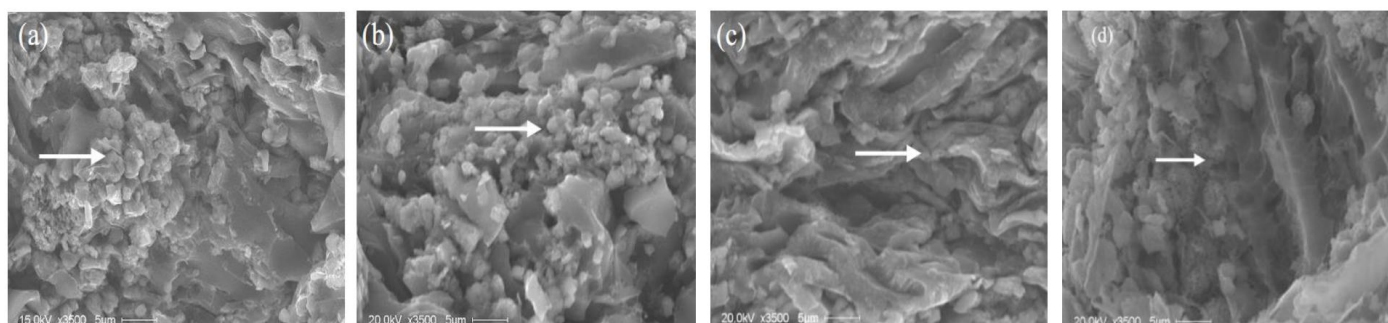


WOOD RESEARCH Journal

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A Review: Effect of Heartwood Proportion in Wood Properties

Rizki Arisandi

Abstract

This study aims to examine the effect of heartwood proportion on wood properties for construction materials by reviewing 98 journal articles and non-articles. The data were collected through an online search using seven keywords: heartwood proportion, heartwood effect, physical properties, mechanical properties, wood dimensional stability, wood gluing, and wood preservation. By eliminating the irrelevant papers, 45 journal articles and non-articles were selected. The review shows that the proportion of heartwood has a positive correlation with wood density and dimensional stability. High wood density will have a positive correlation with the mechanical properties of wood. However, the dimensional stability is not only affected by the proportion of the heartwood but also the microfibril angle and the arrangement of the wood cells. Further, sapwood has a higher moisture content than heartwood. The high moisture content causes the wood drying process to take longer and require more energy. However, it should be noted that the heartwood in some *Acacia* species has a higher moisture content than that in the sapwood, which is commonly called wet heartwood. Therefore, a suitable treatment is needed to minimize the moisture content in the heartwood. In addition, heartwood is difficult to preserve because of the high extractive content in the lumen. The color of the wood is another important indicator to determine the quality of wood, especially the heartwood color, because it is related to the aesthetic value and durability of the wood. Meanwhile, a better understanding of the acid and alkaline properties of extractive substances is necessary to perfectly conduct the wood gluing process.

Keywords: Heartwood proportion, heartwood effect, wood density, mechanical properties, dimensional stability

Introduction

Heartwood is located in the inner layers of the wood and is physiologically inactive in the growing tree; these inner layers are not involved in the physiological process or no longer contain living cells (IAWA committee 1964). The reserve material, such as starch, is removed or converted into heartwood (IAWA committee 1964). Heartwood could optimize the sapwood volume and provide structural support (Taylor *et al.* 2002). Heartwood is one of the most important parameters, including in wood economic values, because it could affect the final use of wood. Heartwood is necessary to the final wood product, especially for wood construction, because it provides natural durability and an excellent color that is associated with heartwood extractives. In contrast, sapwood parts are more susceptible to wood-destroying organisms and have a pale color. The sapwood most often has a light color and low biological resistance while the heartwood has a higher resistance to decay and is darker than sapwood (Moya and Berrocal 2010; Thulasidas *et al.* 2006). Some species form colored heartwood because the xylem parenchyma cells synthesize heartwood substances, such as polyphenol groups, which contribute to wood's color and natural durability before its death (Bamber and Fukazawa, 1985; Hillis 1987; Magel 2000; Taylor *et al.* 2002).

Heartwood proportion has a negative impact on the quality of pulp and paper; such a condition is caused by the high extractives of the heartwood and by pitch problems

(Jansson and Nilvebrant 2009; Lehr *et al.* 2021). However, if the wood is used for construction materials, the large heartwood is highly necessary because it will positively affect the basic properties of the wood, such as physical properties (basic density, moisture content, and wood color), mechanical properties (modulus of elasticity, modulus of rupture, and compression strength from the parallel to the grain), dimensional stability (shrinkage and swelling), wood finishing, and natural durability (Armstrong *et al.* 1984; Rust 1999; Singleton *et al.* 2003; Grabner *et al.* 2005; Ekeberg *et al.* 2006; Pratt *et al.* 2007; Ayobi *et al.*, 2011; Uetimane Jr and Ali 2011). Several previous studies have reviewed the effect of extractives on pulp, paper, and natural durability (Taylor *et al.* 2002; Jansson and Nilvebrant 2009; Lehr *et al.* 2021). However, to date, only a few studies have reviewed the effect of heartwood on its basic properties of the wood. Therefore, this study will review the effects of heartwood on the wood's basic properties.

This study aims to conduct a literature review of the heartwood's effects on the basic properties of wood. This study identified articles and non-articles were through online searches from different search engines. The keywords for searching journals and non-journal articles are "heartwood proportion," "basic density," "wood color," "mechanical properties," "dimensional stability," "wood drying," and "wood finishing." This study collected 98 journal articles and non-journal articles. However, after eliminating some duplicating and irrelevant manuscripts, 45 were combined for this study (Figure 1).

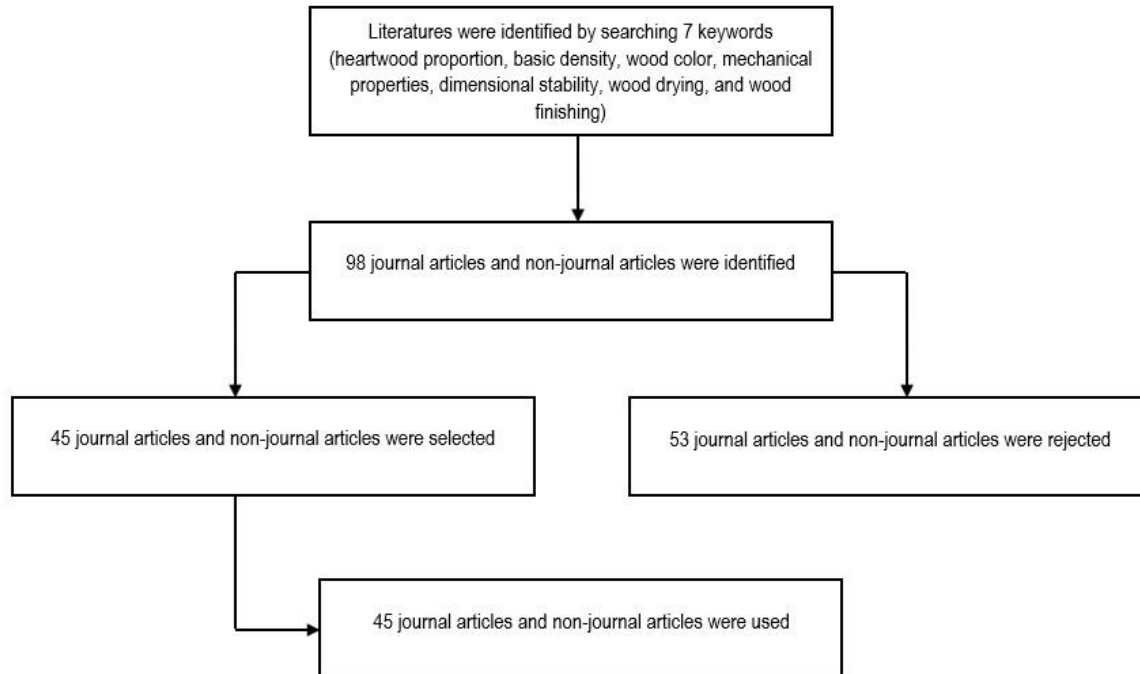


Figure 1. Review processes for this study.

Heartwood and Natural Durability

Heartwood is known to contain a lot of extractives, including phenolic extractives, which provide an attractive appearance to the color of the wood and show natural durability that acts as a potential bio-protectant against various pathogens (Kampe and Magel 2013). Natural durability is intended to wood-decay fungus attack due to extractive antifungal. Martinez-Sotres et al. (2012) report that hexane extract of *Dalbergia congestiflora* wood with medicarpine as the predominant antifungal compound causes inhibition of fungal growth up to 100%. However, wood biodeterioration is caused not only by fungi but also by insects, such as termites, beetles, and marine borers (Kampe and Magel 2013). Tsuruta et al. (2011) report that *Pinus thunbergii* heartwood is rich in alpha-terpineol and longifoline, which are components that inhibit the growth of red tide plankton. Therefore, it is proposed as a useful construction material.

Recent publications emphasize extractives of heartwood or heartwood that exhibit fungitoxic and termiticide activities (Kampe and Magel 2013). This is important because termites cause large economic losses to wood, especially in the tropics region. Dungani et al. (2012) report that quinones appear to be the dominant toxic component for termites in the extracts of the *Tectona grandis* heartwood. Acetone water from the oldest part of the heartwood shows a mortality rate of up to 100% in the termite of *Coptotermes curvignathus*. Rodrigues et al. (2011) report that rubrynolide from *Sextonia Rubra* wood is identified as the most effective protective agent against

termites. Because of its potential to inhibit the growth of tropical and invasive termites, rubrynolide is a potential substitute for synthetic termiticides.

Heartwood, Moisture Content, and Basic Density

One of the most important traits required for the utilization of wood is the moisture content of the logs. Growing trees contain an adequate amount of moisture for about 50% of their fresh weight (Larcher 1995). Most of the moisture must be removed to obtain satisfactory performance for the most frequently used wood. Wood with a higher moisture content dries slower than one with lower moisture content and is generally more susceptible to drying defects (Simpson 1991).

Heartwood is also known to have a lower moisture content than sapwood (Rust 1999). In most tree species, the moisture content of heartwood is different from that of sapwood. Taylor et al. (2002) state that hardwoods depend on species because it has lower moisture content than sapwood in conifers. In general, high wood density has lower moisture content due to the proportion of heartwood with low moisture content. It could be related to the density of the wood.

Heartwood proportion has the highest extractive concentration, which could contribute to basic density. Singleton et al. (2003) explain that extractives could affect basic density values in 19 young-growth western hemlock samples. Moreover, they deploy that the concentration of extractives is slightly higher and near the pith (1-5 rings) and has the highest basic density along the radial profile.

Furthermore, Imamura (1989) explains that wood extractives are mainly located in the lumen cell, which fills empty spaces in wood, reduces porosity, and increases density. Therefore, the presence of a high extractive content in wood is an advantage for materials of construction or furniture. Several authors have also mentioned that the basic density in heartwood is higher than that in sapwood in some species (Ayobi *et al.* 2011; Uetimane Jr and Ali 2011). Aguilera and Zamora (2009) express that the basic density value in the heartwood (0.71 g. cm⁻³) is higher than that in sapwood (0.60 g. cm⁻³). The difference between sapwood's densities and heartwood's densities is partly related to the amount of extractive embedded in the vessels of heartwood and parenchyma cells (Uetimane Jr *et al.* 2009). Thus, the resulted difference between the strength properties of sapwood and heartwood is most likely explained by density due to its widely known effect on several mechanical properties (Armstrong *et al.* 1984; Grabner *et al.* 2005). The same pattern is also found in the mechanical properties (MOR and compressive parallel to the grain) due to the effect of extractive in the heartwood (Ayobi *et al.* 2011). The significant amount of extractives is stored in heartwood twice or three times as much as that in sapwood (Panshin and de Zeeuw 1980).

Heartwood does not always have a lower moisture content than sapwood. Yamamoto *et al.* (2003) argue that the moisture content of *Acacia mangium* (*A. mangium*) and hybrid acacia wood in heartwood is 253% compared to 149% and 154% in sapwood, respectively. It is also mentioned that the moisture content of *A. mangium* from Malaysian heartwood is around 100–110%, and that in sapwood is 80–90% (Anon 1977). Heartwood with high moisture content is usually called wet wood to indicate an abnormal type of heartwood (Ward 1984). However, Yamamoto *et al.* (2003) claim that the heartwood of *Acacia* species is normal because heart rot and high concentrations of inorganic elements in the heartwood are not recognized.

The heartwood of *A. mangium* and *Acacia* hybrid particularly near the pith will be referred to as “wet heartwood” because it has higher moisture content than sapwood. Wet wood or “wet heartwood” causes problems during wood drying. Due to a large amount of water in the logs, especially in the heartwood of *Acacia* species, the drying times become longer (Ward 1984) and could cause problems for sawn timber production in the wood industry. Moisture content could be related to tree growth ecology. Fast-growing species, such as the *Acacia* species, may absorb excessive water from the soil; thus, they could have a negative effect on soil properties and cause high moisture content in the heartwood. Further studies should be carried out to identify suitable conditions to produce acacia wood with lower stem moisture content.

