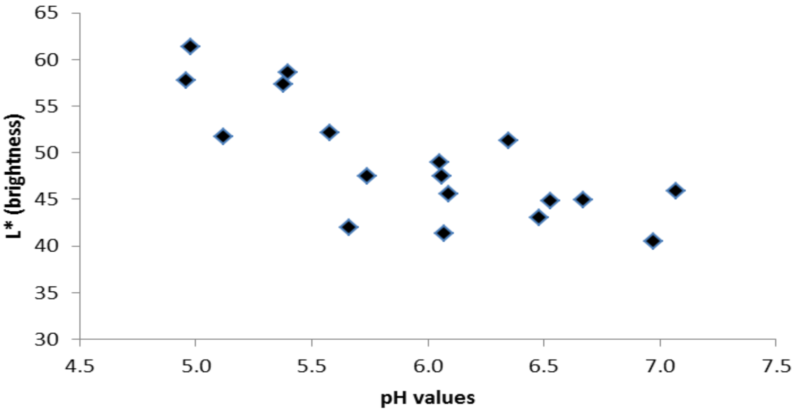

Figure 5. Relation between pH values and L* (brightness) in teak heartwood of black-streak and normal.

Conclusions

The black streak defect of teak wood causes serious losses to the wood industry and this led to the analysis of samples containing this defect in the outer heartwood parts after which they were compared to the normal ones. The black streak area was found to have lower brightness (L*) values up to 10 units, lower levels of yellowness (b*), hue, and chroma in comparison with the normal heartwood. Moreover, the extractive content was discovered to be considerably higher in the blackened portion, particularly in the apolar fraction while the inverse relationship ($r = -0.94$) between the ethyl acetate soluble extractive content levels and brightness values (L*) was also measured. The thick black-streaked heartwood significantly contained more tectoquinone but less squalene while the ash, potassium, calcium, and silica concentration levels were not significantly different among the groups. Furthermore, the variation in the ash contents and individual inorganic elements were unable to adequately explain the differences in the degree of blackening. The increase in pH values was also observed to be corresponding with the blackening of heartwood ($r = -0.75$). Therefore, further research is necessary to elucidate the chemical structures of the ethyl acetate soluble material relating to the formation of the dark-colored compounds in weakly acidic conditions.

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Measurement of Microfibril Angle Using X-Ray Diffraction and Light Microscope on 5-year-old Super and Conventional Teak Wood

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Abstract

The long harvest time causes the processing industry manufactured from teak wood (*Tectona grandis* L. f.) has experienced a lot of declines. To overcome this problem, currently, in Indonesia many types of fast-growing teak have been developed, one of which is Jati Unggul Nusantara (JUN). Trees that are accelerated in growth, are likely to cause changes in their anatomical structure. The anatomical structure of wood is one of the basic properties that greatly influences the use of wood as a raw material. Even small changes in cell shape and size can change the properties of wood as a raw material. One of the anatomical structures of wood, namely the ultramicroscopic structure that affects the quality of wood, is the microfibril angle (MFA). The purpose of this study is to determine the MFA of JUN at the planned cutting age of 5 years, compared to conventional teak at the same age. There are two methods used, namely using X-Ray Diffraction (XRD) and measuring the elongation of the pit apertures slope of the fiber cells using a light microscope, which was obtained from the maceration process. As a result, JUN's MFA is 22.09°, smaller than the conventional teak of 25.29°. This is because JUN was developed from top cuttings so although still young, it already reflects the characteristics of mature teak. The results of the MFA measurements on JUN using two methods (XRD and light microscope), resulted different values. It is different from the MFA measurement results on conventional teak. It is recommended to measure the MFA in JUN wood by using XRD, because possibly, due to accelerated growth, simple pits with an oval shape turn into circular. This difference causes the results of the JUN MFA measurement using a light microscope based on the pit apertures slope to be inconsistent, subjective, and different results in other pits contained in the fiber even though they are closely associated. However, in conventional teak, measurements using a light microscope are possible because the shape of the pit is oval so that the slope of the elongation of the pit aperture can be determined easily, and is more consistent with more uniform values in the same individual fiber.

Keywords: Anatomical structure, JUN, MFA, XRD, light microscope

Introduction

Currently in Indonesia, many types of fast-growing teak distribute under various trade names, such as golden teak, super teak, superior teak, prima teak, and monfori teak, all of which are developed through tissue culture. Similarly, the type of teak developed by the Research and Development Center of Perum Perhutani is known as a Plus Teak Tree (Jati Plus Perhutani/ JPP) (BBPBPTH 2008; Sumarni and Muslich 2008).

From the plant stem of JPP, currently derivatives have been made with various improvements in their characteristics. PT. Setyamitra and the Wanabakti Nusantara Housing Cooperative (Koperasi Perumahan Wanabakti Nusantara/ KPWN) have succeeded in inducing their roots to become stilt roots so that the roots are stronger and the stems grow quicker but do not easily collapse. The superior teak seeds were then given the name of Jati Unggul Nusantara/JUN (Soeroso and Poedjowadi 2008).

Trees accelerated in growth, allowing changes to the anatomical structure due to the growth of the length of the initial cambium cells being constrained and the production of cells with the maximum length is being delayed. The anatomical structure of wood is one of the basic properties that greatly influences the use of wood as a raw material. Panshin et al. (1964), Pandit (2006), and Pandit and Kurniawan (2008) stated that even small changes in the shape and size of cells will cause changes in the properties of wood as a raw material.

For teak wood that has a ring-porous, the earlywood formation produced from rapid growth will result shorter cells. The purpose of developing JUN was provide a teak plantation that can be harvested at a relatively young age. According to Panshin *et al.* (1964), in the first year of stem growth, after the formation of the vascular cambium, the rate of pseudo transverse division is very fast with a very large percentage of survival. This causes the average length of the initial cells of the cambium and its derivate cells to be short, which is known as the juvenile period.

There are at least four levels of structure in a wooden structure that can be identified, where the smaller the size the more advanced equipment is needed. The four levels are macroscopic structure, microscopic structure, nano/ultrastructure structure, and molecular structure level (Booker and Sell 1998).

The ultramicroscopic structure that affects wood quality is the microfibril angle (MFA) (Stuart and Evans 1994). Furthermore, Bendtsen and Senft (1986), in Barnett and Jeronimidis (2003) stated that MFA of the cellulose on the second secondary wall (S2) is a determining factor for the mechanical properties of wood. Microfibrils are the smallest components in the cell wall structure with a diameter of about 3-4 nm and consist of groups of cellulose molecules (protofibrils) covered by hemicellulose sheets. While the MFA is the direction of the slope of the cellulose microfibrils on the secondary wall with the long axis of the fiber or tracheid (Barnett and Bonham 2004, Stuart and Evans 1994). MFA size ranges from 5-34° in Angiosperms (Barnett and Bonham 2004).

The MFA of the cellulose fiber is defined as the angle of the winding that form the spirals of the cellulose chains in the cell wall structure to the fiber axis or the angle formed by the orientation of most of the cellulose microfibrils the long axis of the cell (Stuart and Evans 1994; Barnett and Jeronimidis 2003). Some terms that are also used *include helical angle, spiral angle, and micellar angle.*

The orientation of the cellulose structural unit of the fiber affects the physical and mechanical properties of the fiber, especially density, tensile strength, stiffness, and shrinkage, all of which determine the properties of the paper produced. Small changes in the degree of MFA result in changes in fiber properties (Stuart and Evans 1994).

The MFA can be determined by several techniques, including measuring the alignment of iodine crystals, examining the cell wall, the angle of inside pit aperture, using a confocal microscope, and by using X-Ray Diffraction (XRD) (Barnett and Jeronimidis 2003). The method of measuring the angle of microfibrils on an individual fiber, for example, using a light microscope, takes a very long time. A technique in determining the direction of the microfibril angle automatically is XRD analysis. This method is fast but requires more expensive costs. This study aims to determine the MFA of JUN at the planned harvesting age of 5 years, compared to conventional teak at the same age to estimate the properties of the wood and to determine the most appropriate method in determining MFA in teak.

Materials and Methods

Sampling Site

Sampling was carried out in September 2009. JUN samples were collected from Srengseng Village, Balapulang District, Tegal Regency, Central Java, while the conventional teak samples were from Dukuh Satir Village, Kuta Mendala District, Tonjong Regency, Brebes, Central Java. Laboratory research was carried out from December 2009 to March 2010 at the Plant Anatomy Laboratory and Integrated Instruments and Proximate Center Laboratory of Forest Products Research and Development, Bogor.

Sample Preparation

Samples for ultramicroscopic structure observation were taken from a 5 cm thick disc from the bottom part of the tree. For the measurement of MFA, two methods were used, namely XRD measurement and light microscope.

Sampling was carried out from the pith to the bark according to the amount of incremental growth from each stem. The sample size with a length of 12 mm, a width of 15 mm, and a thickness of 0.5 ~ 1 mm were taken in the tangential section, where from each growth increment the samples were distinct from the earlywood and latewood so that the two samples were obtained from each growth increment. Due to the limitations, radial section sampling cannot be done. However, this condition certainly will not affect the resulting data, because according to Stuart and Evans (1994), samples in the radial and tangential section have relatively the same results.

Microfibril Angle Measurement Using X-Ray Diffraction (XRD)

The MFA was measured by using XRD from Shimadzu with measurement conditions as follows: Cu-Kα radiation (λ= 1.54060 Å), voltage 40 kV and current 30 mA. The auto slit is not used, gap width distribution and receiver are 1 mm and 0.3 mm. Continuous scanning process, Theta/2 Theta, and scan region 0 ~ 360°. Scan speed 90°/min. In data processing, no smoothing of the curve is carried out and the peak of the curve is determined automatically. Shooting is carried out in two orientations, vertical (transmission) and horizontal (reflection). Figure 1 shows the scanning process for measuring the microfibril angle. To calculate the MFA, Cave formula is used: MFA = 0.6 T (Meylan 1976 in Stuart and Evans 1994).

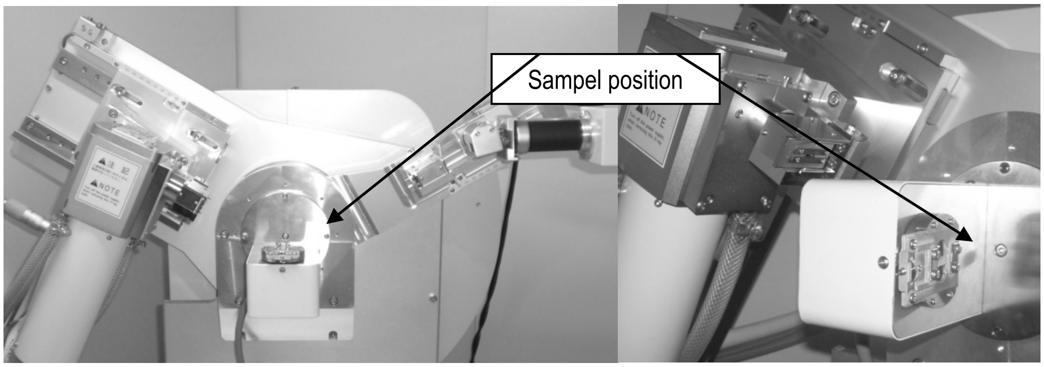

Figure 1. The position of the sample in the scanning process using X-Ray Diffraction

Microfibril Angle Measurement Using a Light Microscope

Measurement of MFA using a light microscope was carried out based on Krisdianto (2008). The fibers that have been decomposed from the maceration process (Tesoro 1989) were observed with a magnification of 500x. The microfibril angle was measured based on the direction of the inclination pit aperture of fiber cell to its long axis using the measurement program available on the Axio Imager Microscope (Zeiss). At each growth increment, the earlywood and latewood were distinct, and for each sample, the measurements were repeated 10 times. How to measure the size of the microfibril angle is presented in Figure 2.