Heartwood and Dimensional Stability

The presence of extractives affects the drying process of wood. Several studies have investigated the effect of

chemical extractives on drying shrinkage of several species (Stamm and Loughborough 1942; Adamopoulos 2002; Hernandez 2006; Hernandez and Almeida 2007) and discovered that removal of wood extractives impacts shrinkage behavior. The dimensional changes of wood could be increased by removing the extractives (Choong and Achmadi 1991; Militz and Homan 1993; Mantanis *et al.* 1994; Adamopoulos 2002). In 1986, a study of 12 *Eucalyptus* species after chemical extraction (Chafe 1986) has revealed positive and negative correlations between extractive content and shrinkage, depending on the selected solvents. This condition indicates that all metabolites do not have the same effects. In addition, Ayobi *et al.* (2011) have revealed that the shrinkage and swelling of the heartwood in *Quercus castaneaefolia* are greater than that in the sapwood. The shrinkage variation is influenced not only by the sapwood-heartwood ratio but also by the microfibril angle, the presence of a gelatinous layer, moisture content of fluctuations from zero to fiber saturation point, wood rays, and different arrangement of the fibers in the cell walls.

Heartwood and Wood Color

Heartwood extractives contribute to the color that is related to the aesthetic values of the wood. The darker color is produced by the secondary metabolites, namely extractives of the heartwood, which give the heartwood natural durability and aesthetic characteristics. Thus, the quality and commercial values of wood are largely based on the extractive quality and quantity of the heartwood (Hillis 1987; Taylor *et al.* 2002; Ekeberg *et al.* 2006). Meanwhile, there is a large color difference between sapwood and heartwood; the selection of wood components based on color also plays an important role in some wood applications (Dzifa *et al.* 2004). Color is an important factor in determining certain uses, such as furniture and decorative coating that refer to pivotal marketing attributes (Mazet and Janin 1990). Wood color in the heartwood is also related to the natural durability of the wood which has been intensively studied (Gierlinger *et al.* 2004; Bhat *et al.* 2005; Kokutse *et al.* 2006; Lukmandaru and Takahashi 2008; Moya and Berrocal 2010). The relationship between color and decay resistance is not direct but is based on extractive effects in both parameters (Gierlinger *et al.* 2004). However, durability and natural coloration do not always correlate with the extractive concentration of the heartwood (Hillis 1987; Taylor *et al.* 2002).

Conclusions

Heartwood extractives play an important role in improving the quality of wood for construction because of their effect on the basic properties of wood. It is positively correlated with the basic density, where a high density will improve the mechanical properties of the wood. Meanwhile, low wood density is commonly found in sapwood with a

higher moisture content than in heartwood. The high moisture content causes the drying process to take a long time. Therefore, the energy required to dry the wood is greater. However, it should be noted that wet-heartwood in some species occurs such as in *Acacia* species. Fast-growing species like *Acacia* can absorb excess water from the soil. Thus, the heartwood can contain more water, which is called wet-heartwood, compared to the moisture content in the normal heartwood. Therefore, the selection of the good or suitable location is should be explored in further research. Extractive content in heartwood also has a negative correlation with the wood preservation process, because preservatives will be difficult to enter into the lumen cells that filled with extractives. Meanwhile, the process of gluing wood requires a good understanding of the acidity and wetness of the extractive substances on the adhesive used. In addition, the presence of heartwood extractives also contributes to stabilize the dimensions of the wood, considering that the shrinkage and swelling of the wood were smaller in heartwood than in sapwood. However, the wood dimensions are not only affected by extractive substances, but also was influenced by the microfibril angles and the arrangement of fibers in the cell wall. Therefore, evaluation of the wood quality for construction materials, is not only the ratio of heartwood and sapwood, but also the investigation of anatomical properties is should be conducted.

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Discolored Components from the Black-streaked Heartwood Extracts of Teak

Ganis Lukmandaru, Tatsuya Ashitani, and Koetsu Takahashi

Abstract

With regard to black-streaked discoloration of teak wood, the ethyl acetate extract from successive extraction was examined. By column chromatography, tectol and two unknown compounds i.e. C-1 (molecular weight of 240) and C-2 (molecular weight of 210) were isolated. Discoloration tests, i.e. air oxidation, acidic (acetic acid), and alkaline (potassium hydrogen carbonate) treatments were conducted to the isolated and other standard quinone compounds (tectoquinone, lapachol, 2-tert-butyl- anthraquinone, 2-hydroxy-methyl-anthraquinone). The results showed that tectol changes its color by the considerable decreasing in brightness whereas C-1 showed huge decrease in yellowness by air oxidation. Tectol did not change its color in pH value of 2.9 to 8.3 but C-1, C-2, and lapachol did change. Tectoquinone was hardly change color under alkaline or acidic treatment. The difference in quinone coloration might be due the structural features of a hydroxyl group and a double bond conjugated.

Keywords : darkening wood, air oxidation, extractives, quinones, tectol.

Introduction

Teak is an economically important tree species indigenous to Java. One of the values of teak wood particularly depends on its aesthetic properties. Coloured wood is in great demand for sawntimber, furniture, and handy craft products. Heartwood color of normal teak is dark brown, but abnormal color due to blackness is not desirable by the people. This discoloration is serious problem that decreases the value of teak products. This natural defect is called 'doreng' in Indonesia and is classified as a cross-sectional defect (BSN 1999).

Color and extractive content of black-streaked heartwood in teak have been investigated (Lukmandaru 2009; Lukmandaru *et al.* 2009). It is commonly known that the phenolic compounds of wood are closely related to the coloration (Takahashi 1996; Paques *et al.* 2013). Unfortunately, the phenols of teak related to the heartwood color are remained unknown. In order to investigate the cause of discoloration, it is expected to identify the extractives contributing to the discoloration and to understand their conversion mechanism. Technically, the causes of discoloration in the wood are various e.g. enzymatic reactions, iron staining, microorganisms, basic and acid conditions of wood etc. (Hon and Shiraishi 2001; Koch *et al.* 2003).

Previous study showed that ethyl acetate (EtOAc) fraction of teak extractives from successively extraction highly correlated with the darkness of heartwood (Lukmandaru *et al.* 2014). Furthermore, it was also found that the lower brightness values correlated with higher pH values. It is thought that some colored components (pigments) were extracted and further examination was conducted with previous methods (Burtin *et al.* 1998; Takahashi and Mori 2006). In this paper, the compounds were isolated and the significance of coloration was described.

Materials and Methods

Chromatography and Physical Property Determinations

Si-gel 20-40 mesh (Wako) and 63-210 mesh spherical neutral (Kanto chemical) were used for flash and column chromatography, respectively. Precoated aluminum sheets silica gel 60 F254 (Merck) were used for thin layer chromatography (TLC). Spots were visualized by UV light irradiation (λ 254 nm and λ 360 nm) and by spraying with vaniline-sulfuric acid (for color test) followed by heating at 110 °C for 10 minutes. Developing solvents used for TLC were hexane/acetone (1:5, v/v). Melting points were determined on a YANACO Micro Melting Point Apparatus.

Extraction and Isolation

Black streaked wood samples from a teak tree (35 years) were collected from Randublatung, Central Java Province. Samples from the tree disc (Fig. 2) were ground in a blender. Further, the ground samples (20-40 mesh, 200 g) were extracted by refluxing with n-hexane, EtOAc, and methanol, successively while heated for 6 hours each. The extracts were rotary-evaporated to yield 7.62 g (38.1 %), 6.70 g (33.5 %) and 5.63 g (28.1%), respectively. The EtOAc extract (4.28 g) were separated into low molecular weight and polymeric fractions by column chromatography. The extract was chromatographed on a silica gel column using n-hexane and acetone as eluents of increasing polarity. The scheme of separation is displayed in Fig. 1. Fractions 2 to 5 contain an unknown compound (C-1) and tectoquinone, respectively. From fraction 8 to 10 (combination), tectol was isolated, whereas from fraction 11 and 12 (combination), another unknown compound (C-2) was isolated from the combination of fraction 8~10.



Figure 1. Teak wood with black streak.

Spectrum Determinations

The ^{13}C (in 400 MHz), ^1H NMR (in 100 MHz) and COSY spectra were determined by a JEOL JNX-400 spectrometer. Chemical shifts are given as δ (ppm) values

with TMS as internal standard. Coupling constants (J) are given in [Hz]. The UV-VIS spectral data were determined with SHIMADZU UV-1600 PC in an acetone solution. The amount of 0.1 mg of tested sample was dissolved in 20 ml acetone (reagent grade). GC and GC-MS analysis were using a Hitachi G-3500 GC equipped with FID and NB-1 capillary 30-m column. Operation temperature was 120 - 300 °C with a heating rate of 4 °C/min and held at 300 °C for 15 minutes. Injector and detector temperatures were set at 250 °C. Helium was used as the carrier gas, the split ratio was 80:1, and the injected volume was 1.0 μL . Mass spectrometry measurements were obtained from GC-MS analysis on a Shimadzu QP-5000 with operation conditions similar to GC analysis. The MS operating parameters were temperature ionization voltage of 70 eV, transfer line temperature at 250 °C, and scan range of 50 – 500 atomic mass unit.

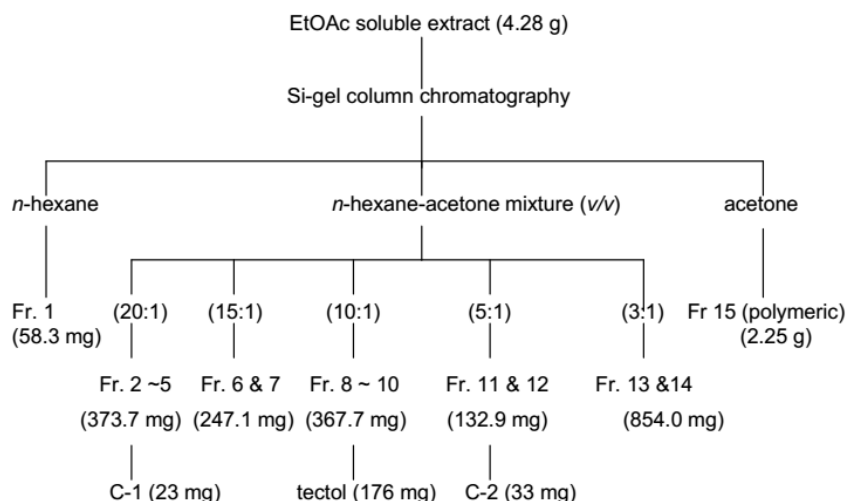


Figure 2. Scheme of compounds isolation from ethyl acetate soluble extract.

Properties of Tectol

Tectol (Fig. 4) was crystallized as a white powder from an n-hexane and acetone solution. Yield : 176 mg; Rf value (solvent n-hexane-acetone = 5 : 1) : 0.32; color reaction (vanillin-sulfuric acid reagent) : blue; mp: 214-216 °C. GC-MS m/z (rel. int.) 450 (98) (M^+), 435 (100), 211 (77), and 210 (54). UV-Vis spectrum λ max acetone : 364 nm. NMR (acetone d_1): δ ^{13}C 27.4 (C-15, C-15'), 27.6 (C-14, C-14'), 76.3 (C-13, C-13'), 111.6 (C-3, C-3'), 116.8 (C-2, C-2'), 121.7 (C-11, C-11'), 122.3 (C-8, C-8'), 123.5 (C-5, C-5'), 126.0 (C-10, C-10'), 126.2 (C-7, C-7'), 126.6 (C-10, C-10'), 126.8 (C-9, C-9'), 130.9 (C-12, C-12'), 142.3 (C-1, C-1'), 145.7 (C-4, C-4'). ^1H 1.47(s, H-15, H-15'), 1.52(s, H-14, H-14'), 5.61 (d, J = 9.8, H-12, H-12'), 5.90 (d, J = 9.9, H-11, H-11'), 7.51(m, H-7, H-7', H-6, H-6'), 7.71 (s, OH), 8.15 (d, J = 8.1, H-8, H-8'), 8.21(d, J = 8.4, H-5, H-5').

Properties of C-1

C-1 was isolated as a reddish crystal from repeated column chromatography. Yield : 23 mg; Rf value (solvent n-hexane-acetone = 5 : 1) : 0.40; mp: 98-100 °C. GC-MS m/z (rel. int.) 240 (16) (M^+), 225 (100), 211 (5), and 197 (34). UV-Vis spectrum λ max acetone : 416 nm. NMR (chloroform- d_1): δ ^{13}C 19.6, 74.6, 77.2, 80.9, 122.4, 126.1, 126.2, 129.9, 131.7, 133.1, 137.5, 140.9, 149.4. ^1H 1.22 (s, 2H), 1.53 (s, 3H), 2.15 (s, 3H), 3.44(s, 4H), 5.70 (d, J = 10.1, 1H), 6.63 (d, J = 9.9, 1H), 7.68 (m, 1H), 8.06 (m, 1H).

Properties of C-2

C-2 was isolated as dark powder from repeated column chromatography. Yield : 33 mg; Rf value (solvent n-hexane-acetone = 5 : 1) : 0.22; mp: 85-87 °C. GC-MS m/z

(rel. int.) 210 (100) (M⁺), 198 (10), and 182 (55). NMR (chloroform-d₁) ¹³C 19.64, 74.63, 77.23, 80.98, 122.39, 126.14, 126.26, 129.99, 131.77, 133.14, 137.57, 140.99, 149.43, 184.46. ¹H 1.23 (s, 1H), 1.69 (s, 3H), 3.81(d, J = 6.3, 1H), 3.97 (t, 1H), 6.12 (s, 2H), 6.44 (d, J = 5.5, 2H), 7.52 (m, 1H), 7.63 (m, 1H), 7.74 (d, J = 7.7, 1H), 8.07 (d, J = 7.8, 1H).