Furthermore, the ultrastructure of wood was observed using a Scanning Electron Microscope (SEM) brand ZEISS type EVO 50. For observations using SEM, the sample size was used with the same cutting pattern as the sample for the MFA measurement. Since this tool does not require coating, there is no prior sample preparation.

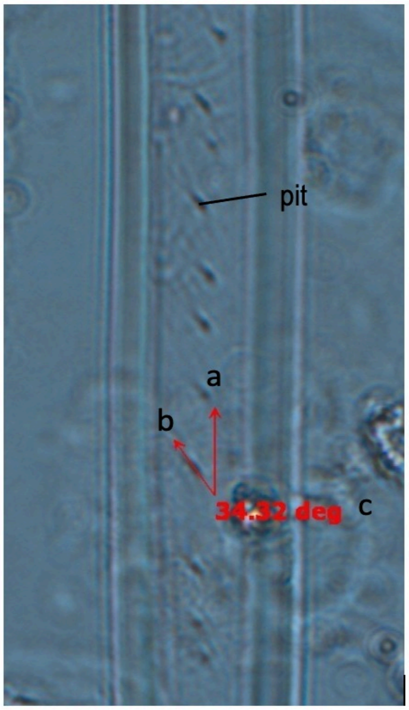

Figure 2. Procedure to measure microfibril angle in one individual fiber cell based on pit orientation (500x magnification). Description: (a) Long axis of fiber cell; (b) Long axis of pit aperture; (c) The size of the microfibril angle.

Data Analysis

MFA data of JUN and conventional teak obtained from measurements using XRD and light microscope were tested using t-student statistics and processed with Excel software. Previously, the F test was performed on the data to determine the diversity of the two samples. Based on a review of various literature, JUN as a species with accelerated growth will have a higher MFA than conventional teak. The hypotheses were:

$H_0: \mu_1 = \mu_2$
$H_1: \mu_1 > \mu_2$ or $\mu_1 < \mu_2$;
where $\overline{X_1}$ = average MFA of JUN and $\overline{X_2}$ = average MFA of conventional teak

The MFA values for the two methods used should have the same value, so to compare the results of the two methods, the following hypothesis was developed:

$H_0: \mu_1 = \mu_2$
$H_1: \mu_1 \neq \mu_2$;
where $\overline{X_1}$ = average MFA using XRD and $\overline{X_2}$ = average MFA using light microscope

Results and Discussion

The data from the MFA measurement using X-Ray Diffraction (XRD) and light microscope are presented in Table 1.

Table 1. Average data of microfibril angle of super teak Jati Unggul Nusantara (JUN) and conventional teak aged 5 years

Types of Teak/ Growth Increment	Microfibril Angle			
	5-year-old JUN		5-year-old conventional teak	
Earlywood	XRD	Light Microscope	XRD	Light Microscope
1	18,48	25,77	30,54	23,63
2	23,28	20,40	19,74	26,30
3	22,26	28,66	29,94	30,92
4	22,62	28,44	20,28	26,78
5	24,87	22,30	20,28	26,94
Mean	22,30	25,11	24,16	26,91
Latewood				
1	20,22	29,64	28,92	24,35
2	21,00	22,95	24,00	31,16
3	18,07	29,22	21,72	33,77
4	15,89	31,02	28,26	26,78
5	22,18	24,67	29,22	18,31
Mean	19,47	27,50	26,42	26,87

Many techniques have been used to measure the MFA value, including a polarizing microscope, light microscope based on the slope of pit aperture and cracks or tears in the cell wall which generally follow the direction of the microfibril slope, iodine infiltration, NIR (Near Infrared Spectroscopy), and others, but the most widely used and the most accurate result at present is using XRD (Barnett and Bonham 2004). Although the measurement of MFA based on the elongation of the pit aperture using a light microscope is the simplest method, it has the disadvantage that it is less effective because it takes time to measure it, and it is less consistent because the direction of pit aperture in one individual fiber cell can be different results of a review by Barnett and Bonham (2004). In addition, the results are doubtful if it is being measured in wood with simple and circular pit.

In this study, the microfibril angle values used mainly in JUN were calculated using XRD. Teak wood fibers have simple to minutely bordered pits, but in JUN, probably due to accelerated growth, it caused a change in simple pits with an oval shape to simple pit that were circular (Figure 3). This difference caused the results of the JUN MFA measurement using a light microscope based on the slope of the pit aperture to be inconsistent, subjective, and different results in another pit in the fiber even though they were closely associated.

In contrast to the MFA measurements of conventional teak, the measurement by using light microscope were easier because the shape of the pit was oval so that the slope of the elongation of the pit aperture can be determined easily and more consistent with more uniform values on the same individual fiber. From Table 1, it can be seen that the results of the MFA measurements on JUN by using two methods (XRD and light microscope based on the elongation of the pit aperture) produced different values, unlike the results of the MFA measurements on conventional teak, which was also supported by the results of statistical analysis.

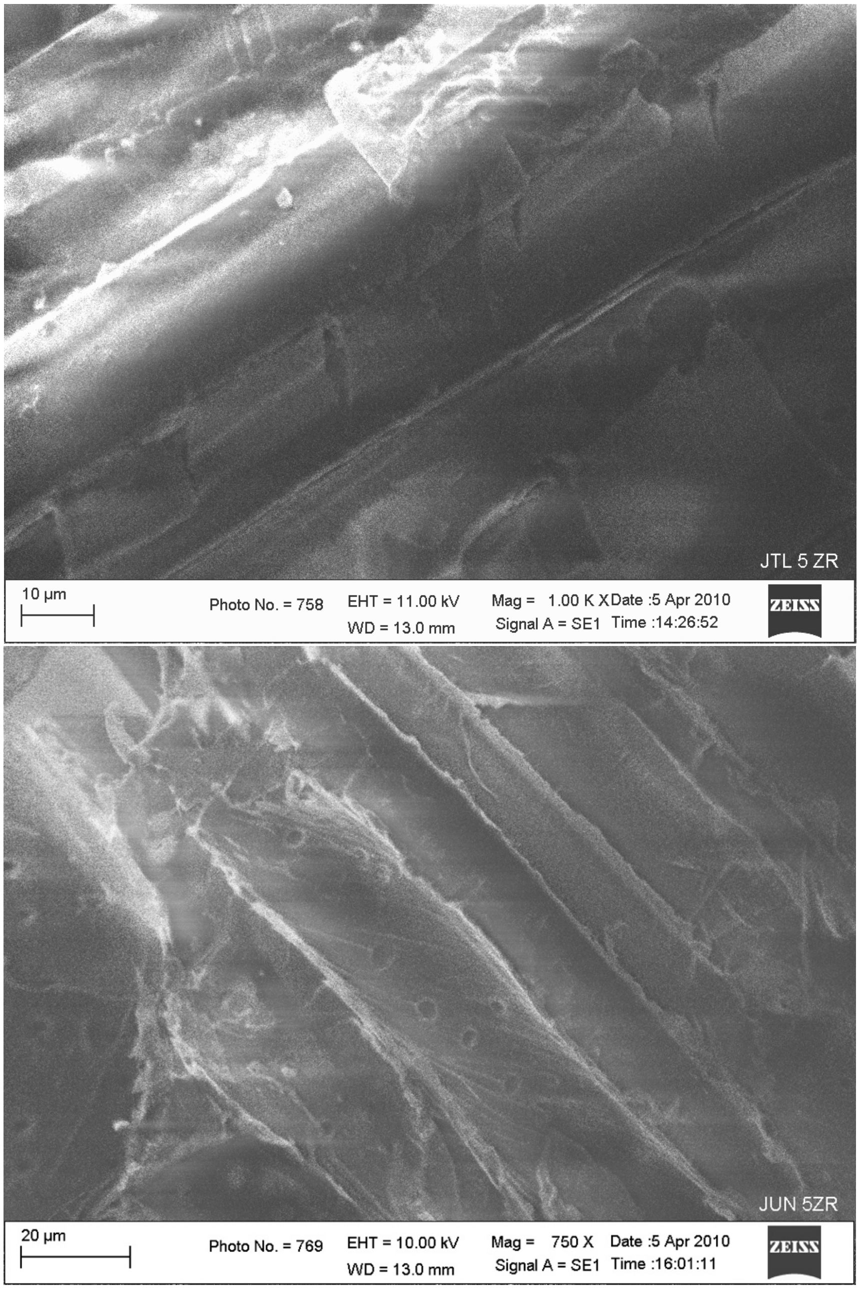

Figure 3. Conventional teak pits are oval (1,000x) and JUN wood pits are circular (750x)

The average MFA of JUN was 22.09° and the MFA of conventional teak was 25.29°. The results of statistical tests showed that the MFA of the two kind of wood was different, whereas the MFA of JUN was smaller than that of conventional teak. The MFA range of JUN wood was 22.30° for earlywood and decreased in the latewood, which was 19.47°. Meanwhile, the MFA of conventional teak wood was 24.16° for the earlywood and became larger for the latewood, which was 26.42°. This result is different from the research conducted by Krisdianto (2008) which carried out measurements using a light microscope on superior teak developed from tissue culture with conventional teak, which was both 7 years old, where the MFA of super teak was 23.29°, greater than that of conventional teak which was 22.05°. The explanation of the results was mentioned because of genetic factors as environmental conditions were considered the same.

Herman et al. (1999) in Barnett and Bonham (2004) stated that fast-grown wood with a large increment width will produce wood with a larger MFA. This shows the relationship that a large growth rate will result in shorter cells so that MFA becomes larger, whereas according to

Pandit (2006), cell length is negatively correlated with MFA. Although JUN wood has a faster growth rate, due to the longer JUN wood fiber (where these properties appear because it is inherited or because it was developed from shoot cuttings so that the young JUN immediately has a fiber structure like mature teak), the MFA value of JUN became smaller. In addition, the slenderness ratio of JUN wood was 41.46 which was higher than that of conventional teak at 32.05, where the results were statistically different. Similar to the fiber length factor, the degree of slenderness was also negatively correlated with MFA.

However, Wahyudi (2000) showed a different pattern where the growth rate had no effect on the amount of MFA, as was the case with fertilization treatment. The value of JUN MFA which is smaller than conventional teak gives different results to the hypothesis that was made earlier. This fact is in line with Donaldson (1996) in Barnett and Bonham (2004) who obtained lower MFA values in young trees derived from shoot cuttings produced from mature trees, compared to young trees of the same type developed from seeds as a control. This is sufficient to explain why MFA JUN is smaller, namely because the use of shoot cuttings causes the characteristics of young JUN to reflect the properties of mature teak. JUN seedlings are shoot cuttings derived from selected old teak trees, where superior parental traits are directly passed on to their breed and produce plants with superior characteristics and appear even though the tree is still young (Purwanto 2005; Wibowo 2005b).

Bendtsen and Senft (1986) in Barnett and Jeronimidis (2003) stated that the angle of the cellulose microfibrils on the wall is a determining factor for the mechanical properties of wood. In Rowell (2005), microfibrils are likened to steel bars to strengthen the concrete structure. The orientation of the cellulose structural unit in this fiber affects the physical and mechanical properties of the fiber, especially density, tensile strength, stiffness, and shrinkage. Small changes in the degree of microfibril angle result in changes in fiber properties (Stuart and Evans 1994). The main characteristic of wood that is affected by the size of the MFA is the shrinkage in the longitudinal direction, where the shrinkage in the longitudinal direction will increase with the increase in the MFA, but has a non-linear relationship (Barnett and Jeronimidis 2003). Likewise, the value of the Modulus of Elasticity (MOE), the larger the angle of the microfibril, the smaller the MOE value so that the wood is only suitable for low-value applications. There is currently no standard that shows what the minimum MFA value is required for wood to be used as a construction material.

Although the MFA value tends to have an effect on longitudinal shrinkage, the smaller JUN MFA compared to conventional teak at the same age will most likely cause the shrinkage (T/R ratio) of JUN wood to be smaller and the wood to be more stable (as evidenced by the results of physical research) so that it will be more profitable when it will be manufactured for veneer, furniture, and other products; higher tensile strength and stiffness, as well as a straighter fiber direction (observable in the longitudinal plane of JUN wood), so as a consequence, less energy is used to process this wood because it is easier to work with.

The structure of the fiber cell walls or tracheids in trees is designed so that the trunk and branches are able to withstand both from external and internal pressures, such as the weight of the tree trunk, the weight of the canopy, and external pressures such as wind and gravity. A large MFA in young trees or seedlings is needed to make the tree more flexible and bend easily without breaking in the wind. Wood formed at the beginning of growth with a large microfibril angle refers to the properties of young wood (Barnett and Bonham 2004). The large MFA value in the young wood area causes the section to become weak with a smaller and less stable MOE value. However, as the tree grows, the trunk becomes stiffer to support the added mass of the trunk and crown, and the lower MFA value in the outer wood allows the tree to do that (Barnett and Jeronimidis, 2003; Barnett and Bonham 2004).

As previously mentioned, naturally trees will form wood with larger MFAs in the early stages of growth. JUN and conventional teak were still very young (5-years age), moreover with the juvenile content is 100%. Besides being developed from shoot cuttings, another possibility that causes the MFA value of JUN to be smaller than conventional teak is thought to be due to the faster growth of the stems with a wide crown shape, so that JUN must adapt to form small microfibril angles. Even though it has a smaller MFA value, JUN will succeed in becoming a tall tree, but not easy to collapse if it is supported by a solid foundation. The weaknesses of superior teak wood are that it grows sideways or collapses quickly once the tree begins to grow, but not with JUN wood. The existence of a stilt root form allows the tree made stiffer by forming small microfibril angles, but does not harm the tree when exposed to internal and external pressures, where this structure is not possessed by conventional teak or other superior teak woods (Figure 4).

Rooting from seed   Rooting from tissue culture   JUN Rooting

Figure 4. The form of taproots in teak growing from seeds, adventitious roots from shoot cuttings and tissue culture, as well as stilt roots in JUN

A small MFA value is one of the parameters chosen in tree breeding. The breeding aim is to reduce the proportion of young wood that has a large MFA so that the properties of the wood will be better and its value will increase economically. However, because the demand for wood is very large, this is a problem because we currently use a lot of fast-grown wood from short rotation cropping (Barnett and Bonham 2004). We can make efforts to minimize the MFA, but it must be ensured that these efforts will not harm the trees. One of the efforts that was quite successful in JUN was by modifying the roots to become stilt roots.

Conclusions

Microfibril angle (MFA) JUN was 22.09°, smaller than the conventional teak 25.29°. The lower value of MFA JUN was due to the fact that the wood was developed from shoot cuttings so that although it was young, it reflected the characteristics of mature teak. Technological input in the form of stilt roots allows JUN to have a small MFA without endangering tree growth due to pressure from inside or outside.

The results of MFA measurements on JUN by using two methods, namely XRD and light microscope, had different values. It was different from the results of MFA measurements on conventional teak. The MFA value used in JUN was proposed to be measured by using X-Ray Diffraction because it is possible that due to accelerated growth, a simple pit with an oval shape turns into circular. This difference causes the results of the JUN MFA measurement using a light microscope based on the slope of the pit aperture to be inconsistent, subjective, and different results in other pits contained in the fiber even though they are closely associated. However, in conventional teak, measurements using a light microscope are possible because the shape of the pit is oval so that the slope of the elongation of the pit aperture can be determined easily, and it is more consistent with more uniform values in the same individual fiber.

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The Effectiveness of Boron Preservatives to Prevent Dry-wood Termite Attack on Mahogany Sapwood

Aryati Larasati and Joko Sulistyo

Abstract

Mahogany wood is utilized for many furniture products and construction purposes. The objective of this experiment was to prevent wood-destroying insects by using boron preservatives such as boric acid and borax. Materials used were mahogany sapwood planks (19 years) obtained from community forest in Kali Bawang District, Kulon Progo. Two preservation methods, i.e., hot-soaking (1, 2, and 3 hours) and the cold-soaking (12, 24, 36, and 48 hours) in 5% concentration, were used. The drywood termites (*Cryptotermes cynocephalus* Light) were used for observation. The result showed that the retention value ranges were 4.25 to 12.99 kg/m^3 for cold-soaking method and 3.09 to 9.53 kg/m^3 for heat-soaking method. Mortaliy rate and mass loss due to termite attacks ranged from 56.0 to 80.6 % (control values : 43.3%) and 850 to 1370 mg (control values : 1930 mg). Significant interaction between soaking time and the type of preservative was observed to discover its effect on the levels of retention (cold soaking) and mortality rate of termites (hot soaking). Boron preservatives tended to enhance the repellent properties than its toxicity.

Keywords: *Swietenia macrophylla*, wood preservation, borax, natural durability, non-pressure method

Introduction

Mahogany wood is one of the commercial woods that are often found in community forests. Mahogany population in Indonesia is concentrated in three provinces, namely West Java, Central Java, and East Java. Mahogany wood is in great demand due its beautiful appearance, good workability, and ability of being finished and dried without significant defects (Martawijaya *et al*. 2005). Nonetheless, the mahogany wood produced from community forests is assumed to have low quality because it is harvested at young stage. Most of the raw materials in the small-scale furniture industry are mahogany which comes from young stands. The concern is that the wood has a fairly high proportion of sapwood, which generally exhibits a low natural durability.

Wood preservation process is an effort to extend the duration of mahogany wood utilization. Boric acid and borax preservatives are commonly used due their water-borne properties, cheap price, and availability. In addition, it is also possible to accelerate their dissolving by increasing the temperature of the solvent. The easiest method to do is the soaking method, especially for communities around forests and small-scale industries. Cold soaking with borax and boric acid on several types of wood is quite effective in preventing termite damage (Abdurrahim 1994; Lelana *et al*. 2011; Sumaryanto *et al*. 2013). Therefore, this research was conducted on the preservation of mahogany wood using the active ingredient boron by cold soaking and hot soaking methods.

Materials and Methods

Material Preparation

The material used was wood from a 19-year-old mahogany tree from Kajoran Pelem Hamlet, Banjaroyo Village, Kali Bawang District, Kulon Progo Regency, Yogyakarta (Figure 1). The sapwood part was separated from the wood plank that previously was cut using a chainsaw. The size of the test specimens for preservation and termite resistance test was 3 cm (radial) x 3 cm (tangential) x 10 cm (longitudinal). The oil paint was used to to cover the transverse side (x) to avoid penetration from the longitudinal direction.

Figure 1. Boards (left side) of mahogany wood and mahogany logs (right side) from trees grown in community forest in Kulon Progo

Soaking Process

The commercial grade boric acid (H_3BO_3) and anhydrous borax (Na_2B4O_7) purchased from a local chemical store were prepared for the process. The concentration of preservative solution used in both preservative methods was 5%. The test samples were initially arranged, then were soaked completely in a solution tank. The test samples were soaked for a predetermined time variation of 12, 24, 36, 48 hours (cold-soaking method). The same procedure was applied to hot-soaking method. The tank was heated to a temperature of 80ºC for the specified time variations of 1, 2, and 3 hours. Experimental controls were untreated sapwood specimens. All treatments were replicated 3 times. After the soaking treatments, the samples were conditioned to the weather in order to determine the amount of retained preservatives (retention). The conditioning step was carried out by placing the test sample in an oven at 49ºC for 24 hours. This weather conditioning treatment was carried out for 10 days. After 10 days, the test samples were removed and air-dried at room temperature for 2 days. Retention value was determined by weighing the weight after treatment minus weight before treatment in a given volume (Baysal *et al*. 2006).

Termite Test

A glass tube with a diameter of approximately 2.5 cm and a height of 4 cm was installed on an unpainted wood cross section. The installation was carried out using a wood glue. The glass tube was used to prevent termites from spreading out of the attack area (Figure 2). After that, the test sample was weighed to determine the air-dry weight before feeding. As many as 50 active drywood termites (*Cryptotermes cynocephalus* Light.) at nymph stage (N) were used in each test sample. (Figure 3). The test samples were fed to dry wood termites and were placed in a cool and dark place for 28 days. To measure the termiticidal activity, dead termites were counted at the end of observation. The weight loss was measured to quantify the extent of the termite attack on the wood (SNI 2006).

Figure 2. Specimens of termite test

Figure 3. Dry-wood termite (*Cryptotermes cynocephalus* Light.)

Statistical Analysis

A two-way analysis of variance (ANOVA) test was carried out to determine the factors (soaking time and preservative type) that had a significant effect on the 5% test level. The two factors were arranged in a factorial design. The post-hoc Tukey HSD (Honestly Significant Difference) was applied to see the difference in the mean value of the treatment (Gaspersz 1991). SPSS 16 software for Windows was used to do all calculations.

Results and Discussion

Retention is measured to evaluate the effectivity of preservation process. The recommended retention of boric acid preservative is 8 kg/m^3 to prevent termites, other insects, and fungi in tropical countries such as Indonesia (SNI 1999). The results of ANOVA showed that the interaction between the type of preservative and soaking time factors showed a significant effect on the retention value ($p<0.01$). Tukey test showed that the highest cold soaking retention value was 17.26 kg/m^3 at 48 hours soaking time with borax, while the lowest retention value was 4.24 kg/m^3 at 12 hours with boric acid (Figure 4). The borax retention value in this study was lower than boric acid retention value. This is probably because boric acid is easier to dilute using hot-water to get more preservatives retained in the wood cells. Previously, Yamauchi *et al*. (2007) demonstrated that the aqueous solution impregnates the cell walls of wood with boric acid more easily than the methanolic solution.

The hot-soaking time showed a significant effect on the amount of retention ($p<0.01$), while the difference between the two preservatives was not significant. Based on Tukey tests, it was shown that the 3-hours hot soaking was significantly different from the 1-hour hot soaking in the retention value. Previous studies with the same preservative reached 3-12 kg/m^3 in teak with cold soaking (Sumaryanto *et al*. 2013) or in the cold soaking range with borax preservative (Abdurrohim 1992). The same trend in the soaking time factor was also observed by Barly and Lelana (2010), who observed cold soaking of tusam and sengon woods, and Rinaldi *et al*. (2014), who preserved sengon wood with hot and cold soaking of kecubung leaf extract. This tendency was also observed by Djarwanto and Sudrajat (2002) on mangium wood that was preserved with hot-cold soaking of boron-based preservatives.