Air Oxidation Test

The three samples prepared as mentioned above were dissolved in acetone. The solution was then applied to a TLC plate and left in the laboratory desk for 5 days (ambient temperature). The color of TLC before and after exposure was measured with a CIEL*a*b* system, described in using a colorimeter (NF777). L*a*b* system gives the brightness (L*), redness (a*), and yellowness (b*). The resulting total color difference (ΔE^*_{ab}) was evaluated using the following equation : $(\Delta L^*^2 + \Delta a^*^2 + \Delta b^*^2)^{1/2}$. Tectoquinone (2-methyl anthraquinone, 25753-31 Kanto Chemical), along with several commercially available compounds, which previously reported to occur in the teak extract (Sandermann and Simatupang 1966; Windeisen *et al.* 2003; Lukmandaru and Takahashi 2009), i.e. lapachol 142905 Sigma-Aldrich), 2-hydroxymethyl anthraquinone (17241-59-7 Acros Organics) were also measured.

Alkaline and Acidic Treatment of Quinones

The 0.5 ml solution of each compound mentioned in discoloration test (1 mg/ml) was placed in a test tube. 100 μ l of potassium hydrogencarbonate (KHCO₃) and acetic acid (CH₃COOH) solution at different concentrations (0.01, 0.1, and 1 %), correspond to pH of 3–9, was added to each sample. The color change of each solution was observed after 4 h.

Results and Discussion

Identification of Components

Teak heartwood meals were extracted with EOAc and treated successively with n-hexane and acetone. Polymeric parts were fairly large in the EtOAc extract (52 %). In the low molecular weight parts, a combination of fractional crystallization and chromatographic methods led to the separation of tectol and 2 other unknown compounds. Tectol was also isolated in considerable amount. The identification of tectol was confirmed by comparing the NMR spectra data reported by Lemos *et al.* 1999). Tectoquinone was detected by GC-MS as one of major compounds. C-1 was separated as orange crystals and as determined by analyzing its GCMS molecular ion at m/z 240.

¹³C-NMR spectrum of C-1 showed 13 carbon signals, including three methylene carbons (δ C 74.6, 77.2, 80.9), three olefinic carbons (δ C 137.5, 140.9, 149.4), one methyl carbon (δ C 19.6) and six aromatic carbons (δ C 122.4, 126.1, 126.2, 129.9, 131.7, 133.1). In the ¹H-NMR spectrum, the resonances of methylene proton (δ H 3.4), aromatic proton (δ H 6.6), methylenedioxy protons (δ H 5.6, 5.7), and vinyl protons (δ H 7.68, 8.0) were found.

C-2 was separated as dark powders, and was determined by analyzing its GC-MS molecular ion at m/z 210. ¹³C-NMR spectrum of C-2 showed 13 carbon signals, including carbonyl carbon (δ C 184.4), two methylene carbons (δ C 77.2; 80.9), three olefinic carbons (δ C 133.1; 137.5; 149.4), two methyl carbons (δ C 19.6; 74.6) and four aromatic carbons (δ C 122.3; 126.1; 126.2; 131.7). In the ¹H-NMR spectrum, it revealed methylene proton (δ H 3.8; 3.9), aromatic protons (δ H 6.1; 6.4), and vinyl protons (δ H 7.5; 7.6; 7.7; 8.0). Due to the presence of aromatic rings and carbonyl carbons, this compound is suggested to be a naphthaquinone compound.

Air Oxidation Test

The results of air oxidation of the compounds are shown in Table 1. It was revealed that tectol changes its color (ΔE^*_{ab} = 27.2) as indicated by the considerable decreasing in brightness and increasing in yellowness index (Fig. 3). Lapachol and C-1 were moderately changed, whereas tectoquinone was slightly changed. The color change in C-1 was mostly from its yellowness. The changes of the color in other compounds were small.

Table 1. Color changes of compounds after 5-day exposure

Compounds	Color measurement			Color changes after exposure			
	L*	a*	b*	ΔL^*	Δa^*	Δb^*	ΔE^*_{ab}
Tectol	91.4	0.6	2.7	-13.1	5.1	23.3	27.2
C-1	85.3	4.0	24.7	3.1	-2.5	-10.3	11.0
C-2	84.3	0.1	15.7	1.5	1.3	1.6	2.5
Tectoquinone	91.7	-1.3	6.4	-0.4	-6.0	4.3	7.3
Lapachol	83.0	9.0	17.6	6.9	-7.9	8.6	13.5
2-tert-butyl-AQ	92.1	0.9	-0.1	-0.3	-0.3	2.1	2.1
2-hydroxy-methyl-AQ	92.1	1.0	-0.1	-0.5	-1.1	3.7	3.8

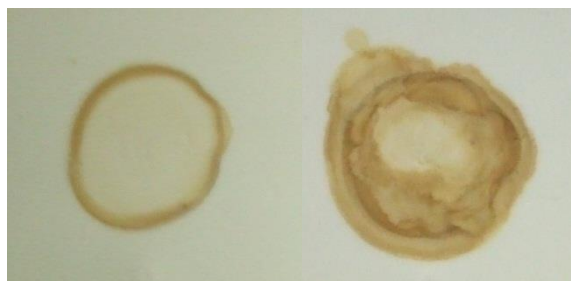


Figure 3. Air oxidation of tectol after 1-day (left) and 3-day exposures (right).

Alkaline and Acidic Treatment of Quinones

Compounds were treated in acetic acid and potassium hydrogencarbonate in the pH range of 3-9 to investigate the influence of pH values. After the treatment, changes in color and UV-VIS absorption were examined. The results (Table 2, Fig. 4) revealed that C-1, C-2, and lapachol changed their color after alkaline treatment at 0.1 % KHCO_3 (pH 8.3), whereas tectol changed its color at 1 % KHCO_3 (pH 9.3). Tectol showed no clear absorption spectrum, although tectol changed color to dark green. In acidic condition, only C-1 and lapachol changed their color at acetic acid 0.1 % solution (pH 3.9). C-1 showed absorption maxima at 416 (at pH 3.9 and 8.3) and 520 nm (at pH 9.5). It was concluded

that C-1, C-2, and tectol is sensitive to pH changes, while other quinones hardly change color even at high pH. The pH changes does not correspond to the changes in the color of the heartwood that were caused by acidic or alkaline treatment since the pH of black streak part ranges from 5.5 to 7.0 as described in the previous report (Lukmandaru *et al.* 2009; 2014). Furthermore, the cause of pH change in the discolored part is remained unknown. This trend was also differed in another species related to pH values (Starck *et al.* 1984; Takahashi and Mori 2006). Thus, the question about the reason of color changes of woods upon pH change cannot be answered in a definite way.

Table 2. Color changes and UV-VIS measurement of compounds after 4-hr acidic and alkaline treatment.

Compounds	Acetic acid				Potassium hydrogen carbonate	
	pH 2.9	pH 3.9	pH 5.9	pH 6.9	pH 8.3	pH 9.5
Tectol	x	x	x	x	x	Deep green (362 nm)
C-1	x	Weak reddish (416 nm)	x	x	Weak reddish (416 nm)	Reddish (520 nm)
C-2	x	x	x	x	Weak brownish	Weak brownish
Tectoquinone	x	x	x	x	x	x
Lapachol	x	Weak reddish (378 nm)	x	x	Weak reddish (368 nm)	Deep reddish (484 nm)
2-tert-butyl-AQ	x	x	x	x	x	x
2-hydroxy-methyl-AQ	x	x	x	x	x	x

Remark : x = no color change

AQ = anthraquinone

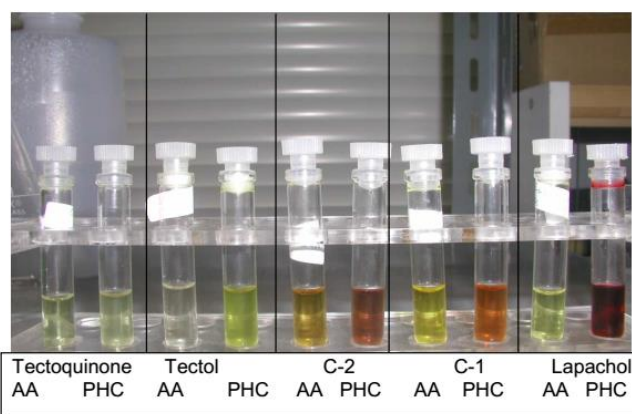


Figure 4. The color changes of compounds after the treatment of acidic and alkaline. (AA = acetic acid 1 %; PHC = potassium hydrogen carbonate 1 %).

Relationship between Structure and Coloration of Quinone

Previously, the discoloration behaviour of teak during irradiation was observed which the concentration tectoquinone and phenol decreased substantially (Li *et al.* 2019). Furthermore, darkened wood samples by heat treatment showed the total extractives content were higher in the treated teakwood (Gasparik *et al.* 2019; Lengowski *et al.* 2021). Table 1 and 2 shows how quinones are colored with air oxidation, acidic, and alkaline treatment. Fig. 5 displayed the chemical structure of the treated compounds. Tectoquinone and other two anthraquinones are remained stable, whereas tectol, C-1, C-2 and lapachol changed their color. It is thought that the color changes are due to the structural differences among those compounds.

The structural differences are the structure of double bond conjugated and hydroxyl groups. The structure of tectoquinone, 2-tert-butyl-anthraquinone, 2-hydroxy-methyl-anthraquinone which is not colored, are lack of hydroxyl group and double bond conjugated (Table 3). Thus, it is reasonable to assume that the structural features of a hydroxyl group and a double bond conjugated have a significant effect on quinone coloration (Takahashi and Mori 2006). Tectol with two hydroxyl groups and a possibility to extend its double bonds conjugated system, changes its color through air oxidation and through treatment at pH 9.5. Lapachol with one hydroxyl group and a possibility to extend its double bonds conjugated system changes to weak reddish at pH 3.9 and 8.3 as well as moderately changed in color through air oxidation.

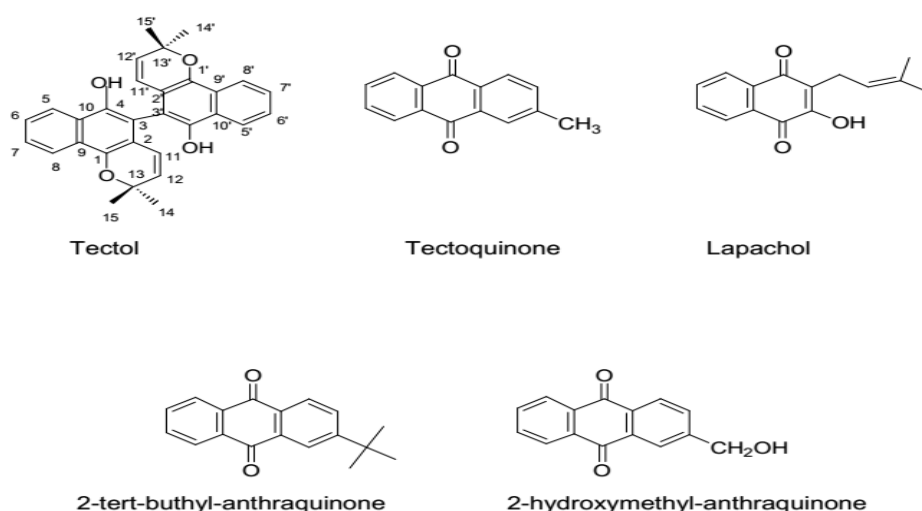


Figure 5. Compounds from the extractives of teak heartwood.

Table 3. Structural differences among the compounds from teak extractives.

Compounds	Structure	
	Hydroxyl group	Extension of double bond conjugated
Tectol	2	2
Tectoquinone	0	0
Lapachol	1	1
2-tert-buthyl-AQ	0	0
2-hydroxy-methyl-AQ	1	0

The Contribution of Components to the Discoloration of Teak Wood

As tectol providing the most intense color on TLC plates and showing the most abrupt decrease in brightness, it could be regarded as a major heartwood color precursor or pigment. Tectol can easily be oxidized, therefore, this could be the first stage of tectol before being polymerized by enzymatic reaction to produce special colored compounds. This similar phenomenon was also observed in a napthaquinone, hydrojuglone glucoside, in *Juglans* sp wood

(Burtin *et al.* 1998). The yellowness value of C-1 was decreased considerably after air exposure. This fact is in line with characteristic of black streak part of teak in the previous study (Lukmandaru 2009; Lukmandaru *et al.* 2009), which has lesser value in yellowness. In an earlier report, lapachol was also detected in *Tabebuia serratifolia* wood extract which it contribute in yellow color of wood (Romagnoli *et al.* 2013).

Heartwood and sapwood of teak were measured to be weakly acidic (Qiu *et al.* 2019). In addition, the main

different substances between heartwood and sapwood were 4-tert-butyl-2-phenyl-phenol, tectoquinone, and 2,3-dimethyl-1,4,4a, 9a-tetrahydro-9,10-anthracenedione#. The sensitivity to pH treatment also suggests that C-1 and C-2 could be the one of precursors of colored substances although the changes did not occur in the weakly acid range. It is assumed that a structure changed to a p-quinone or o-quinone structure after acidic/alkaline treatments due to the formation of a large conjugated system (Takahashi and Mori 2006). The exact structure of and C-1 and C-2 will be elucidated after finishing the measurements COSY CH, HMBC, and HMQC- NMR and will be reported in the future. This study proved that tectoquinone is not easily to change its color although this compound was observed in comparatively higher amount (Lukmandaru *et al.* 2009; 2014). Various constituents other than quinones are found in the teak heartwood, therefore, more detailed investigations are needed.