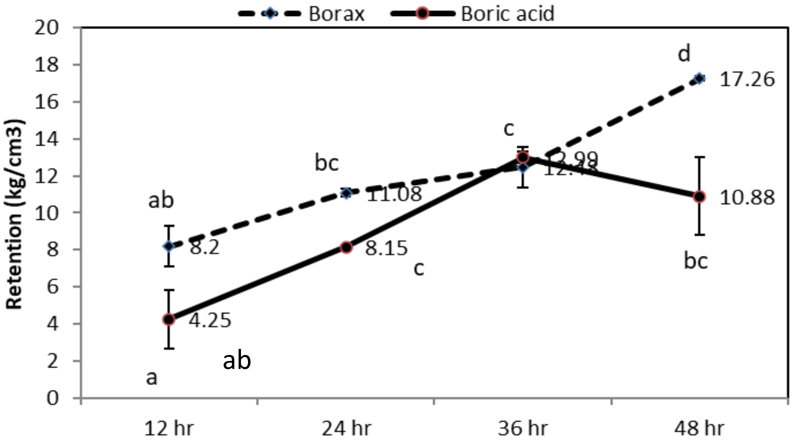

Figure 4. Retention of mahogany sapwood after cold soaking in boron preservatives (5% concentration). Average of 3 replications with the standard deviation error bar. The same letters are not statistically different at $p < 0.05$ by Tukey's test.

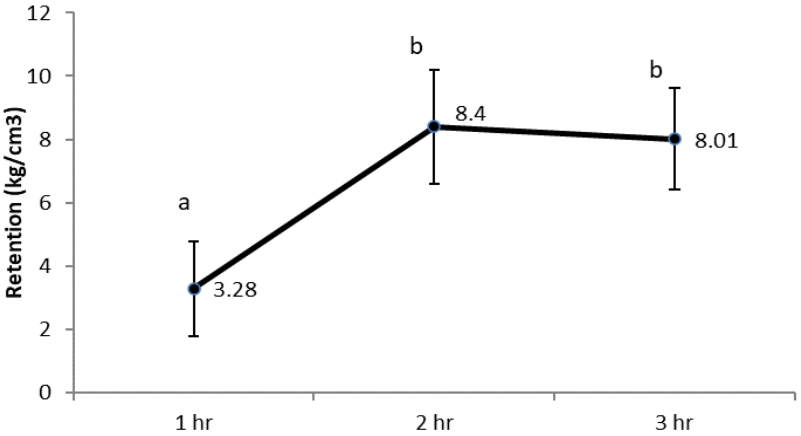

Figure 5. Retention of mahogany sapwood after hot soaking in boron preservatives (5% concentration). Average of 3 replications with the standard deviation error bar. The same letters are not statistically different at $p < 0.05$ by Tukey's test.

The drywood termite mortality and weight loss are presented in Table 1. The ANOVA results showed that the soaking time and the type of preservatives did not have a significant effect on the mass loss due to drywood termite attack in both methods. The cold soaking time and the type of preservative also had no significant effect on the mortality of dry wood termites. The interaction of the type of preservative and the duration of hot soaking showed a significant effect on drywood termite mortality (p<0.01). The results of the Tukey test between soaking time and type of preservative showed that the highest value (80.6%) was found in boric acid preservative with 3 hours of soaking time.

Comparison with controls without preservatives showed a drastic reduction in weight loss. However, there was no much increase in termite mortality because almost all treatments gave values below 70%. This indicates that the concentration used (5%) has more antifeedant effect than toxic effect. The tendency to increase retention with soaking time also cannot directly explain the effect on these two parameters. This is thought to be related to preservative penetration, which was unfortunately not measured in this experiment. Likewise, the type of preservative had no effect on the weight reduction parameters. This is because the active ingredients contained in both types of preservatives are the same (boron). It is asssumed that both preservatives have the same effectiveness against drywood termites. The same trend was also observed by Sumaryanto *et al*. (2013) in teak sapwood with boric acid and borax treatments. This indicates that the sapwood of teak and mahogany behaves the same towards boron preservatives. Further research needs to be done to explain this phenomenon.

Table 1. Termite test of mahogany sapwood after soaking in boron preservatives (5% concentration) and 28-day observation. Average of 3 replications. The same letters are not statistically different at $p < 0.05$ by Tukey's test.

Treatment	Mortality rate (%)		Weight loss (mg)	
Cold soaking (hour)	Borax	Boric acid	Borax	Boric acid
12	74.0	70.6	1090	850
24	62.0	69.3	930	900
36	66.6	65.3	940	870
48	72.6	67.3	920	940
Average	68.8	68.1	970	890
Hot soaking (hour)				
1	69.3 ab	56.0 a	960	1370
2	60.6 a	67.3 ab	1040	850
3	60.0 a	80.6 b	900	950
Average	63.3	68.0	970	1060
Control (untreated)	43.33		1930	

Conclusions

The interaction between soaking time and the type of preservative using the cold-soaking method gave a significant effect on the retention and mortality rate of termites, but did not have a significant effect on weight loss. The interaction between soaking time and preservatives with the hot-soaking method did not have a significant effect on retention and weight loss. The highest cold soaking retention value was 17.26 kg/cm^3 at 48 hours soaking time with borax whereas the 2-hours hot soaking obtained the highest retention value (8.04 kg/cm^3). The effective duration to prevent drywood termite attack was 1 hour of hot soaking in borax preservatives or 2 hours in boric acid preservatives while 12 hours of cold soaking with borax or boric acid preservatives was sufficient. Although the minimum retention has been achieved, the penetration of preservatives was not measured in this test although it is also an important factor for indicators of the effectivity of wood preservation.

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Study of Provenance and Site Variability on Calorific Value and Other Fuel Properties of Teak Stem

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Abstract

Currently Perum Perhutani has conducted efforts to improve the productivity of teak forest by provenance trial. However, only a few studies have so far considered the variation of these main fuel properties of wood under the influence of external factors such as location and provenance. On the other side, the huge amount of waste was regularly generated from primary and secondary wood processings. Therefore, in this research, the calorific value and other fuel properties were investigated and related to provenance and growth site. This research used the stem wood and bark of five provenances (1 to 5) of teaks that were planted at three sites of Perhutani stand (Bojonegoro, Ngawi, Ciamis). The fuel characterisctics of bark were only evaluated at Ciamis site. Compared to bark, wood generally had lower values in ash content, volatile matter content, and density, but had higher values in fixed carbon content, calorific value, and Fuelwood Value Index levels. The caloric values of teak wood and bark were 4,191~4,520 cal/g and 3,545~3,939 cal/g, respectively. Provenance and site interaction had significant effect to the ash content, density, and calorific value in wood. The samples from Ciamis site (code Ft) had the highest level in calorific value. However, the relation between calorific value and density is not clear in this experiment. With regard to bark, provenance 3 (Ft) showed the best energy properties.

Keywords: wood waste, fuelwood, fixed carbon, ash content, heating value

Introduction

Teak is one of the most important timber species and categorized as fancy wood to produce multiple end-uses from handicrafts to heavy construction. In Indonesia, the teak plantations are mostly managed by the state-owned company, Perum Perhutani. Not only does Perum Perhutani manage the plantations, but it also has wooden industries to produce sawn woods, plywoods, and other wood-based panels. Consequently, the logging and wooden industrial wastes have been generated in considerable amounts. Those wastes are utilized for heat and electricity production in those wooden factories and are donated to communities around the forest.

Biomass has been proved as useful and cost-effective alternative renewable energy source in its various forms. The logging residues of final felling operations primariliy include tops, branches, and twigs that have been allowed to remain at the site, whereas the industrial wastes are mainly in the form of slab and sawdust. Along with wood parts, bark wastes are also found in huge numbers. Debarking these logs would be impractical due to their small size. The bark portion in the teak stem was varied depending on site or tree age. The percentage of bark of Indonesian teak reached 25% (Lukmandaru *et al.* 2010), whereas that of Indian teak reached 43% (Tewari *et al.* 2013) although the measurement method was different between the two. Hence, it is necesary to estimate the contribution of the wastes by exploring their fuel properties. However, literature on energy characteristics for teak is available in scanty numbers because this timber is not intended to be used as a commercial fuel. The study reported here serves to fill that gap. It is important to understand the physical and chemical nature of feedstock. The calorific value is the most important characteristic for comparing the effectiveness of any fuel. Any variations in the calorific value between species or in tree parts indicate differences in their chemical and physical compositions.

The quality of teak timber could be improved by intensive management. The potential for managing teak in different sites and under different situations is well documented. Provenance trials to evaluate growth performance, stem form, and productivity in teak trees have been conducted. This trial is the first step in a genetic improvement programme component of plantation establishment. Selection for desirable wood properties, however, was not much emphasized. The effect of site and provenance on the basic properties of teak wood has been investigated in Indonesian teak (Lukmandaru 2012; Hidayati *et al.* 2013) and teak grown overseas (Kjaer *et al.* 1999; Varghese *et al.* 2000; Bhat and Priya 2004; Bhat *et al.* 2005). Significant differences in several parameters were observed among provenances and sites. It is hypothesised that ecological differences between regions of provenance of teak have led to differences in energy properties.

The main aim of this study was to analyse variation in the calorific value and other fuel characteristics of teak stem from main resource bases, depending on the growth-site and provenance. This work used three different sites (Bojonegoro, Ciamis, and Ngawi Forest Management Unit) and five provenances. The information gathered will be useful for further research on the tree improvement aspects of teak with reference to energy properties and to bring out their potential utility for future afforestation programmes. In addition, the best performing provenances can be used for bioenergy production.

Materials and Methods

Field Sampling

The stem samples were taken at different sites (Bojonegoro, Ngawi, and Ciamis Forestry Management Units), whereas five provenances (code 1 to 5) planted in each site were observed. The stem samples were procured from slab wastes of a sawmill in each site. The slab wastes were randomly selected for each provenance. The codes of the provenaces are presented in Table 1. From the slab, wood and bark samples were then separated by hand. The fuel properties of the bark that were determined were only those of samples from Ciamis. The fuel properties of each part, which was obtained at different weights by sawing, were determined. The 2 g of specimens were for moisture content, density, ash content, volatile matter content tests, while 1 g of specimen was for calorific value test.

Table 1. Codes for observed provenaces in three sites

Provenance	Bojonegoro (D)	Ngawi (E)	Ciamis (F)
1	D9	E47	Fi
2	D11	E149	Fk
3	D16	E502	Fp
4	D18	E52	Fr
5	D20	E4	Ft

Laboratory Methods

Densities of dried samples (ca. 2 g) were determined by water displacement volume method (ASTM D 2395-02). An air dried sample (1 g) was burned in an oxygen bomb calorimeter (Parr Instrument Company Inc, no. 1341 3403 series) for determining the calorific value.

Moisture content of sample (2 g) was determined after oven-drying (ASTM D 4442-92). The ash content and volatile matter content (2 g dry basis) were determined using ASTM D5142. Fixed carbon content (FCC %) was calculated from the equation:

FCC (%) = 100 - (% Ash content + % Volatile matter content) ……………………………………………...................(1)

Fuelwood value index (FVI) was based on the properties of calorific value, wood density, and ash content (Purohit and Nautiyal 1987):

Fuelwood Value Index (FVI) = Calorific Value (kJ/g) × Wood density (g/cm^3) / Ash content (g/g) ....(2)

Statistical Analysis

Analyses of variance (ANOVA) were performed for evaluating site and interaction on wood samples. For the bark part, the differences among provenances were analysed using one-way ANOVA models. A Tukey's test was used to show which groups were significantly different. All data were analyzed using SPSS 18 for Window.

Results and Discussion

Fuel Properties of Wood

Generally, woody biomass is a renewable fuel because the amount of carbon dioxide resulting from burning is equal to that absorbed during the tree growth. The understanding of fuel properties, i.e., calorific value, ash content, volatile content, fixed carbon content, ultimate carbon, and hydrogen, is very important for utilization of any material as fuel. An ideal fuelwood species should have high calorific value, high wood density, and low ash content. The measurement of proxymate analysis is described in Table 2. The moisture content in the wood was in the narrow range (11~12%), indicating homogenous condition in the field. Ash content was widely varied (0.43~1.87%) and still in the range reported by the previous study (Lukmandaru 2011) on teak grown in Randublatung stand (0.7~3.0%). The ranges of volatile matter and fixed carbon contents were 78.4~83.9% and 15.5~21.7%, respectively. For comparison, the values of volatile matter and fixed carbon contents on teak wood (4 years) from Nigeria were 74.7% and 16.6%, respectively (Chow and Lucas 1988).

The data of density, calorific value, and FVI are presented in Table 3. The density range obtained here was 0.55~0.69 g/cm^3. Previously, the density of teak wood from community forest in Gunungkidul, Yogyakarta, was 0.50~0.67 g/cm^3 (Marsoem *et al.* 2014) while the density of teak wood from Perhutani stand (clonal, 12 years) was 0.51~0.52 g/cm^3 (Hidayati *et al.* 2014). Furthermore, the specific gravity of the wood was 0.62~0.75 (Martawijaya *et al.* 2005). The wide variation was also found in calorific value (4,191~4,520 cal/g). Those levels are lower than those of Martawijaya *et al.* (2005) (5,081 cal/g) and teak grown in Nigeria (4,580 cal/g) (Chow and Lucas 1988). Studies on local commercial species for fuel (Matheson 1990; Cahyono *et al.* 2008) showed the calorific value of 4.197 cal/g for lamtoro (*Leucaena leucocephala*), 4,168 cal/g for gamal (*Gliricidia maculata*), and 3,329~3,514 cal/g for kaliandra (*Caliandra calothyrsus*).

By ANOVA, no significant factor affected the proxymate data in moisture, fixed carbon, and volatile matter contents (Table 3). Provenance × site interaction was significant ($p < 0.05$) for ash content, density, and calorific value. This interaction was manifested in the Ciamis site having smaller values for ash content for several provenances, whereas the highest value was observed in samples from Bojonegoro site. The highest density level (0.69 g/cm^3) was found in samples of Bojonegoro (D18). The highest calorific value (4,520 cal/g) was observed in Ciamis site (Ft). The site and provenance effects, as a single factor, significantly affected FVI, the highest value of which was measured in Ciamis (20.9) and provenance 2 (17.8) (Figure 1).

The provenance indicates various locations that are distinct from each other either geographically or in eco-agri systems. In an earlier report, significant effect of 21 provenances (13 locals and 8 from outside Indonesia) was observed on physical properties measured by non-destructive evaluation (Hidayati *et al.* 2013). Furthermore, variation in heartwood proportion, calcium, and silica contents was measured among the provenances in teak wood from Puerto Rico (Kjaer *et al.* 1999). The effect of provenance on anatomical properties was also observed by Bhat and Priya in Indian teakwood (2004). In this study, the variabilility in ash content, density, and calorific value among provenances led to conclusion that geographic variation may influence the wood properties. Because all trees were growing under similar environmental conditions, the observed differences among provenances may partly be due to genetical variation.

Table 2. Proxymate analysis of teak wood waste (average of three replications).

Sites/provenances	Moisture content (%)	Ash content (%)	Volatile matter content (%)	Fixed carbon content (%)
Bojonegoro				
D9	11.7	1.68 c	80.8	17.5
D11	12.2	0.87 ab	81.3	17.8
D16	11.8	1.61 c	80.5	17.9
D18	12.0	1.13 b	82.2	16.7
D20	12.4	1.87 c	80.7	17.4
Average	12.02 (0.28)	1.43 (0.41)	81.1 (0.68)	17.46 (0.47)
Ngawi				
E47	11.8	1.05 b	81.3	17.6
E149	11.5	0.67 a	78.4	20.9
E502	11.8	1.27 b	80.0	18.7
E52	11.5	0.86 ab	80.6	18.6
E4	12.0	1.08 b	82.1	16.9
Average	11.72 (0.21)	0.98 (0.22)	80.48 (1.40)	18.54 (1.51)
Ciamis				
Fi	12.2	0.62 a	79.8	19.6
Fk	11.6	0.48 a	80.8	18.8
Fp	12.5	0.43 a	77.9	21.7
Fr	12.0	0.84 ab	79.6	19.6
Ft	12.0	0.60 a	83.9	15.5
Average	12.06 (0.32)	0.59 (0.15)	80.4 (2.21)	19.04 (2.25)

Remarks: The same letters on the same column are not statistically different at $P < 0.05$ by Tukey's test.

Table 3. Density, calorific value, and fuel value index of teak wood waste (average of three replications) T

Sites/provenances	Density (g/cm^3)	Calorific value (cal/g)	Fuel value index
Bojonegoro			
D9	0.55ab	4211 d	6.4
D11	0.58b	4243 de	12.2
D16	0.60b	4397 e	7.0
D18	0.69c	4343 de	11.8
D20	0.64b	4239 d	6.1
Average	0.61 (0.05)	4286.6 (79.4)	8.7 (3.03) g
Ngawi			
E47	0.63b	4210 d	10.8
E149	0.56ab	4237 de	15.6
E502	0.62b	4254 de	10.6
E52	0.59b	4274 de	12.8
E4	0.52a	4379 e	8.9
Average	0.58 (0.04)	4270.8 (64.8)	11.74 (2.56) g
Ciamis			
Fi	0.67bc	4388 e	19.8
Fk	0.65bc	4320 e	25.5
Fp	0.56ab	4191 d	25.3
Fr	0.59b	4379 e	12.9
Ft	0.66bc	4520 f	21.1
Average	0.62(0.04)	4359.6 (119.2)	20.9(5.14) h

Remarks: The same letters on the same column are not statistically different at $P < 0.05$ by Tukey's test.

Table 4. Site and provenance analysis of variance in fuel properties and density of teak wood waste

Source of variations	df	Mean square						
		MC	AC	VMC	FCC	Density	CV	FVI
Site (A)	2	0.17	0.38**	9.178	10.9	0.001	2136.7	51.5*
Provenance (B)	4	0.51	2.65**	2.205	9.3	0.008*	33536.1*	606.9**
A x B	8	0.25	0.19*	6.209	5.8	0.010**	26329.9*	2.2
Error	30	0.23	0.08	5.385	5.7	0.001	8719.3	17.0

Remarks: df = degree of freedom, MC = moisture content, AC= ash content, VMC = volatile matter content, FCC = fixed carbon content, CV = calorific value, FVI = fuel value index. ** Significant at the 1% level (one-way analysis of variance); * significant at the 5% level (one-way analysis of variance)

Calorific value of plants is defined as the amount of heat energy released during combustion of plant tissue. The calorific value is mainly affected by elemental composition, moisture content, and quantity of ash produced (Kumar *et al.* 2011). The higher the moisture content is, the less efficient the wood becomes as a fuel since the net calorific value for heating is reduced. After felling, green wood starts to lose moisture quickly at first as it loses free water and then at a slower rate, it loses bound water (Shmulsky and Jones 2011). The moisture content gradually approaches an equilibrium state that fluctuates with temperature and relative humidity as discovered in this study (11~12%). The small variation in moisture content values showed the homogenity of the slabwood samples. Thus, it is not very important as there is no significant difference among the factors.

The highest calorific value in Ciamis site (Ft) need attention in terms of fuel purpose. This tendency is supported by comparatively low ash content levels in Ciamis site. It is known that the fuel quality reduces with the amount of ash present in the biomass. When wood is used as a fuel, the accumulation of ash will interfere with combustion and reduce the efficiency of the furnace. On the other hand, density is one of the important parameters that directly affect the quality of a fuel. The species having higher density are preferred as fuel because of the high-energy content per unit volume and their slow burning property. Previous study showed positive correlation between density and calorific value (Munalula and Menicken 2009; Chin *et al.* 2013). This pattern was not observed in this study as the highest values was measured in Bojonegoro site (D18). The reasons for the dissimilarities were probably due to differences in the chemical composition of the wood, particularly in relation to the polysaccharide fraction and lignin. The higher value of the heat of combustion of lignin, compared with polysaccharides, results from the higher ratio of carbon to hydrogen in that substance (Shmulsky and Jones 2011). In addition, high fixed carbon content adds to high-energy value of plant material. However, by ANOVA, it is discovered that this variation also does not have significance. Variations of cell wall composition indicated in this experiment might be also related to the differences of growing site (soil type, annual rainfall, and temperature).

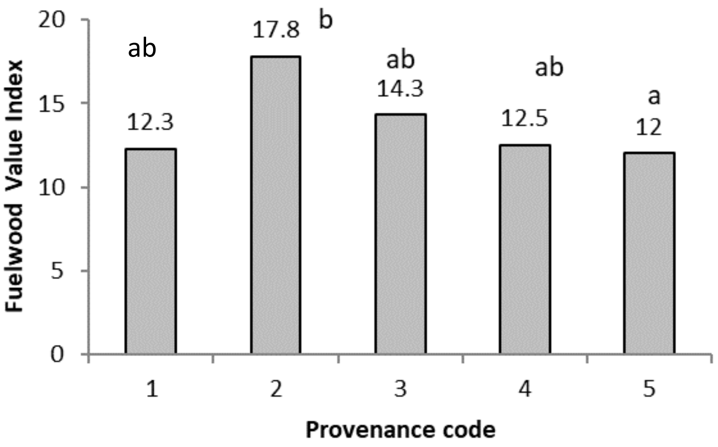

Figure 1. Fuelwood value index of teak wood waste (average of three replications). The same letters are not statistically different at $P < 0.05$ by Tukey's test.

Fuel Properties of Bark

It is essential to achieve maximum utilization of all above-ground portions of each harvested tree, including the bark. Therefore, a detailed analysis of biomass with high feasibility and abundant availability is a crucial step in producing biomass fuel as a commercial fuel. Due to differences in chemical structure, bark and wood showed huge differences in fuel characteristics. Compared to the wood, bark generally had higher values in ash content, volatile matter content, and density, but had lower fixed carbon content, calorific value, and FVI (Table 4). Based on calorific value and FVI, it was found that bark was less effective as fuel than wood.

The comparatively low calorific value in bark could be related to the low value of fixed carbon content and high value of ash and volatile matter contents even though the density is higher compared to the wood. A biomass having low ash content is considered better feedstock. The bark of all evergreen hardwood species usually presents significantly higher ash content than the wood. Majority of ash in a tree is concentrated in the bark tissues because of its importance to physiological functions. Extractives content has positive effect on calorific value of a biomass (Kataki and Konwer 2001). Unlike wood, bark contains suberin and polyphenols, more extractives, and less polysaccharides (Fengel and Wegener 1984). In addition, volatile content is inversely proportional to fixed carbon content and a biofuel rich in fixed carbon (low content in volatiles) will burn slowly. During the combustion process, when the biomass is heated, the volatiles escape first and burn in gaseous state, leaving behind the fixed carbon as char, which burns later in solid state.

By using one-way ANOVA involving only one site (Ciamis) at a time (Table 5), it was known that provenance was significant for any other variable tested ($p < 0.05$). This variability might reflect adaptive responses to geographic variation and environmental conditions. Fp gave the highest significant values in density (0.85 g/cm^3), calorific value (3,939 cal/g), FVI (3.64), and fixed carbon content (18.0%), and the lowest value in ash content (3.84%) and volatile matter content (78.1%). It is noticed that the highest density value of bark was also found in the same provenance (Fp) and this pattern is not found in wood. This implies that calorific value in bark is more related to other characteristics and more predictable than that of the wood. Unfortunately, the evaluation has been conducted only on Ciamis site. It would be interesting to find the trend in bark that is related to the site and to compare it with the wood. Future works should be conducted on more sites as well as to estimate the actual contribution of both wood and barks as fuel.