The higher extractive contents of discolored heartwood to those of normal wood mean that both high and low molecular weight substances could be studied using HPLC and GC-MS analysis. The significantly high *n*-hexane and EtOAc extractive content in the black streak part (Lukmandaru *et al.* 2009; 2014) indicated that the intense production of pigmented heartwood substances. It was also observed that the final color of the wood after extraction was still darker than that of the normal heartwood. Above a certain degree a polymerization, some compounds remain bound to the matrix. To understand more about the background of the blackening, the acidolysis treatment (Kai and Swan 1990) might be necessary to characterize the polymeric parts, as well as, enzymatic or derivation treatment to the low molecular weight substances. The blackening process was assumed to be a kind of protective function against biological origins. This hypothesis was supported by the comparatively high level of tectoquinone in that region (Lukmandaru *et al.* 2009; 2014). However, tectoquinone was relatively stable at low and high pH, as well as in air oxidation. In studying the blackening *Diospyros kaki*, Yasue *et al.* (1975) observed that a quinone compound is indicated as a precursor of polymeric substances. On the other hand, tectol, a dimeric naphtquinone, provided dark colored after air oxidation. Thus, it is proved that the structural of quinone will affect the ability to change its color. Unfortunately, two isolated compounds remain unidentified, as well as, another dimeric quinone as not isolated, therefore, the conclusions with regard to structural differences of quinone could not be drawn more thoroughly. The structure of tectoquinone, 2-tert-butyl-anthraquinone, 2-hidroxy-methyl-anthraquinone which is not colored, are lack of hydroxyl group and double bond conjugated.

Conclusions

By column chromatography, tectol and two unknown components (C-1 and C-2) were isolated from the low molecular weight parts of ethyl acetate extract. By air

oxidation test, tectol, a dimeric naphtquinone, showed an abrupt decrease in brightness. Therefore, tectol could be a precursor of colored compounds by enzymatic reactions. Tectoquinone was relatively stable at low and high pH, as well as in air oxidation. The discoloration sensitivity might be due the structural differences in double bond conjugated and hydroxyl groups among the tested quinones. All tested components did not change their color after weak acidic treatment which suggest the other unisolated colored substances and high molecular parts from ethyl acetate extract might be involved in discoloration process under the weakly acid range.

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Investigation of Flavonoid Extractives and their Contribution to Color of *Dalbergia latifolia* Roxb Wood

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Abstract

Dalbergia latifolia wood is a beautiful wood with color of dark purple to dark brown and rich in flavonoid compounds. This study aimed to investigate the presence of flavonoid compounds from *D. latifolia* wood and their contribution to its color. The *D. latifolia* wood sample was powdered and extracted with ethanol-toluene (1/2, v/v). The ethanol- toluene extract then was column chromatographed to obtain fraction 1 to fraction 12. Methylation was conducted to each fraction to detect flavonoid compounds by GC-MS. The results of GC-MS analysis showed that ethanol- toluene extract gave Fr- 1- Fr. 3 as soluble flavonoids (34.2%) and Fr. 4- Fr. 12 as insoluble polymers (62.6%). Furthermore, 12 flavonoids i.e latifolin, dalbergiphenol, chalcone, dalbergin, and their derivatives were characterised and these compounds might be significance in contributing to color of *D. latifolia* wood.

Keywords: *D. latifolia*, color, extractives, flavonoids, latifolin, dalbergiphenol, chalcone, dalbergin

Introduction

Dalbergia latifolia Roxb, known as *sonokeling* in Indonesia is a member of Fabaceae family. In Indonesia, *D. latifolia* is found growing naturally in the forest of East and Central Java, favoring moist and well drained soils but also known to be drought resistant (Krishnamurthy *et al.* 2010; Praciak 2013). *D. latifolia* is known for its high-quality wood (Dwianto *et al.* 2019). Further, *D. latifolia* wood is highly valued for its beautiful dark purplish pattern with reddish brown color and also rich in fragrant. By those qualities, it made *D. latifolia* wood become popular for furniture, musical instruments, and various high-class home furnishing material. (Khalid *et al.* 2015; UNEP-WCMC 2017).

Color is one of an important aspect of wood quality. The color of dark purple to dark brown in the wood of *D. latifolia* was strong suggested by the presence of flavonoids and quinones. The earlier reports, the heartwood of *D. latifolia* have shown the presence of katinone, neoflavonoid dalcridon, latinone, latifolin, 4-methoxydalbergione, and obtusaquinol (Rastogi and Mehrotra 1993a; and 1993b; Thurlough *et al.* 1981; Sekine *et al.* 2009a; Khalid *et al.* 2015). Latifolin from *D. latifolia* has been assayed for its antitermite and antifungal activity (Sekine *et al.* 2009b). Recent study has also identified a new diaryl 1, 2-diketone from the heartwood of *D. latifolia* and assessed its antibacterial activity (Liu *et al.* 2018).

Wood color variation is associated with the composition of its extractive components. Flavonoid type compounds have been mentioned for its contribution to coloration of plant parts (Giusti and Wrolstad 2003; Iwashina 2013; Panche *et al.* 2016). Previous researchers (Imamura *et al.* 1980; Yazaki *et al.* 1985; Kai and Swan 1990) showed some flavonoids to be responsible for coloration of wood. Several compounds with color have been isolated from *D. latifolia* wood such as dalbergiphenol, 5-O-methylatfolin,

and 3'-hydroxy-2,4,5-trimethoxydalbergiquinol which are yellow color (Meng *et al.* 2019). However, study of the relationship of flavonoids on their contribution to the color of *D. latifolia* has not been reported. In this study, the fractionation of ethanol- toluene extract of *D. latifolia* wood through column chromatography was conducted and each fraction were further examined for their contributions to color of *D. latifolia* wood.

Materials and Methods

Sample Collection and Extraction

The sample of *D. latifolia* wood (15-year-old) was collected and purchased from a woodworking industry in Bantul, while the tree origin is from Community Forest in Bantul, Yogyakarta, Indonesia. The heartwood and sapwood (2/1, w/w) were mixed and milled to powder then 10 g of sample was extracted by ethanol/ toluene (2/1, v/v) for 6 h in Soxhlet apparatus.

Column Chromatography and GC-MS Analysis

The ethanol- toluene extract (3.4 g) was loaded into Si-gel (60 N, spherical 63-210 μ m, neutral Kanto Chemical Co., Inc., Japan) column chromatography. For the fractionation, the solvent of *n*-hexane, ethyl acetate (EtOAc), acetone, methanol (MeOH), and water were used as eluent. Each fraction then was evaporated and weighed as results (percentage of dry extract).

The GC-mass spectrometry (GC-MS) data were collected with a GCMS-QP 2010 (Shimadzu, Japan). The 1 μ l of sample (1 mg/ml) was prepared for direct injection sample and methylation sample. The methylation protocol: to 2 mg of sample was dissolved into 1 ml of MeOH. Further, 100 μ l of TMAH (tetramethylammoniumhydroxide, Sigma Aldrich, Germany) was added. The GC condition: Rtx-5MS

capillary column (30 m x 0.25 mm I.D. and 0.25 μ m; GL Sciences, Tokyo, Japan); detection temperature of 285 $^{\circ}$ C; column temperature from 70 $^{\circ}$ C (1 min) to 290 $^{\circ}$ C at 5 $^{\circ}$ C/min; injection temperature of 250 $^{\circ}$ C; acquisition mass range from of 50-500 amu using helium as the carriers gas. The sample was compared to NIST library and literatures (Balakhrisna *et al.* 1962; Khan *et al.* 2006; An *et al.* 2008; Sekine *et al.* 2009a, and 2009b; Meng *et al.* 2019; Cuong *et al.* 2019).

Color Properties Determination ($\lambda = 300-700$ nm)

The sample (1 mg/ml) from 12 fractions was read at wave length of 300-700 nm for color measurement by an Ultraviolet (UV)/ Visible spectrophotometer (model SP-3000 Nano, Optima, Tokyo, Japan).

Results and Discussion

Extraction, Fractionation, and GC-MS Analysis

The woodmeal of *D. latifolia* was extracted by ethanol-toluene (2:1, v/v) and then was fractionated (Masendra *et al.* 2020). The fractionation was conducted by column chromatography with solvent *n*-hexane and increasing the polarity with EtOAc, acetone, MeOH, and water. Figure 1 showed the result of fractionation of ethanol-toluene extract (in total 3.28 g or 96.8% of initial sample). The results showed Fr. 1, Fr. 2, Fr. 11, and Fr. 12 had great amount of extractive contents ($\geq 10\%$). The Fr. 1 was eluted with *n*-hexane, Fr. 2 with *n*-hexane- EtOAc (8/2), Fr. 11 and Fr. 12 were obtained with polar solvent such as MeOH and water.

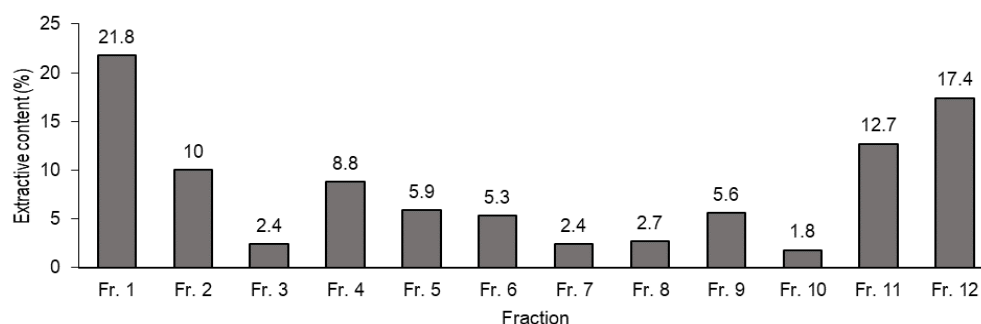


Figure 1. Fractionation results of ethanol- toluene extract of *D. latifolia* wood; Fraction (eluent): Fr. 1 (*n*-hexane), Fr. 2 (*n*-hexane- EtOAc; 8/2), Fr. 3 (*n*-hexane- EtOAc; 7/3), Fr. 4 (*n*-hexane- EtOAc; 5/5), Fr. 5 (*n*-hexane- EtOAc; 3/7), Fr. 6 (*n*-hexane- EtOAc; 2/8), Fr. 7 (*n*-hexane- EtOAc; 1/9), Fr. 8 (EtOAc), Fr. 9 (EtOAc- acetone; 5/5), Fr. 10 (acetone), Fr. 11 (MeOH), Fr. 12 (MeOH- water; 5/5).

The analysis of GC-MS by direct injection showed the Fr. 1- Fr. 3 have one peak and it was identified as latifolin (Masendra *et al.* 2020). Therefore, the methylation was conducted in all fractions. By methylation, many other flavonoids were observed (Figure 2 and Table 1) and were appeared at retention of 30- 40 minutes. That result was

similar with that of direct injection of Fr. 1- Fr. 3. However, there were no peaks were detected in the Fr. 4- Fr. 12. The percentage of latifolin was dominant in Fr. 2 and Fr. 3, while 3-hydroxy-2,4,5-trimethoxydalbergiquinol was in a high concentration in Fr. 1.

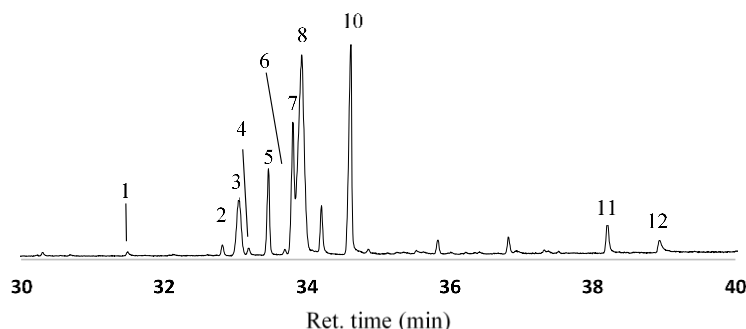


Figure 2. Chromatogram of GC-MS from Fr. 1; 1. dalbergiphenol (retention time/ RT (min): 31.5), 2. latifolin dimethyl ether (32.8), 3. 2,3-dimethoxy-2,4-dihydroxychalcone (33.1), 4. latifolin dimethyl ether isomer (33.2), 5. 5-O- methyl latifolin (33.5), 6. 2-O- methyl latifolin isomer (33.7), 7. 2-O- methyl latifolin (33.8), 8. 3-hydroxy-2,4,5-trimethoxydalbergiquinol (33.9), 9. 2,4,5-trimethoxydalbergiquinol (34.2), 10. latifolin (34.6), 11. O-methyl dalbergin (38.2), 12. dalbergin (38.9).

Table 1. Flavonoids from *D. latifolia* wood detected by GC-MS

Compound	Rt (min)	Constituents	Relative abundance (%)			Color
			Fr. 1	Fr. 2	Fr. 3	
1	31.5	dalbergiphenol	0.29	0.86	-	brown
2	32.8	latifolin dimethyl ether isomer	0.91	2.56	14.32	colorless
3	33.1	2,3-dimethoxy-2,4-dihydroxychalcone	8.78	1.29	-	yellow
4	33.2	latifolin dimethyl ether	0.64	-	21.61	colorless
5	33.5	5-O- methyl latifolin	7.35	3.47	-	yellow
6	33.7	2-O- methyl latifolin isomer	0.36	-	-	yellow
7	33.8	2-O- methyl latifolin	13.23	4.43	-	yellow
8	33.9	3-hydroxy-2,4,5-trimethoxydalbergiquinol	38.83	14.52	-	yellow
9	34.2	2,4,5-trimethoxydalbergiquinol	4.00	0.59	8.17	yellow
10	34.6	latifolin	21.33	58.30	25.48	colorless
11	38.2	O-methyl dalbergin	2.98	2.53	30.41	yellow
12	38.9	dalbergin	1.32	11.46	-	yellow

Remarks : the identification and color of constituents were assigned based on previous studies

Characterization of Fr.1- F. 3

In this study, flavonoids of *D. latifolia* wood were detected by GC-MS with direct injection and methylation method and the mass spectra of flavonoids detected in the sample were compared with previous works (Balakhrisna *et al.* 1962; Khan *et al.* 2006; An *et al.* 2008; Sekine *et al.* 2009a, and 2009b; Meng *et al.* 2019; Cuong *et al.* 2019). The chemical structure of compound 1- 12 was displayed in Figure 3.

Dalbergiphenol (1); MS, m/z (relative abundance): 270 [M⁺] (100), 253 (15.4), 237 (14.6), 223 (21.2), 209 (15.8), 195 (6.9), 177 (12.7), 165 (23.3), 153 (14.6), 139 (123.3), 115 (52.9), 103 (14), 91 (47.3), 77 (28.8), 69 (25.7), 51 (27.2), 39 (5). The MS compound 1 was compared to previous works (Khan *et al.* 2006; Sekine *et al.* 2009b). *Dalbergiphenol* has a light brown oil color and it was isolated from *D. odorifera*, *D. latifolia* and *Ranunculus repens* (Khan *et al.* 2006; An *et al.* 2008; Sekine *et al.* 2009b). *Latifolin dimethyl ether* (2); MS, m/z (relative abundance): 314 [M⁺] (100), 299 (13.6), 285 (31.5), 268 (10.2), 253 (7.3), 239 (9.3), 225 (6), 209 (6), 193 (4), 181 (11.2), 165 (9), 151 (21), 128 (11), 115 (16.8), 105 (9.7), 91 (10.4), 77 (14.7), 69 (10.5), 43 (7). The MS compound 2 was compared with a previous literature and this compound was isolated from *D. latifolia* heartwood (Sekine *et al.* 2009a). *2,3-Dimethoxy-2,4-dihydroxychalcone* (3); MS, m/z (relative abundance): 300 [M⁺] (48.2), 285 (2.2), 269 (100), 253 (6.4), 239 (4.1), 225 (8.5), 210 (2.6), 181 (6.3), 168(6.6), 153 (9.6), 131 (7.4), 115 (8), 103 (4.4), 91 (6.6), 77 (7.2), 69 (10.1), 39 (3.9). The compound 3 was predicted from a chalcone group which have yellow color. *Latifolin dimethyl ether isomer* (4); MS, m/z (relative abundance): 314 [M⁺] (100), 299 (19.8), 283(20.8), 269 (5.2), 257 (6.7), 241(4.6), 221 (4.7), 208 (6.9), 191 (7.5), 181 (15), 165 (11.6), 145 (16.1), 131 (14.4), 121 (21.6), 105 (8.3), 91 (21), 77 (11), 69 (12), 51 (8.3), 41 (5.5). Compound 4 was suggested to close with compound 2 with m/z 314 as molecule intake. *5-O- methyl latifolin* (5); MS, m/z (relative abundance): 300 [M⁺] (53.6), 285 (3.3), 269 (27.5), 253 (5.5), 241 (4.1), 225 (6.6), 210 (4.4), 194 (5.9), 168 (100),

167 (9.1), 153 (39.5), 131 (16.1), 107 (11), 91 (8), 77 (16.6), 69 (12.1), 51 (6.6), 39 (7.8). The compound 5 was similar to 5-O- methyl latifolin that isolated from *D. latifolia* heartwood and *D. odorifera* heartwood with yellow color (Sekine *et al.* 2009a; An *et al.* 2008; Meng *et al.* 2019). *2-O- methyl latifolin isomer* (6); MS, m/z (relative abundance): 300 [M⁺] (100), 285 (13.7), 271 (30.8), 253 (10.4), 239 (10.2), 225 (10), 211 (5.2), 194 (12.2), 181 (8), 153 (12.2), 137(25.4), 126 (7.6), 105 (18), 91 (25), 79 (10.5), 69 (15.4), 55 (12.5), 39 (8). The MS of compound 6 was compared to a previous work (Sekine *et al.* 2009a), it was isolated from *D. latifolia* heartwood. *2-O- Methyl latifolin* (7); MS, m/z (relative abundance): 300 [M⁺] (100), 285 (9.3), 283 (9.8), 271 (20.3), 253 (7.6), 237 (8.1), 209 (5.6), 192 (10.3), 177 (7.6), 167 912.7), 137 (19.3), 115 (24.3), 105 (8.6), 91 (29.6), 77 (15.6), 65 (8.8), 53 (6.2), 41 (2.9). Same as compound 6, compound 7 was similar to 2-O- methyl latifolin that was isolated from *D. latifolia* heartwood (Sekine *et al.* 2009a). *3-hydroxy-2,4,5-trimethoxydalbergiquinol* (8); MS, m/z (relative abundance): 300 [M⁺] (19.4), 286 (35.2), 271 (5.4), 255 (100), 240 (8.5), 225 (4.7), 211 (6.2), 197 (3.7), 181 (6.1), 165 (10), 152 (7.2), 128 (11.2), 115 (14.2), 105 (6.2), 91 (11.7), 77 (7.7), 69 (13.5), 43 (6), 35 (5). The MS of compound 8 was similar with previous studies, and it also was isolated from the heartwood of *D. tonkinensis* and *D. latifolia* in yellow color (Cuong *et al.* 2019; Meng *et al.* 2019). *2,4,5-trimethoxydalbergiquinol* (9); MS, m/z (relative abundance): 284 [M⁺] (100), 269 (7), 253 (3.5), 239 (8.3), 237 (35.2), 223 (3), 209 (22), 183 (4.3), 181 (16.4), 152 (10.9), 128 (13), 115 (9.1), 102 (4.7), 91 (3.3), 77 (6.2), 69 (14.9), 43 (11), 35 (5). This compound was isolated from heartwood of *D. odorifera* (Yun *et al.* 2015). *Latifolin* (10); MS, m/z (relative abundance): 286 [M⁺] (59.2), 269 (6.2), 255 (37.5), 239 (5), 227 (5), 211 (6.4), 197 (4), 180 (9), 154 (100), 153 (15.5), 139 (23), 107 (12), 91 (10.3), 77 (20), 69 (17.2), 53 (9), 39 (11). The compound 10 was compared and reported from previous works as a colorless compound (Balakhrisna *et al.* 1962; Sekine *et al.* 2009a). *O-Methyl dalbergin* (11); MS, m/z (relative abundance): 282 [M⁺] (100), 267 (11), 254 (44.4), 239 (25.7), 235 (32.4), 207

(7.6), 183 (13.1), 181 (3.3), 155(17), 152 (18.5), 139 (30.2), 115 (4.8), 102 (6.4), 89 (3.7), 77 (19.5), 69 (21.1), 51 (8), 39 (3.9). The compound **11** was suggested as O-methyl dalbergin that was isolated from the heartwood of *D. sissoo* (Ahluwalia *et al.* 1957; Ahluwalia and Seshadri 1956). *Dalbergin* (**12**); MS, m/z (relative abundance): 268 [M^+] (100), 253 (3.2), 225 (93.3), 197 (9), 183 (3), 169 (3), 155

(7), 141 (12), 127 (18), 115 (8), 101 (7), 89 (5), 77 (12), 69 (32), 53 (9), 39 (6). The compound **12** was suggested to similar with dalbergin, a yellow color compound that isolated from heartwood of *D. latifolia*, *D. odorifera*, *D. melanoxylon*, and *D. sissoo* (Ahluwalia and Seshadri 1956; Chan *et al.* 1997; Mutai *et al.* 2013; Meng *et al.* 2019).

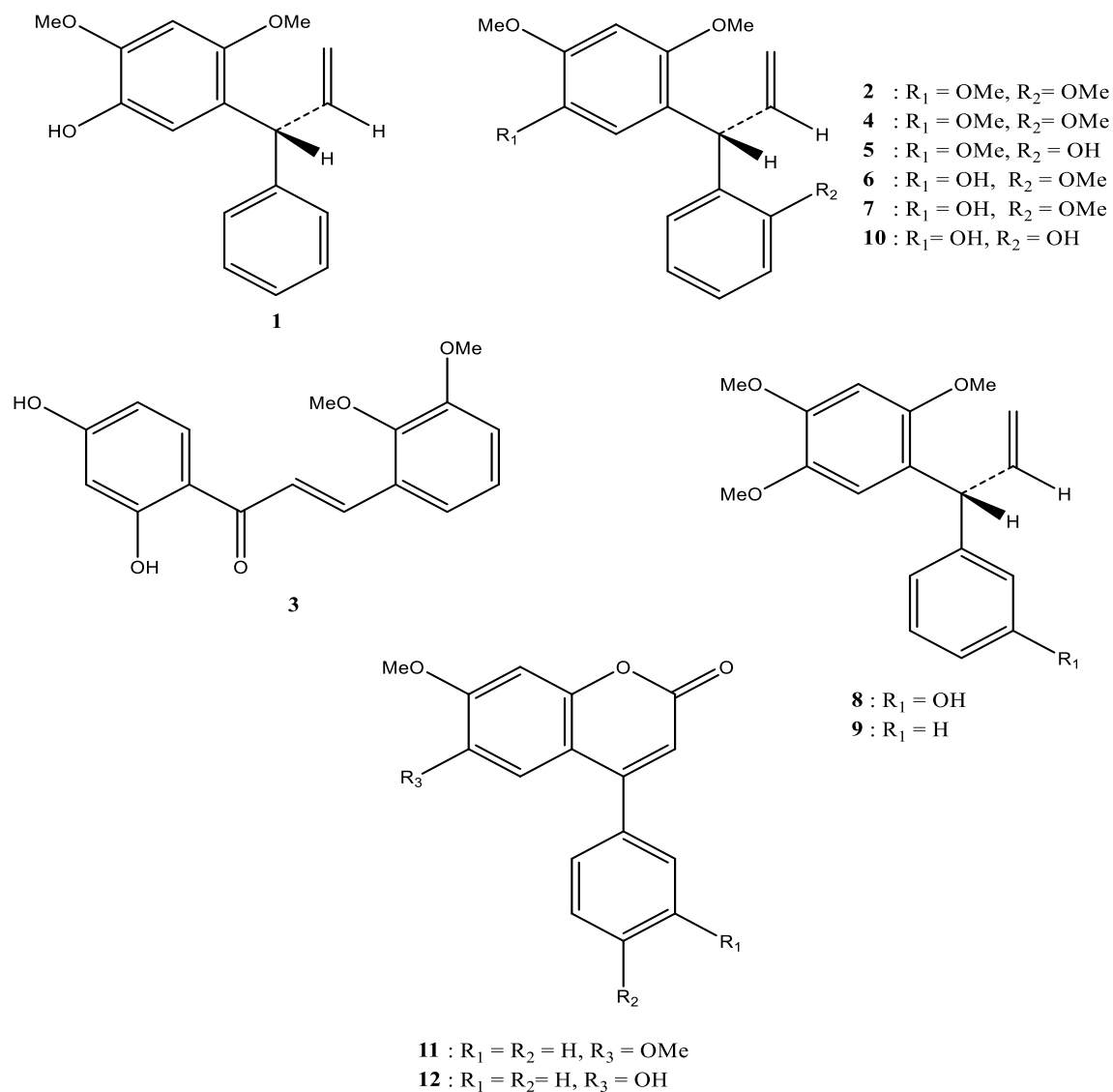


Figure 3. Chemical structure of flavonoids detected in *D. latifolia* wood; **1**. dalbergiphenol, **2**. latifolin dimethyl ether isomer, **3**. 2,3-dimethoxy-2,4-dihydroxychalcone, **4**. latifolin dimethyl ether, **5**. 5-O- methyl latifolin, **6**. 2-O- methyl latifolin isomer, **7**. 2-O- methyl latifolin, **8**. 3-hydroxy-2,4,5-trimethoxydalbergiquinol, **9**. 2,4,5-trimethoxydalbergiquinol, **10**. Latifolin, **11**. O- methyl dalbergin, **12**. Dalbergin.

Color Properties and Extractives Contributing to Color

In some wood species, flavonoids significantly involved in coloration and discoloration of wood (Yazaki *et al.* 1985; Kai and Swan 1990) and might decrease the quality of wood. Thus, the study of correlation between flavonoids and their contribution to the wood color is to support and develop the prevention of wood from damage when it is utilized. The fractionation of ethanol-toluene extracts in Figure 1 obtained 12 fractions which three fractions (Fr. 1- Fr.3) as soluble flavonoids and nine fractions (Fr.4- Fr. 12) as insoluble polymers. The yield of soluble flavonoids was 34.2% of ethanol- toluene extract dried sample. The solubility of flavonoids from Fr.1- Fr.3 generally obtained from solvent with a low polarity. By GC-MS analysis, flavonoids were almost from neoflavonoid

group (Table 1). In comparison, neoflavonoids also were able to dissolve in solvent of *n*-hexane and dichloromethane (Sekine *et al.* 2009a, and 2009b; Wu *et al.* 2011).