Table 5. Fuel properties and density of bark waste from Ciamis site (average of three replications).

Provenance	Moisture content (%)	Ash content (%)	VMC (%)	FCC (%)	Density (g/cm^3)	Calorific value (g/cm^3)	Fuel Value Index
Fi	12.4 a	5.30 e	79.0 h	15.7 kl	0.84 n	3813 pq	2.53 s
Fk	12.7 ab	5.87 ef	79.2 h	15.0 jk	0.83 mn	3756 o	2.23 rs
Fp	13.4 b	3.84 d	78.1 h	18.0 l	0.85 n	3939 q	3.64 t
Fr	12.5 a	7.19 g	80.1 i	12.8 j	0.77 m	3545 o	1.59 r
Ft	12.4 a	6.50 ef	79.5 hi	14.0 jk	0.81 mn	3619 o	1.91 r
Average	12.68(0.42)	5.74(1.27)	79.18(0.73)	15.1(1.95)	0.82(0.03)	3734.4(156.2)	2.38(0.78)
Sign.	0.01*	<0.01**	0.01*	<0.01**	0.01*	0.01*	0.03*

Remarks : VMC = volatile matter content, FCC = fixed carbon content,. ** Significant at the 1% level (one-way analysis of variance); * significant at the 5% level (one-way analysis of variance). The same letters on the same column are not statistically different at $P < 0.05$ by Tukey's test.

Conclusions

The effect of provenance and site on fuel properties of teak wood and bark has been studied. The ranges of caloric value in wood and bark were 4,191-4,520 cal/g and 3,545-3,939 cal/g. Significant interaction between those factors was found in ash content, density, and calorific value. Based on the calorific value and ash content, provenance 5 in Ciamis site (code Ft) was found to be the most promising fuel source. There was no particular trend observed betwen density and calorific value. Provenance effect was also found in FVI and the highest value was observed in provenance 2. Characterization on bark showed that provenance factor significantly affected all tested parameters. It is measured that provenance 3 (Fp) had the best fuel properties for the bark part.

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Characteristics of Carbon from Oil Palm Shell Activated by Low Concentration of Zinc Chloride Activator

Joko Sulistyo, Purnama Darmadji, and Sri Nugroho Marsoem

Abstract

Currently, a large amount of oil palm shell has been dumped as waste from palm oil processing in Indonesia. Using a low concentration of zinc chloride ($ZnCl_2$), thermal treatment during pre-carbonization was applied in the preparation of activated carbon from oil palm shells at various temperatures and reaction durations. This study, therefore, aims to investigate the physical and chemical characteristics of activated carbon prepared. Oil palm shells collected from a plantation in Palembang were carbonized by two methods, one-stage carbonization (at 300°C for 3 hours) and two-stage carbonization (at 300°C for 3 hours, then at 600°C for an hour) before chemical activation using $ZnCl_2$, at a concentration of 10 and 15%wt. Activation of oil palm shell charcoal was conducted at 600, 700, and 800°C and reaction times of 60, 120, and 180 minutes. The results showed two-stage carbonization, high temperature, and prolonged reaction time is bound to increase burn-off as well as methylene blue adsorption, and decrease the yield and volatile matter content of the activated carbon prepared. Meanwhile, high $ZnCl_2$ concentration increased the ash content and the methylene blue adsorption. In addition, the two-stage carbonization had higher iodine adsorption compared to the one-stage carbonization. The activated carbon with high iodine (769.3 mg/g) and methylene blue adsorption (133.7 mL/g) levels was obtained by two-stage carbonization using 15%wt $ZnCl_2$ at a temperature and reaction time of 800°C and 180 minutes, respectively.

Keywords: charchoal, agricultural wastes, chemical activator, pyrolysis, NWFP

Introduction

Indonesia is one of the main producers of palm oil in the world. Furthermore, palm oils and palm kernels are processed into crude palm oil (CPO) and palm kernel oil (PKO) with yields of about 20~24% and 4%, respectively (Poku 2002). Meanwhile, solid wastes from the production of CPO and PKO amount to 74%, in the form of empty fruit bunches, palm fruit fiber, palm kernel shells, and palm kernel waste, comprising 20.5%, 27.3%, 10.2%, and 15.5%, respectively (Saono and Sastrapradja 1983). Thus, each hectare of oil *palm* plantation produces about 16 tons of dry matter/year biomass (Foo-Yuen *et al.* 2011).

Solid waste from oil palm plantations has been used as liquid smoke for carbonization processes. Carbonization is carried out between 300~400°C to eliminate polyaromatic hydrocarbons in liquid smoke products (Stolyhwo *et al.* 2005). According to Hattula *et al.* (2001), polyaromatic hydrocarbons, including benzo[α]pyrene, are carcinogenic compounds. The carbonization process gives rise to a char-like residual solid material reported to contain high levels of volatiles, leading to the limited specific internal surface area, as well as low porosity formation, limiting further utilization of the charcoal-like material (Guo and Luo 2000; Pastor-Villegas *et al*. 1993). Currently, several studies have reported the use of oil palm shell material to produce activated carbon with different methods (Lua and Guo 2001; Hesas *et al*. 2010; Herawan *et al*. 2013). This study, therefore, aims to utilize this material in activated carbon production.

Activated carbon/charcoal is a high-porosity carbon material with an enormous specific internal surface area, and consequently, the ability to absorb various gases and volatiles from gas mixtures and separate or disperse materials from a solution (Roy 2002). Generally, activated carbon is manufactured in two stages, carbonization and activation. The activation process is carried out using chemical activators oxidizing charcoal at high temperatures to obtain a final product with an accessible internal pore structure, and consequently, a high adsorption capacity. Zinc chloride ($ZnCl_2$) is a chemical activator commonly used for carbonaceous materials. The physical activation process generally uses $ZnCl_2$ in low concentrations, as reported to Hussein *et al*. (1996), where a 25% concentration was used for oil palm shells. Meanwhile, the chemical activation process using $ZnCl_2$ at a higher concentration was reported by Ahmadpour and Do (1997) with up to 500% concentrations in macadamia seed shells. In this study, however, the manufacture of activated charcoal from charcoal produced by carbonization at 300°C, used a chemical activation method with a low concentration of $ZnCl_2$. This study also examined the effect of the carbonization method and activation process conditions, including temperature and reaction time, on the activated charcoal's physical as well as chemical properties, including the ash content, volatile matter content, fixed carbon content, and the benzene, iodine, as well as methylene blue adsorption capacities.

Materials and Methods

Materials and Instruments

The materials used were oil palm shells (OPS) collected from oil palm plantations in Palembang - South Sumatra, and $ZnCl_2$ for carbon activation and analysis of the activated carbon. Meanwhile, the equipment used in this study include an electric retort, 60 mesh sieve, digital analytical balance, muffle furnace, oven, UV-VIS spectrophotometer, and a MMS-300 multi-shaker.

Manufacture of Charcoal from Oil Palm Shells

Oil palm shells (OPS) with an average moisture content of 11.25% were carbonized using an electric retort. The retort was connected by a stainless exhaust pipe and an upright glass cooler, while carbonization was carried out at 300°C for approximately 3 hours. Subsequently, the process was terminated by turning off the retort and cooling overnight. A portion of the OPS charcoals was heated at 600°C for 1 hour after the carbonization process. The OPS charcoals were then ground into flour and sieved to obtain a particle size below 60 mesh.

Manufacture of Activated Carbon from Oil Palm Shell Charcoal

The mixing ratio of OPS charcoal to $ZnCl_2$ was 10 and 15 g of $ZnCl_2$ for each 50 g of dry charcoal. Subsequently, the required quantity of $ZnCl_2$ was then dissolved in 100 mL of distilled water to form a solution with a 10% and 15% concentration. The OPS charcoal was then immersed for 24 hours in a solution containing the activating ingredients. This process was assisted by stirring with an electric stirrer for 20 minutes at the initial stage of immersion. This was followed by washing the material with 100 mL of distilled water and repeating 5~8 times until a pH of 6~7 is reached. The mixture was then filtered with a filter paper to separate the solvent and solid charcoal. Subsequently, the charcoal was air-dried, then oven-dried at 115°C± 5°C, for 3 hours. The OPS charcoal was then placed in a tightly closed porcelain dish and then heated in a muffle furnace at variations of 600°C, 700°C, and 800°C, as well as reaction times of 60, 120, and 180 minutes. This was followed by cooling the furnace for 24 hours.

Activated Carbon Test

The activated carbon analyses were performed based on American Standard for Testing Materials (ASTM) to determine the ash content (ASTM D 2866-94), volatile matter content (ASTM D1762-84), fixed carbon content, and moisture content (ASTM D 2867-04). Meanwhile, the benzene, iodine, and methylene blue adsorption capacities were analyzed based on the SNI 06-3730-1995 standard. In addition, the yield and burn-off fraction of the activation process were also determined.

Data Analysis

This study used a completely randomized design arranged in a factorial manner, comprising four factors: carbonization stage, $ZnCl_2$ concentration, activation temperature, and activation time. Based on this study design, for the 1-stage carbonization, carried out in 3 replications, the treatment combination was 2 x 3 x 3 x 3, giving 54 samples. Meanwhile, for the 2-stage carbonization carried out in 2 replications, the treatment combination was 2 x 3 x 3 x 2, giving 36 samples. Thus, a total of 90 test samples were obtained. In this study, the treatment test parameters were yield, burn-off fraction, moisture content, volatile matter content, ash content, fixed carbon content, as well as adsorption of benzene, iodine, and methylene blue. Furthermore, the factor effect was analyzed by analysis of variance (ANOVA). A four-way analysis of variance with interaction was performed for each of the studied parameters, by using the following linear mixed effects model (Steel and Torrie 1995):

$$Y_{ijkl} = \mu + \rho_i + \alpha_j + \beta_k + \gamma_l + (\rho\alpha)_{ij} + (\rho\beta)_{ik} + (\rho\gamma)_{il} + +(\alpha\beta)_{jk} + (\alpha\gamma)_{jl} + (\beta\gamma)_{kl} + (\rho\alpha\beta)_{ijk} + (\alpha\beta\gamma)_{jkl} + (\rho\alpha\gamma)_{jkl} + (\rho\alpha\beta\gamma)_{ijkl} + \varepsilon_{ijkl}$$

where: Y = parameter mean; μ = mean, ρ_i= carbonization stage effect; α_j= $ZnCl_2$ concentration effect; β_k= temperature effect; γ_i= reaction time effect; $(\alpha\beta)_{jk}$= interaction effect between $ZnCl_2$ concentration and temperature; $(\beta\gamma)_{kl}$= interaction effect between temperature and reaction time; $(\alpha\beta\gamma)_{jkl}$= interaction effect among $ZnCl_2$ concentration, temperature and reaction time; ε_{ijkl}= random error. Subsequently, Tukey's test was performed for results with statistically significant differences. All calculations were conducted by SPSS version 10 under Windows.

Results and Discussion

Tables 1 and 2 show the average yield and properties of OPS activated carbon prepared using 1-stage and 2-stage carbonization. The summary of analysis of variance was presented in Table 3.