The GC-MS analysis showed latifolin, dalbergin, dalbergiphenol, chalcone, and their derivatives were in Fr. 1- Fr. 3. The absorbance measurement of Fr. 1 and Fr. 2 resulted the high absorption in the beginning of UV-Vis spectra (Figure 4). This finding in Fr. 1 and Fr. 2 might be correlated with the presence of soluble flavonoids. On the contrary, the Fr. 11 and Fr. 12, as insoluble polymers, showed the absorption in a higher wavelength. With regard to a previous study, Santos-Buelga *et al.* (2003) reported that flavonoids with maximum absorption at 310- 370 nm is might from quercetin and maximum absorption at around 450-550 nm is from anthocyanins.

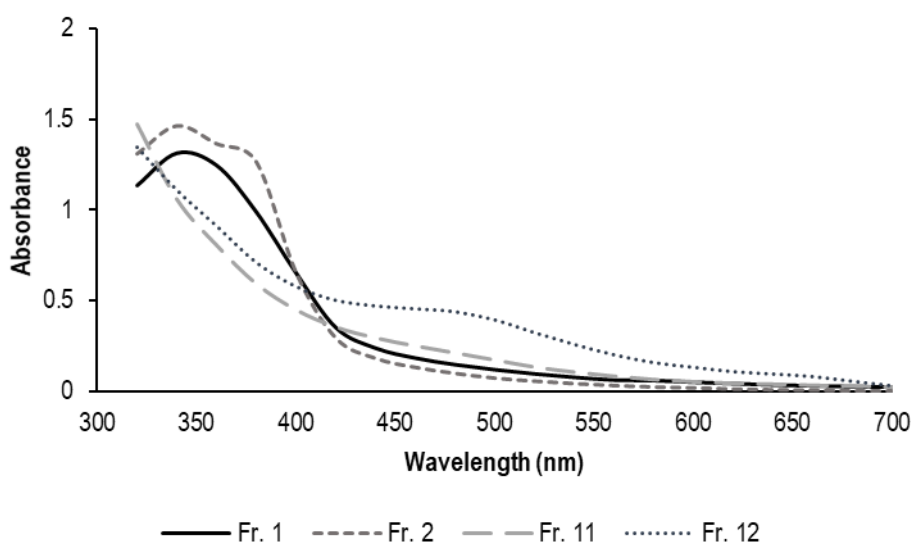


Figure 4. Absorbance of Fr. 1, Fr. 2, Fr. 11, and Fr. 12 from *D. latifolia* wood extract.

Based on yield extraction, the color properties of *D. latifolia* wood was dominated by Fr. 1 (21.8 %) and Fr. 12 (17.4%). Further, after GC-MS analysis of direct injection and methylation in the 12 fractions, only 3 fractions (Fr.1- Fr.3) showed the information of flavonoids. In the case of other fractions (Fr. 4- Fr. 12), the absent of flavonoids in GC-MS detection indicates that insoluble polymers were exist. The percentage of flavonoids in Fr. 1- Fr. 3 and insoluble polymers in Fr. 4- Fr. 12 were 34.2% and 62.6% (Figure 1), and thus the contribution of insoluble polymers was higher than soluble polymer to color of *D. latifolia* wood.

In this study, the absorbance measurement was conducted to each fraction using UV-Vis spectrophotometry. Due to Fr. 1, Fr. 2, Fr. 11 and Fr. 12 that represent soluble flavonoids and insoluble polymers had a high extractive content, the absorption of these fractions were further discussed. The appearance of color and absorbance for some fractions have been captured in Figure 4 and 5. The Fr. 1 and Fr. 2 had the high absorbance at 300- 400 nm, while Fr. 11 and Fr. 12 had a high absorbance at 400- 550 nm.

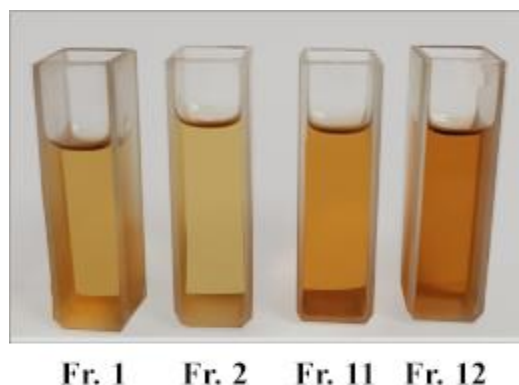


Figure 5. Color appearance of fractions from *D. latifolia* wood extract.

In the appearance (Figure 5), the color of Fr. 12 has the darkest color (brown) following by Fr. 11, Fr. 1, and Fr. 2. With regard to flavonoid presences, the Fr. 1 contained 3-hydroxy-2,4,5-trimethoxydalbergiquinol or compound **8** as the main compound (38.83%). In Fr. 2, compound **8** was 14.52% and it was a predominant compound. This compound (**8**) has a yellow color and it was derivative from dalbergiphenol, a compound with light brown oil color (Khan *et al.* 2006). In the case of Fr. 2, latifolin or compound **10** (58.3%) was the major compound (Table 1). However, due to the compound **10** is colorless, a single compound **10** may

not contribute to the color of *D. latifolia* wood. This colorless compound (**10**) also may contribute the color of Fr. 2 that was not too dark as other fractions (Figure 5). Further, a comparison between color and colorless compounds was made in Figure 6. The Fr. 1 was dominated by color compounds, while the colorless compounds were in considerable proportion in Fr. 2. Thus, the presence of compound **8** and other colored compounds (**1, 3, 5, 6, 7, 9, 11, 12**) in Fr. 1 and Fr. 2 might contribute to the color of *D. latifolia* wood.

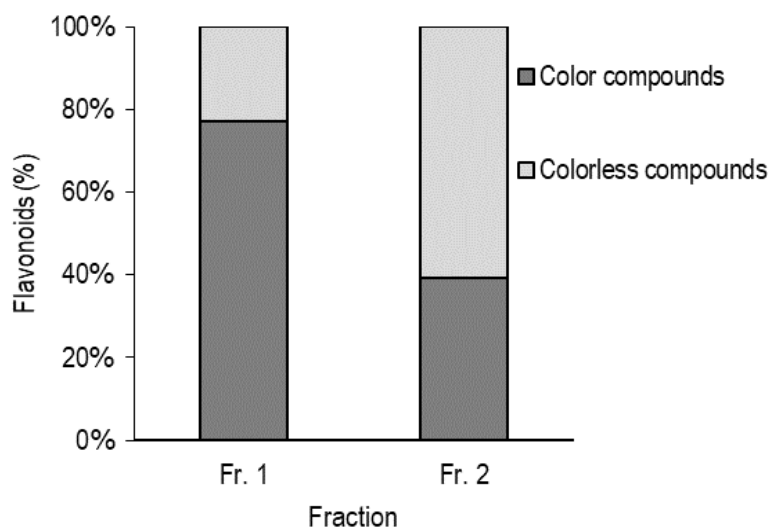


Figure 6. Comparison of extracts with color and colorless flavonoids detected in *D. latifolia* wood.

However, it should be considered that latifolin was detected in a high concentration with direct method injection of GC-MS, especially found in Fr. 1- Fr. 3. This suggests latifolin is a precursor in insoluble polymers (Fr. 4- Fr.12), which subsequently affected considerably to the color of *D. latifolia* wood. This phenomenon similar to previous works on catechin, a colorless compound and a precursor of condensed tannin in some wood species (Roux 1972;

Yazaki *et al.* 1985). To the best of our knowledge, this is the first information of the correlation between flavonoids and color of *D. latifolia* wood. Thus, the identification of insoluble polymers from *D. latifolia* wood is necessary to be studied in the future work in order to find out the compounds that represent 62.6% of color contribution such as by acidolysis methods (Kai and Swan 1990).

Conclusions

The investigation of flavonoids from the ethanol-toluene extract of the *D. latifolia* wood and their contribution to the color has been conducted. The correlation showed that soluble flavonoids from Fr.1- Fr. 3 gave attribution of 34.2% to color of *D. latifolia* wood, while insoluble polymer was 62.6% in Fr. 4- Fr. 12. By methylation, 12 flavonoids that were grouped into latifolin, dalbergiphenol, chalcone, dalbergin were identified and their presence may contribute to the color of *D. latifolia* wood.

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Thermoelectric Properties of Porous SiC/SiO₂/C Composite from Carbonized *Cryptomeria japonica* Wood

Joko Sulisty, Hiroyuki Kitagawa, and Sri Nugroho Marsoem

Abstract

Electric power generation by thermoelectric material utilizing radiated heat of from roof's house, engine and others is potential clean energy in tropical areas such as Indonesia. In this study, thermoelectric materials such as silicon carbide (SiC/SiO₂/C) composites were developed from carbonized *Cryptomeria japonica* wood infiltrated ethyl silicate-40 by sintering at 1400, 1600 and 1800 °C for 30 min under N₂ atmosphere. This study aimed to examine the morphology, microstructure and thermoelectric properties of porous SiC/SiO₂/C composites. SiC/SiO₂/C composites sintered at 1600 °C with low value of thermal conductivity was potential for the development of thermoelectric material. The oxidation of SiC/SiO₂/C composite sintered at 1600 °C which removed parts of residual silica and carbon, transformed the composite exhibiting p-type semiconductor with low values of Seebeck coefficient of to that exhibiting n-type semiconductor with high values Seebeck coefficient. A maximum of figure of merit of $6.25 \times 10^{-5} \text{ K}^{-1}$ was obtained at 140 °C in the oxidized SiC/SiO₂/C composite sintered at 1600 °C. The comparatively high figure of merit indicates the potentiality the material for thermoelectric purpose.

Keywords: Thermoelectric properties, silicon carbide, carbonized wood, silica.

Introduction

Recently the development of green and clean energy from biomass has received a great attention for replacing fossil fuels. One of the biggest concerns associated with the development of green and clean energy is to reduce the amount of carbon in the atmosphere and minimize the impact on global climate change. Various alternative energy sources have been studied for example the generation of liquid fuels from biomass conversion such as bio-ethanol (Sassner *et al.* 2008), bio-diesel (Oliveira *et al.* 2009), bio-oil by a fast pyrolysis (Balat *et al.* 2009), and aromatics by a catalytic fast pyrolysis (Carlson *et al.* 2009; French and Czernik 2010). Another potential energy is electric power generation using thermal or heat as initial energy form that is defined as thermoelectric power (Carpenter 2014). Indonesia as a tropical country with the long daylight provides potential the heat radiated from houses' roofs and walls. The other sources of heat are from engines of million motorcycles and cars or factories. The implementation of the electric power generation from the heat of houses will support the development of smart houses in which several electronic devices such as sensors, and others will be powered by this kind clean energy.

Thermoelectric power conversion employs thermoelements based on the effects of origination of thermoelectromotive forces (Anatychuk 2012). Thermal conduction for heat releasing from hot and cold side cause electrons move from cold to hot side in the p-type semiconductor, and from hot to cold side in the n-type semiconductor. It has been reported that porous SiC/C composite from carbonized wood which was prepared at 1400 °C for 30 min generated thermoelectric power with a maximum figure of merit of $3.38 \times 10^{-7} \text{ K}^{-1}$ at 200 °C

(Fujisawa *et al.* 2005). The open porous foam structure of thermoelectric oxide materials such as Ca₃CO₄O₉ makes the possibility to design efficient thermoelectric modules for waste heat sources (Noudem *et al.* 2008). The direct large area physical contact of thermoelectric foam elements with hot media will make them efficient electric power generators. The open porous thermoelectric materials with introduced porosities can be good candidates to confine phonons (lattice vibrations) in order to reduce the thermal conductivity if the pores can be made sufficiently small.

Porous SiC/SiO₂/C composites were produced from carbonized wood submerged in etylsilicate-40 solution under vacuum of 1 kPa following by a pre-treatment at room temperature that determined a solid-solid reaction during the sintering at 1400 – 1800 °C (Sulisty *et al.* 2010). The purpose of this study was to examine the morphology, microstructure and thermoelectric properties of porous SiC/SiO₂/C composites. Furthermore, the effect of oxidation of SiC/SiO₂/C composite was studied on the improvement of the thermoelectric properties. The morphology was observed by scanning electron microscope (SEM). The microstructure was analyzed by Raman spectroscopy and X-ray diffraction. The thermal conductivities were measured by a laser flash method. The thermoelectrical properties were measured by thermoelectric measurement apparatus.

Materials and Methods

Preparation of SiC/SiO₂/C Composites

Sugi (*Cryptomeria japonica*) wood particles were heated at a rate of 4 °C/min up to 700 °C in a laboratory scale electric furnace. The particles were held at 700 °C for 1 h under a N₂ gas flow of 100 mL/min. The resulting carbonized wood was then granulated using a blender and

sieved to yield particle sizes of 45~150 μm . A silica solution was prepared by diluting ethylsilicate-40 (Colcoat, Japan) with ethyl alcohol to obtain a 15% SiO_2 concentration by weight. The carbonized wood was submerged in the silica solution and held under a vacuum of 1 kPa for 90 min. The carbonized wood infiltrated with ethylsilicate-40 was then simply kept at room temperature until it dried. The final SiO_2 content calculated by the molar ratio was found to be 50% based on the dry charcoal weight. A dry weight of 1 g of carbonized wood infiltrated with SiO_2 was then placed into a 10 mm-internal-diameter graphite die with a length of 5 cm equipped with two graphite punches with a total length of 5 cm. To evaluate the effect of sintering temperature, $\text{SiC/SiO}_2/\text{C}$ composites were heated to 1400, 1600, and 1800 $^\circ\text{C}$ at a rate of 250 $^\circ\text{C}/\text{min}$ with a holding time of 30 min under a pressure of 15 MPa and a N_2 gas flow of 1 L/min using a pulse current sintering device (VCSP II, SS Alloy, Hiroshima), hereafter denoted as non-oxidized $\text{SiC/SiO}_2/\text{C}$ composite, respectively. The 5-mm-thickness samples obtained were cut into discs with a thickness of approximately 0.8 mm. Some samples prepared at 1600 $^\circ\text{C}$ were oxidized at 900 $^\circ\text{C}$ for 2 hr, in order to determine the improvement of thermoelectric properties, denoted as oxidized $\text{SiC/SiO}_2/\text{C}$ composite. The bulk density of these samples with and without oxidation treatment was determined by the Archimedes method.

Characterization

The microstructure of non-oxidized and oxidized samples was analyzed using Raman spectroscopy (Renishaw inVia) with an air-cooled CCD detector. An argon laser with a wavelength of 514.5 nm was used as an excitation source. The spectra were measured in the 400~1,800 cm^{-1} range. Seven 10-s accumulations were collected to give an adequate signal-to-noise ratio. The wave number was calibrated using the 520 cm^{-1} line of a silicon wafer. Spectral processing was performed using WiRE 2 software. X-ray diffraction (XRD, Rigaku-RINT-ultra X18) at 45 kV and 200 mA was used to determine the crystalline phase formed during sintering in non-oxidized and oxidized composite prepared at 1600 $^\circ\text{C}$. The data were collected as continuous scans, with a step size of $0.02^\circ 2\theta$ and a scan rate of $1^\circ 2\theta/\text{min}$ between $10^\circ 2\theta$ and $90^\circ 2\theta$. The bulk samples were analyzed without powdering since a random orientation of crystallites was assumed to be already present.

The morphology of samples with and without oxidation treatment was observed using scanning electron microscopy (SEM, JEOL-JSM-5310). The samples were observed directly without any coating. The thermal diffusivity (α) and the specific heat (C_p) were measured under a vacuum at room temperature and in a temperature range from room temperature to 150 $^\circ\text{C}$ by the laser flash method using a thermal constant analyzer (Ulvac, TC-7000H). The thermal conductivity (K_T) was calculated by the following equation:

$$K_T = \rho C_p \alpha \quad \dots\dots\dots (1)$$

where ρ is the bulk density of the specimen (g/cm^3), C_p is specific heat ($(\text{J}/\text{g})/\text{K}$), and α is the thermal diffusivity (m^2/s). The Seebeck coefficients and the electrical conductivity were measured under a vacuum in a temperature range from room temperature to 150 $^\circ\text{C}$ using a Seebeck coefficient/electrical resistance measuring system. The figure of merit of the specimen was calculated using the following equation:

$$Z = \frac{S^2 \sigma}{K_T} \quad \dots\dots\dots (2)$$

where Z is figure of merit (K^{-1}), S is Seebeck coefficient (V/K), σ is electrical conductivity ($\Omega^{-1} \text{m}^{-1}$), K_T is thermal conductivity ($\text{W}/(\text{m K})$).

Results and Discussion

The Raman spectra are shown in Fig. 1. In non-oxidized $\text{SiC/SiO}_2/\text{C}$ samples prepared at 1600 and 1800 $^\circ\text{C}$ and oxidized sample prepared at 1600 $^\circ\text{C}$, the transverse optic (TO) peak was observed at around 783~796 cm^{-1} , corresponding to phonon mode of cubic $\beta\text{-SiC}$ (Shiryaev *et al.* 2008) (Fig. 1a and b). The TO peak became more intense and narrower as the heat treatment temperature increased to 1800 $^\circ\text{C}$. Narrowing of the TO peak in both $\text{SiC/SiO}_2/\text{C}$ samples heated at 1600 and 1800 $^\circ\text{C}$ is related to ordering of the $\beta\text{-SiC}$ crystals. The Raman spectra of non-oxidized samples heated at 1400 $^\circ\text{C}$ did not appear the TO peak, indicating less formation of $\beta\text{-SiC}$. The Raman spectra of non-oxidized composite samples exhibited broad D and G bands at around 1349~1357 and 1582~1589 cm^{-1} , respectively, attributed to carbon material with a turbostratic structure (Ishimaru *et al.* 2007). The width of D and G band peaks corresponds to the degree of order in the carbon microstructure. The narrowing D and G bands was found with the increase of sintering temperature indicating the improvement the amount of ordering in the carbon microstructure. The D and G bands were not observed in the spectra of composite sample that had been oxidized, indicating that parts of the residual carbon had been removed.

The XRD patterns of non-oxidized and oxidized $\text{SiC/SiO}_2/\text{C}$ composites prepared at 1600 $^\circ\text{C}$ as shown in Fig. 2. Major diffraction peaks are observed at around $2\theta = 14$ and 17° , corresponding to the SiO_2 crystal phase, around $2\theta = 26$, 44 , and 79° , corresponding to the (002), (101), and (110) turbostratic carbon phase, respectively, and around $2\theta = 35$, 42 , 60 , and 72° , corresponding to the (111), (200), (220), and (311) reflections of the cubic $\beta\text{-SiC}$ phase (Cheung and Ng 2007; Shin and Exarhos 2007). As can be seen from the XRD patterns, both non-oxidized and oxidized composite samples prepared at 1600 $^\circ\text{C}$ contained 3 crystal

phases including SiO_2 , turbostratic carbon and $\beta\text{-SiC}$, supporting the Raman spectroscopy analysis. The intensity of peaks of SiO_2 crystal phase and turbostratic carbon decreased with the oxidation of sample at 900 °C for 2 h due

to residual silica (SiO_2) and carbon decreased. After the oxidation treatment the residual silica and carbon was still exist in the composite.

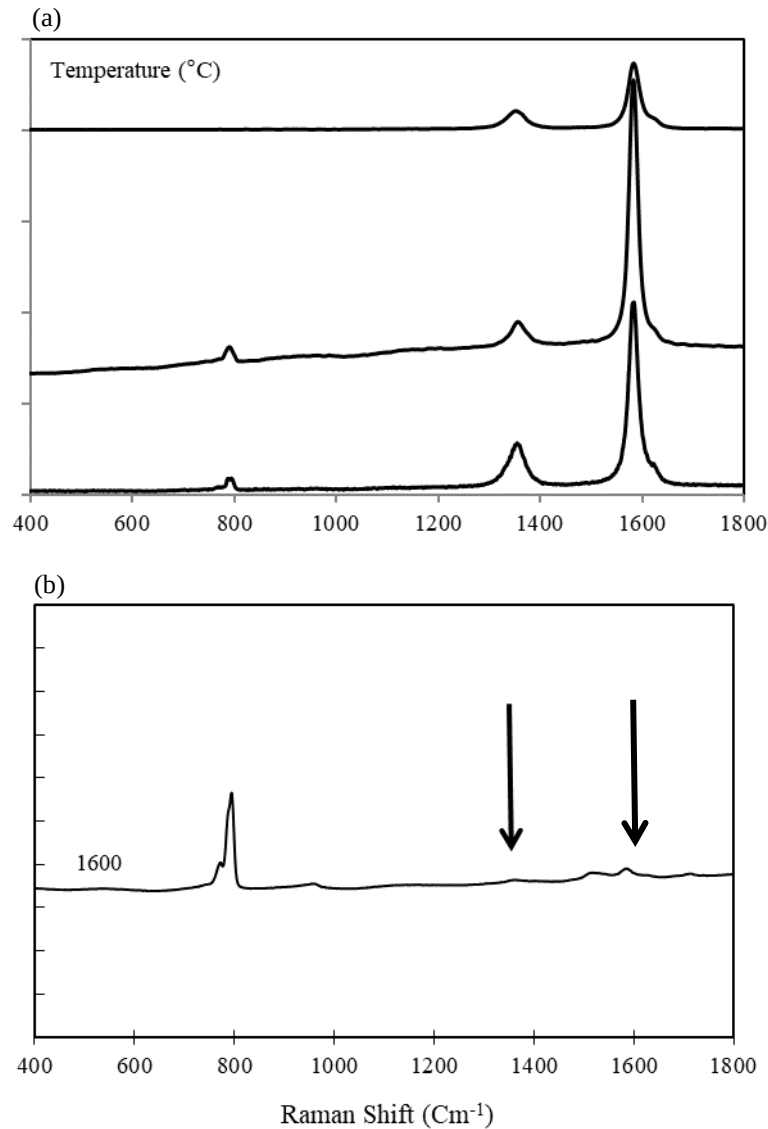


Figure 1. Raman spectra in the ranges of 400~1800 cm^{-1} of (a) non-oxidized $\text{SiC/SiO}_2/\text{C}$ composite samples prepared at different sintering temperatures and (b) oxidized $\text{SiC/SiO}_2/\text{C}$ composite sample prepared at 1600 °C. *TO* transverse optic, *D band* disorder, *G band* graphite. The arrows indicate the less intensive of the transverse optic peak.

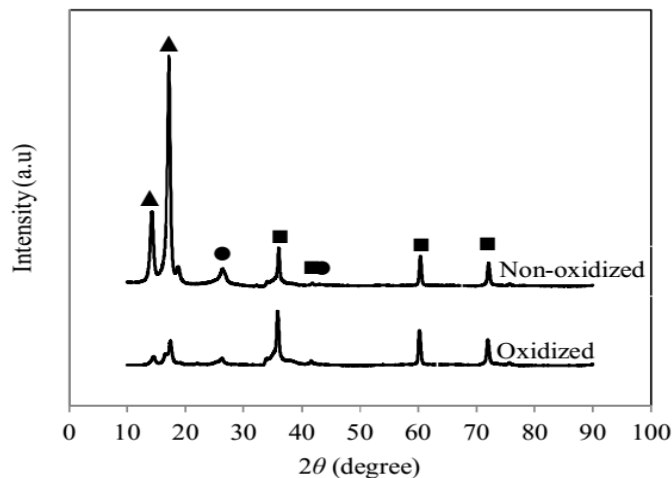


Figure 2. X-ray diffraction pattern of non-oxidized and oxidized SiC/SiO₂/C composite prepared at 1600 °C. (●) C, (■) β-SiC, (▲) SiO₂.

Figure 3 (a-c) shows SEM images of the morphology of non-oxidized SiC/SiO₂/C composites prepared at 1400, 1600 and 1800 °C. In the non-oxidized SiC/SiO₂/C composite prepared at 1400 and 1600 °C the particles were closely packed with spherical bodies distributed over the surface of the particles, as indicated by arrows, while in the samples that had been sintered at 1800 °C the particles were even more closely packed with smaller spherical bodies found on the surface of particles, as shown by arrow in Fig. 3 (c). It is considered that the morphological difference depends on the sintering temperature. Figure 3 (d) shows SEM images of the morphology of the SiC/SiO₂/C

composites sintered at 1600 °C followed by an oxidation at 900 °C for 2 h. The pores were clearly visible on the surface of the particles, as indicated by arrow. Oxidation of the residual silica and carbon of sample influenced the pore development. The morphology of oxidized composite possessed more porosity due to the removal of the excess silica and carbon comparing to that of non-oxidized composites. The removal of parts of the excess silica and carbon was confirmed by the disappearing of D and G bands on the Raman spectra and the decreasing intensity of both crystal phases on the XRD patterns.

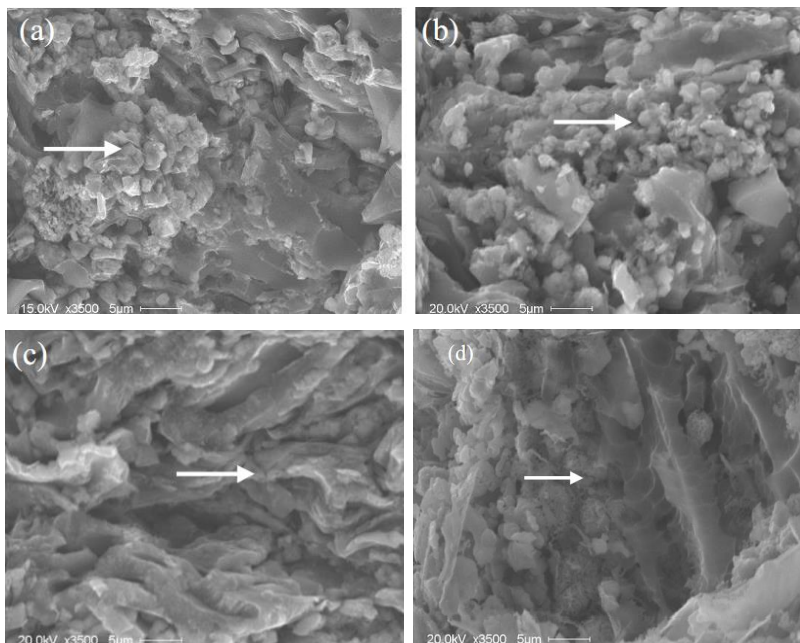


Figure 3. SEM images of non-oxidized SiC/SiO₂/C composites sintered at (a) 1400, (b) 1600, (c) 1800 °C and oxidized SiC/SiO₂/C composite sintered at (d) 1600 °C.

The bulk density of sample prepared at 1800 °C showed drastically increase value compared with the others samples as shown in Fig.4. The high density of samples prepared at 1800 °C were consistent with SEM observation which is showed the close packed particles with small spherical bodies on this sample. The bulk density of sample heated at 1600 °C was lower than that prepared at 1400 °C.

The large spherical bodies on the surface of particles and large pore size that was consistent with the SEM image influenced the low bulk density of sample prepared at 1600 °C. The oxidation of the excess silica and carbon that opened the large pore size, as shown in SEM image, decreased substantially the bulk density of sample prepared at 1600 °C.