Table 1. Average of yield and properties of oil palm shell activated carbon by 1-stage carbonizations

Parameters		ZnCl$_2$ of 10%			ZnCl$_2$ of 15%		
		600°C	700°C	800°C	600°C	700°C	800°C
Yield (%)	60 min	85.29	82.14	73.62	73.36	82.42	89.40
	120 min	74.22	76.53	75.44	84.40	85.71	74.61
	180 min	86.51	83.58	74.77	81.17	75.16	71.93
	Average	82.01	80.75	81.62	79.64	81.09	78.65
Burnt-off fraction (%)	60 min	14.71	17.86	26.38	26.64	17.58	10.60
	120 min	25.78	23.47	24.56	15.60	14.29	25.39
	180 min	13.49	16.42	25.23	18.83	25.39	28.07
	Average	17.99	19.25	25.39	20.36	18.91	21.35
Moisture content (%)	60 min	2.13	3.64	1.89	1.61	1.17	2.64
	120 min	3.19	3.99	3.80	2.71	4.12	3.80
	180 min	3.57	3.80	3.38	2.94	2.77	3.27
	Average	2.97	4.00	3.03	2.43	2.69	3.24
Volatile content (%)	60 min	15.29	11.20	15.96	15.87	11.66	7.46
	120 min	13.32	4.98	1.59	14.19	5.44	5.01
	180 min	5.73	8.49	3.19	10.49	5.85	3.29
	Average	11.45	8.22	6.91	13.52	7.65	5.26
Ash content (%)	60 min	9.81	9.36	6.36	6.78	11.73	6.82
	120 min	12.45	8.07	7.79	13.13	9.12	4.56
	180 min	6.06	7.79	5.77	9.04	14.02	17.22
	Average	9.44	9.80	6.64	9.65	11.62	9.53
FCC (%)	60 min	72.77	75.78	75.79	75.73	75.43	83.08
	120 min	71.03	82.95	86.82	69.96	81.32	86.62
	180 min	80.71	75.18	87.65	74.78	77.35	76.21
	Average	74.84	77.97	83.42	73.49	78.03	81.97
AOB (%)	60 min	16.39	12.65	13.85	19.03	14.29	15.83
	120 min	13.06	13.97	14.13	17.43	12.13	13.90
	180 min	15.59	34.99	13.30	13.32	13.53	10.99
	Average	15.01	20.53	13.76	16.60	13.32	13.57
AOMB	60 min	122.67	122.05	122.25	122.39	122.97	120.12
	120 min	122.59	122.85	122.67	121.74	121.65	120.82
	180 min	122.82	122.67	123.31	121.48	121.79	122.89
	Average	122.69	122.13	122.74	121.87	122.14	121.28
AOI (mg/g)	60 min	434.70	277.14	332.05	445.92	388.91	366.23
	120 min	410.71	556.33	412.05	354.33	342.94	421.23
	180 min	546.91	342.65	276.92	410.95	422.23	510.69
	Average	464.11	392.04	340.42	403.73	384.69	432.75

Remarks: FCC = fixed carbon content; AOB = adsorption of benzene; AOMB = adsorption of methylene blue; AOI = adsorption of iodine

Table 2. Average of yield and properties of oil palm shell activated carbon by 2-stage carbonizations

Parameters		ZnCl$_2$ of 10%			ZnCl$_2$ of 15%		
		600°C	700°C	800°C	600°C	700°C	800°C
Yield (%)	60 min	72.39	78.56	71.71	72.05	77.53	72.16
	120 min	79.49	82.89	70.37	81.10	79.80	74.13
	180 min	79.26	70.37	70.13	79.98	73.41	67.42
	Average	77.05	79.52	70.74	77.71	76.92	71.23
Burnt-off fraction (%)	60 min	27.61	21.44	28.29	27.95	22.47	27.84
	120 min	20.51	17.11	29.63	18.90	20.20	25.87
	180 min	20.74	22.90	29.87	20.02	26.59	32.58
	Average	22.95	20.48	29.26	22.29	23.08	28.77
Volatile content (%)	60 min	3.42	5.90	1.60	4.70	9.07	2.97
	120 min	8.83	6.97	3.00	9.25	3.05	3.80

	180 min	5.05	5.62	5.00	13.52	4.37	3.32
	Average	5.77	6.16	3.20	9.16	5.50	3.36
FCC (%)	60 min	80.30	79.08	81.96	79.09	74.99	80.82
	120 min	77.62	74.64	80.73	76.38	78.08	76.11
	180 min	78.49	77.08	78.24	72.03	80.18	81.58
	Average	78.81	76.93	80.31	75.83	77.75	79.51
Ash content (%)	60 min	16.27	15.02	15.43	16.22	15.94	16.21
	120 min	13.35	18.39	16.90	14.37	18.87	17.78
	180 min	16.47	17.30	16.49	14.45	15.44	14.99
	Average	15.43	16.90	16.49	15.01	16.75	17.13
AOB (%)	60 min	12.64	14.37	13.89	16.75	12.98	17.70
	120 min	14.37	13.50	15.44	12.89	15.09	13.25
	180 min	12.50	15.44	14.61	15.14	13.74	14.39
	Average	13.17	13.61	14.65	14.93	13.94	15.11
AOMB (ml/g)	60 min	118.94	116.24	118.44	118.83	131.03	136.96
	120 min	115.53	117.18	134.35	131.23	116.79	131.17
	180 min	117.07	117.85	132.79	132.22	132.47	133.67
	Average	117.18	117.09	128.53	127.43	126.76	133.93
AOI (mg/g)	60 min	605.72	638.44	671.17	605.72	572.99	540.27
	120 min	556.63	605.72	671.17	556.63	572.99	572.99
	180 min	589.36	638.44	752.98	523.91	687.53	769.34
	Average	583.90	627.53	698.44	562.09	611.17	627.53

Remarks: FCC = fixed carbon content; AOB = adsorption of benzene; AOMB = adsorption of methylene blue; AOI = adsorption of iodine

Table 3. Summary of analysis of variance of properties of oil palm shell activated carbon

	Parameters							
Source of variation	Yield	Burn-of fraction	VC	FCC	AC	AOB	AOMB	AOI
Carbonization stage (A)	**	**	**	ns	**	*	**	**
$ZnCl_2$ concentration (B)	ns	ns	ns	ns	**	ns	**	ns
Temperature (C)	**	**	**	**	**	ns	**	ns
Reaction time (D)	ns	ns	**	ns	*	ns	**	ns
A × B	ns	ns	ns	ns	**	*	**	ns
A × C	ns	ns	*	**	**	*	**	*
A × D	**	**	**	**	**	ns	**	ns
B × C	ns	ns	*	ns	*	**	**	ns
B × D	**	**	ns	ns	ns	**	**	ns
C × D	**	**	**	*	**	**	**	ns
A × B × C	ns	ns	ns	ns	ns	*	**	ns
A × B × D	*	*	*	**	**	**	**	ns
A × C × D	ns	ns	*	**	**	**	**	ns
B × C × D	**	**	**	*	**	*	**	ns
A × B × C × D	**	**	ns	*	**	*	**	ns

Remark: VC = volatile content, FCC = fixed carbon content, AOB = adsorption of benzene; AOMB = adsorption of methylene blue; AOI = adsorption of iodine; ns = not significant; ** = significant at the 1% level; * = significant at the 5% level.

Yield and Burn-off Fraction

The average yield of OPS activated carbon produced in this study using the 1- and 2- stage carbonization methods were 79.46% and 75.53%, respectively. This chemical activation process produced a higher yield compared to the report by Srinivasakannan and Abu Bakar (2004), where a yield of 33~63% was obtained using H_3PO_4 at a 60% concentration. Furthermore, this experiment produced a higher yield compared to the physical activation process with N_2 gas carried out by Ahmadpour and Do (1997), where a value between 42.6~48.1% was obtained using the ratio weight of $ZnCl_2$ at a 100% concentration, or the study by Mozammel *et al*., (2002), where a value between 43~53% was obtained, using $ZnCl_2$ at a 110% concentration, in physical activation with hot steam and CO_2.

The burn-off fraction in the 1- and 2- stage carbonization treatments were about 20.54% and 24.47%, respectively. This value was lower, compared to the report by Ahmadpour and Do (1997), where a value between 54.2~57.4% were obtained using a weight ratio of $ZnCl_2$ at a 100% concentration, in the physical activation process with N_2 gas. Meanwhile, a wide variation of burn-off fraction, ranging between 35.2~77.4%, was reported by Wan Daud *et al.* (2002) using N_2 gas in OPS charcoal activation, at temperatures between 800 and 900°C. The high yield and low intensity of the burning fraction of OPS activated carbon is possibly due to the high content of volatile substances in the carbon's pore structure, allowing a reaction between $ZnCl_2$ and the deposits of volatile substances, including tar and hydrocarbon compounds formed during the activation or carbonization process (El-Shobaky and Youssef 1978). The high level of volatile substances in OPS activated carbon certainly indicates the devolatilization process performed to open the pores from closing by carbonization products and form new pores, had not been effectively achieved.

Moisture Content

OPS carbon produced by 1- and 2-stage carbonizations had an average moisture content of 0.94% and 1.82%, respectively. During activation, water in the charcoal is removed at temperatures of up to 170°C (Cheremisinoff and Moressi 1978). Based on the analysis of variance, the activation time and concentration of $ZnCl_2$ had a significant effect on the water content of OPS activated carbon. However, after Tukey's test, the moisture contents were discovered to differ insignificantly. This might be caused by error control on the data or unbalanced replications. Consequently, the moisture content of OPS activated carbon in this study was only observed in 1-stage carbonization. However, to avoid the adverse effects of moisture in the research material, drying was carried out in an oven at 150 ± 5°C for 3 hours before analyzing the activated carbon's physico-chemical properties.

Volatile Matter Content

The volatile matter content in OPS activated carbon manufactured by activation process using $ZnCl_2$ was higher for the 1-stage carbonization (8.83%), compared to the 2-stage carbonization treatment (5.52%). Generally, the volatile matter content of OPS activated carbon ranges between 1.60 and 15.87%. The volatile matter content obtained in this study was higher, compared to the report by Guo and Lua (2000), where a value ranging from 0.1 to 0.5% was obtained for oil palm kernels charcoal activated using nitrogen gas flow. According to the analysis of variance, the interaction of $ZnCl_2$ concentration, temperature, and activation time factors, influenced the volatile matter content. The combination of 10% $ZnCl_2$ concentration treatment, 800°C temperature, and 120 minute-activation time, produced the lowest volatile content (2.3%). Similarly, variations in temperature between 700 and 800°C, combined with an activation time of 120 and 180 minutes with either 10 or 15% $ZnCl_2$ concentration, produced low volatile levels. This is because the devolatilization process increases with increasing temperature and activation time, starting from low to high molecular weight materials (Vitidsant *et al*. 1999; Guo and Lua 2000; Mozammel *et al*. 2002).

Ash Content

Ash is a residual mineral material from combustion, usually expressed as the ash content of a substance. The results indicated OPS activated carbon manufactured by 1-stage carbonization had lower ash content, ranging from 6.06 to 17.22% with an average of 9.45%, compared to the 2-stage treatment counterpart, ranging from 15.02 to 20.09%, with an average of 16.29%. Guo and Lua (2000) reported the ash content of activated carbon from oil palm seeds ranged from 9.1~19.5% and was affected by the activation temperature. This means a higher activation temperature produces higher ash content in the activated carbon. Similarly, Vitidsant *et al*. (1999) and Shimada *et al*. (2004) reported the ash content of activated charcoal increases with increased activation time. These findings indicate the interaction of carbonization treatment, $ZnCl_2$ concentration, temperature, and activation time factors, has a highly significant effect on the ash content.

Generally, 2-stage carbonization treatment for each variation of $ZnCl_2$ concentration, temperature, and activation time, produced higher ash content, compared to the 1-stage carbonization counterpart. Carbon produced by 2-stage carbonization underwent a longer carbonization process to generate the high ash content. This is because longer heat treatment caused more carbon on the burning charcoal's surface to become ash during the activation process. In this study, OPS activated carbons manufactured using 15% $ZnCl_2$ concentration, a temperature of 800°C, and a 180 minute-activation time produced the highest ash content (16.15%), and this value differed significantly from the counterparts manufactured under lower temperature and shorter activation time. Guo and Lua (2000) discovered higher activation temperature is bound to increase the conversion of carbon into gaseous products, resulting in higher ash content of the final activated carbon products. In addition, Vitidsant *et al*. (1999) and Shimada *et al*. (2004) demonstrated an increase in activation time leads to an increase in the ash content of activated carbon.

Fixed Carbon Content

The interaction of carbonization treatment, $ZnCl_2$ concentration, temperature, and activation time factors, showed an increase in the fixed carbon content, as the activation temperature increased from 600 to 800°C. As the activation temperature increases, the volatiles in carbon's pore structure is removed, starting from low to high molecular weight materials (Goa and Lua, 2000; Vitidsant *et al*. 1999). This removal of volatiles causes a rise in the carbon content per unit dry weight. In this study, carbonization treatment, $ZnCl_2$ concentration, and activation temperature factors showed a different pattern of fixed carbon content with the activation time factor. Increased activation time also provides an opportunity for heat to penetrate the carbon's inner section, thus, releasing more volatiles. This devolatilization process increases the carbon content in the charcoal per unit weight. The 1-stage carbonization showed a tendency to increase the fixed carbon content from an activation time of 60 to 180 minutes, while the 2-stage carbonization treatment exhibited an opposite trend. This is probably due to the burning of carbon on the surface to form gas products, and consequently, produce more ash in the charcoal (Guo and Lua 2000).

Adsorption of Benzene

Benzene adsorption number is the easiest parameter to estimate an activated carbon's suitability as an adsorbent for the gas phase adsorption process. The pore structure plays an important role in the gas phase adsorption process due to the micropores (Rodriguez-Reinoso and Linares-Solano 1989). Based on the results, activated carbon from the 1-stage carbonization had a higher adsorption capacity with an average of 15.47%, compared to the 2-stage counterpart, with an average of 14.23%. It also indicates that the surface of activated carbon generated from the 2-stage carbonization contained more polar nature of non-carbon molecules to reduce the adsorption level (Pari and Sailah 2000). This is possible because the 2-stage carbonization was unable to effectively increase the micropore surface area and total pore volume, as the specific surface area increases. This 2-stage carbonization treatment merely increases the mesoporous surface area and total mesoporous volume. The additional carbonization treatment only widened the existing pores by burning the carbon on the surface, without creating a new surface. This finding showed the interaction of the four factors affects the adsorption of benzene. From the interaction between $ZnCl_2$ concentration, temperature, and activation time factors, the combination of 10% $ZnCl_2$ concentration, 700°C activation temperature, and a 180-minute activation time, produced the highest benzene adsorption capability (24.19%). The 15% $ZnCl_2$ concentration only required a lower temperature and shorter activation time of 600°C and 60 minutes, respectively, to obtain sufficient micropore surface area and micropore volume, to provide more adsorption.

Adsorption of Iodine

Determining the iodine number is a simple way to predict the specific surface area of activated carbon methods (Jankowska *et al.* 1991). It is a measure of the micropore (0~20 Å) content of the activated carbon by adsorption of iodine from solution. The specific range is 500~1200 mg/g, which is equivalent to surface area of carbon between 900 and 1100 m^2/g (Saka 2012). The 1-stage carbonization treatment produced activated carbon with iodine adsorption capability of 402.96 mg/g, while the 2-stage counterpart was 618.44 mg/g. These values are lower compared to the experiment by Srinivasakannan *et al*. (2004), where the iodine number of carbon activated with phosphoric acid from rubberwood powder was between 693 and 1,096 mg/g, depending on the temperature and activation time. However, the values were higher than the report by Vitidsant *et al*. (1999) on physically activated OPS carbon using nitrogen gas (338.08~543.64 mg/g) iodine adsorption capacity depends on the temperature and activation reaction time. Several factors responsible for this low iodine adsorption include high volatile matter content in activated carbon and inadequate burn-off fraction from the activation process. Consequently, the formation of new surfaces and pores was less effective. The results indicate iodine adsorption of iodine is only influenced by the carbonization treatment factor.

The 2-stage carbonization showed higher iodine adsorption, compared to the 1-stage treatment. This 2-stage carbonization had lower volatile matter content in the activated carbon (5.52%), compared to the 1-stage counterpart (8.83%). According to Bansal *et al.* (1988), the volatile matter concentration is related to the activated carbon's specific internal surface area. High-temperature treatment for a long time increases the loss of volatile matter from the pore cavity and charcoal surface, consequently, increasing the specific internal surface area. This rise in the specific internal surface area is bound to increase iodine adsorption. Similarly, Mozammel *et al*. (2002) reported increased temperature and activation time led to an increase in iodine adsorption, in a fourth-order polynomial trend.

Adsorption of Methylene Blue

The methylene blue adsorption capacity is an indicator of the activated carbon's adsorption towards molecules with similar dimensions as methylene blue. This value also indicates the specific surface area of carbon with a pore dimension above 1.5 nm (Jankowska *et al*. 1991). The 1-stage carbonization produced a methylene blue adsorption value of 122.14 mL/g, while the 2-stage counterpart was 125.15 mL/g. These values are lesser, compared to the experiment by Vitidsant *et al*. (1999), where values between 146.76 and 176.06 mL/g were measured for OPS carbon activated using nitrogen gas, as well as the report by Xia *et al*. (1998), where values between 100~171 mL/g were obtained for activated carbon manufactured from bagasse. Several factors responsible for the low methylene blue adsorption include high volatile matter content in activated carbon and inadequate burn-off fraction from the activation process. These lead to limited formation of new surfaces and pores in an activation process. The interaction of the temperature and activation time factors showed increased temperature and activation time affected increasing the methylene blue adsorption. In addition, the devolatilization process increases with increasing temperature and activation time, starting from low to high molecular weight materials (Guo and Lua 2000; Vitidsant *et al*. 1999;

Mozammel *et al*. 2002; Lua and Guo 1998). The interaction of the $ZnCl_2$ concentration and activation time factors showed the use of 15% concentration and higher activation temperature led to higher methylene blue adsorption. Meanwhile, the interaction between the $ZnCl_2$ concentration and activation temperature factors indicated a rise in the $ZnCl_2$ concentration and activation temperature leads to an increase in methylene blue adsorption.

Quality of Oil Palm Shells Activated Carbon

Table 4 shows a comparison of the quality of OPS activated carbon manufactured through 1- and 2- stage carbonization treatments, with a combination of several $ZnCl_2$ concentrations, temperature, and activation time, against the specific requirements for technical activated carbon according to SNI 06-3730-1995. Based on this comparison, OPS activated carbon manufactured using both treatments does not meet the requirements for iodine adsorption. However, the 2-stage carbonization treatment at an activation temperature and reaction time of 800°C and 180 minutes, respectively, produced activated carbon with iodine adsorption of 752.98 – 769.34 mg/g (Table 2), and this is up to the SNI standard.

Table 4. Comparison of Properties of Oil Palm Shells Activated Carbon with regard to Specific Requirements of Activated Carbon according to SNI 06-3730-1995.

No	Parameters	Unit	Requirement	1	2
1.	Loss parts after heating at 950 °C	%	max. 25	8.83	5.52
2.	Moisture content	%	max. 15	3.07	n.d
3.	Fixed carbon content	%	min. 65	78.29	78.19
4.	Ash content	%	max. 10	9.45	16.29
5.	Adsorption of benzene	%	min. 25 (granular)	15.47	14.23
6	Adsorption of methylene blue	mL/g	min 120	122.14	125.15
7.	Adsorption of iodine	mg/g	min. 750	402.96	618.44

Remarks: 1. Oil palm shells activated carbon with 1-stage carbonization
2. Oil palm shells activated carbon with 2-stage carbonization
The values presented are average for various treatments for each carbonization stage (temperature 600, 700, 800°C; reaction time 60, 120, 180 min; concentration $ZnCl_2$ of 10 and 15%).

Conclusions

OPS activated carbon manufactured using the 2-stage carbonization treatment had higher burn-off fraction, ash content, as well as iodine and methylene blue adsorption but had lower yield, volatile matter content, and benzene adsorption, compared to the 1-stage treatment counterpart. The increase in $ZnCl_2$ concentration from 10% to 15% produced OPS activated carbon with higher ash content and methylene blue adsorption capacity. Furthermore, increased activation temperature generated higher burn-off fraction, fixed carbon content, and methylene adsorption, but led to reduced yield and volatile matter content. The comparatively high ash content and methylene blue adsorption, as well as the low volatile matter content, were obtained by prolonging the activation time. Also, the combination of 2-stage carbonization treatment, 15% $ZnCl_2$ concentration, 800°C activation temperature, and 180-minute activation time produced activated charcoal with optimum yield (67.42%), burn-off fraction (32.58%), volatile matter content (3.32%), ash content (15.09%), fixed carbon content (81.58%), and adsorption of benzene (14.39%), iodine (769.34 mg/g), as well as methylene blue (133.67 mL/g). The OPS activated carbon manufactured using low $ZnCl_2$ concentration at various temperatures and activation times met the quality requirements of SNI 06-3730-1995 for volatile matter content, moisture content, fixed carbon content, and methylene blue adsorption.

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Example of Table and Figure

Table 1. Effects of temperature on *in vitro* growth of seedlings.

Temp. (°C)	Shoot length (mm)	Number of leaf	Fresh weight (g)
25	59.2 ± 10.6^{c}	4.5 ± 0.8^{a}	0.29 ± 0.13^{a}
27	88.5 ± 9.3^{a}	4.8 ± 0.9^{a}	0.40 ± 0.12^{a}
29	75.0 ± 11.1^{b}	3.8 ± 0.6^{a}	0.30 ± 0.07^{a}

Note: Values (average ± standard deviation) with different letters are statistically significant according to Tukey's multiple comparison test. Data were recorded after 4 weeks of culture. MS medium was used as a basal medium without any PGRs. Number of sample = 10.

Source: Chujo *et al* 2010.

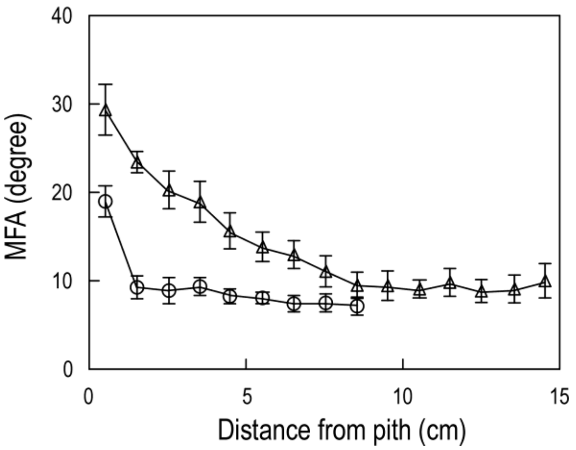

Figure 3. Radial variation of microfibril angle of the S2 layer in tracheid. Open circle, *Agathis* sp.; open triangle, *Pinus insularis*; Bars indicate the standard deviation. (Source: Ishiguri *et al* 2010)

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