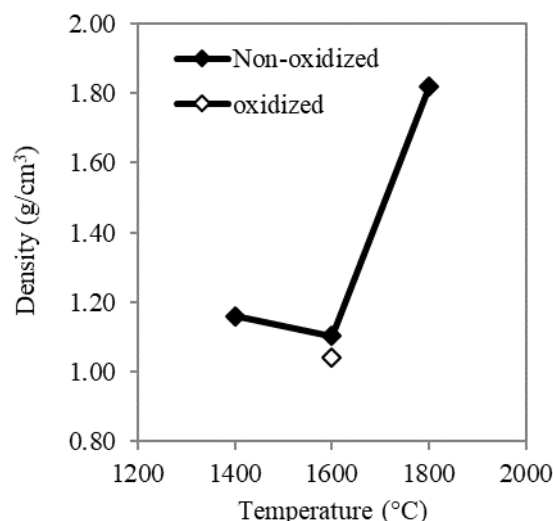


Figure 4. Relationship between bulk density of non-oxidized and oxidized SiC/SiO₂/C composites and sintering temperature.

Figure 5 shows the temperature dependence of the thermal conductivity of non-oxidized SiC/SiO₂/C samples prepared at 1400, 1600 and 1800 °C and also oxidized SiC/SiO₂/C sample prepared at 1600 °C. The thermal conductivity of the oxidized sample prepared at 1800 °C was higher than those prepared at 1400 and 1600 °C, as a result of a greater amount of β -SiC crystals indicated by the appearing the TO peak on the Raman spectra and the intensity of peaks $2\theta = 35, 42, 60,$ and 72° on the XRD patterns. The thermal conductivity of the non-oxidized SiC/SiO₂/C sample prepared at 1800 °C decreased with the increase of measuring temperature. The porosity contribution is dominated in the decreasing of thermal conductivity with the increasing temperature (Pappacena *et al.* 2007). The thermal conductivity of oxidized SiC/SiO₂/C sample prepared at 1600 °C was much lower than that non-oxidized sample. The thermal conductivity decreases with increasing porosity (Pappacena *et al.* 2007; Wang *et al.* 2007; Wei *et al.* 2007) as discussed previously. Pores influence the thermal conductivity of material as heat conduction is being scattered by pores. SiC/SiO₂/C composite prepared at 1600 °C with and without oxidation that exhibited low values of thermal conductivity was potential candidate for thermoelectric material. These sample were then measured its Seebeck coefficient as follow.

Figure 6 shows the temperature dependence of the Seebeck coefficient of non-oxidized and oxidized

SiC/SiO₂/C composite samples prepared at 1600 °C. The SiC/SiO₂/C composite prepared at 1600 °C, without oxidation (non-oxidized sample), showed a positive sign which was expected to be p-type semiconductor. The maximum value of Seebeck coefficient of SiC/SiO₂/C composite without oxidation was $7.51 \mu\text{VK}^{-1}$ at measuring temperature of 150 °C which was lower than that of polycrystalline 3C-SiC films with value about $51 \mu\text{VK}^{-1}$ at measuring temperature of 244 °C (Ivanova *et al.* 2006), SiC foam with value about $120 \mu\text{VK}^{-1}$ at measuring temperature of 800 °C (Wei *et al.* 2007), indium arsenide nanofilm with value around $55 \mu\text{VK}^{-1}$ at similar measuring temperature (Mavrokefalos *et al.* 2007) and β -FeSi₂ with SiO₂ and TiO dispersion with value of $200 \mu\text{VK}^{-1}$ at measuring temperature of 400 °C (Ito *et al.* 2006). The oxidation of SiC/SiO₂/C composite (oxidized sample) showed a negative sign corresponding to an n-type semiconductor. The oxidation treatment transformed p-type to n-type semiconductor and also improved much higher the Seebeck coefficient of SiC/SiO₂/C composite than that of SiC/SiO₂/C composite without oxidation. It has been reported that porous SiC ceramics have a high Seebeck coefficient (Fujisawa *et al.* 2008). The oxidation treatment removed parts of residual silica and carbon in SiC/SiO₂/C composite, as confirm by Raman spectra and XRD pattern, and changed the microstructure by developing large amount of pores in the composite, as confirm by SEM image. The highest Seebeck coefficient value of SiC/SiO₂/C composite

at measuring temperature of 150 °C was comparable with porous SiC composite (Fujisawa *et al.* 2008) and with CSMO foam with value of $-178 \mu\text{VK}^{-1}$ (Noudem *et al.* 2008).

The electrical conductivity and figure of merit of oxidized SiC/SiO₂/C composite sample prepared at 1600 °C in relationship with measurement temperature as shown in Fig. 7 (a-b). The electrical conductivity increased with the increase in measurement temperature which is similar with previous report in SiC/C composite (Fujisawa *et al.* 2005). The figure of merit of oxidized SiC/SiO₂/C composite which was calculated using Eq. (2) also increased as the

measurement temperature increased. A maximum value of the figure of merit of $6.25 \times 10^{-5} \text{ K}^{-1}$ was obtained at 140 °C in the oxidized SiC/SiO₂/C composite sample prepared at 1600 °C. The result of maximum figure of merit of oxidized SiC/SiO₂/C composite at measurement temperature range from 30~150 °C was higher than that on the previous result of SiC/C composite that obtained $3.38 \times 10^{-7} \text{ K}^{-1}$ at 200 °C (Fujisawa *et al.* 2005), SiC foam that obtained $1 \times 10^{-7} \text{ K}^{-1}$ at 800 °C (Wei *et al.* 2007), and porous SiC composite that obtained $2.01 \times 10^{-5} \text{ K}^{-1}$ at 700 °C (Fujisawa *et al.* 2008).

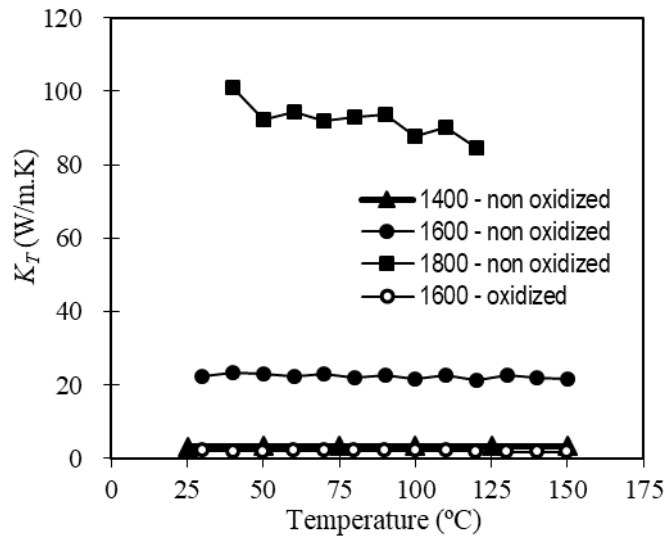


Figure 5. Thermal conductivities of non-oxidized SiC/SiO₂/C composite samples prepared at 1400, 1600 and 1800 °C and oxidized SiC/SiO₂/C composite sample prepared at 1600 °C measured in the ranges of 30~150 °C

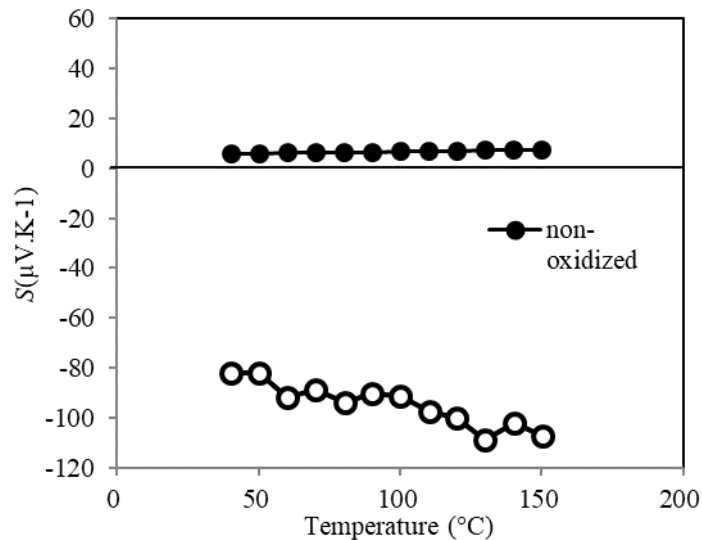


Figure 6. Seebeck coefficient of oxidized SiC/SiO₂/C composite sample prepared at 1600 °C measured in the ranges of 30~150 °C.

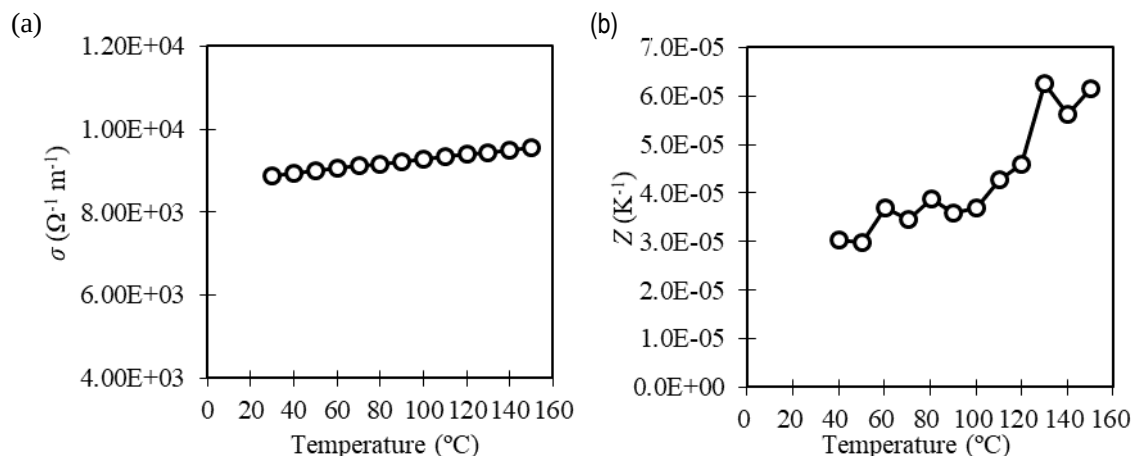


Figure 7. (a) Electrical conductivity and (b) figure of merit of oxidized SiC/SiO₂/C composite sample prepared at 1600 $^{\circ}\text{C}$ measured in the ranges of 30~150 $^{\circ}\text{C}$.

Conclusions

Porous SiC/SiO₂/C composites were developed from carbonized wood infiltrated with ethylsilicate-40 using a pulse current sintering apparatus at temperature range from 1400~1800 $^{\circ}\text{C}$. The SiC/SiO₂/C composite sintered at 1600 $^{\circ}\text{C}$ with the low value of thermal conductivity was potential for thermoelectric material. The oxidation of SiC/SiO₂/C composite sintered at 1600 $^{\circ}\text{C}$ which removed parts of residual silica and carbon, transformed the composite exhibiting p-type semiconductor with low values of Seebeck coefficient to that exhibiting n-type semiconductor with high value Seebeck coefficient. A maximum of figure of merit of $6.25 \times 10^{-5} \text{ K}^{-1}$ was obtained at 140 $^{\circ}\text{C}$ in the oxidized SiC/SiO₂/C composite sintered at 1600 $^{\circ}\text{C}$. This achieved figure of merit suggests that this treatment would suitable for further development in term of thermoelectric materials.

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Fuel Properties of Slab Wastes from Sengon Sawmills: A Case Study in Sleman and Wonosobo Regencies

Joko Sulisty, Binsar Edward Sianturi, and Raditya Ananta Rustantoputro

Abstract

Sengon (*Paraserianthes falcata* (L.) Nielsen) is a fast-growing and versatile species that has been established in community forests. Many sawmills utilize sengon wood as a raw material which generates wastes in the form of sawdust and slab consisting of a mixture of bark and wood. Those wastes are widely used by communities and home industries as fuel. The objective of this study was to characterize the energy properties of slab wastes from sengon sawmills in Wonosobo dan Sleman Regencies. The results showed that the calorific value and fuelwood value index (FVI) ranges were 4,089 to 4,749 cal/g and 2.71 to 18.74, respectively. The values of density ranged from 0.23 to 0.94 g/cm³. The proximate analysis showed that the values of moisture and ash contents ranged from 13.90 to 20.03% and from 0.30 to 4.59%, respectively, whereas volatile matter and fixed carbon contents ranged from 75.84 to 88.94% and from 10.23 to 20.62%, respectively. In general, the slab samples from Wonosobo gave higher values in fixed carbon content and FVI but smaller values in density, moisture content, volatile matter content, and ash content than those of the samples in Sleman. The bark part showed higher amounts in density, moisture content, fixed carbon content, and ash content but lower in volatile matter content, calorific value, and FVI than the wood part. Based on the wood consumption, sawmill recovery, calorific value, and dry weight biomass value, the potential annual energy from slab wastes in Sleman and Wonosobo reached $1,374 \times 10^{13}$ cal (equivalent to 1,525,222 L of kerosene) and 1.521×10^{14} cal (equivalent to 16,884,016 L of kerosene), respectively.

Keywords: falcata wood, sawn wood, biomass energy, calorific value, community forest

Introduction

Sengon (*Paraserianthes falcata* (L.) Nielsen syn *Albizia falcata*) is a fast-growing species and has various benefits in all parts of the tree, from leaves to roots. The characteristics and potentials of sengon wood are in accordance with industrial demands. This makes more and more industries, such as the sawmill and plywood industries, use sengon wood as raw material.

The abundance of sengon wood utilized by the industry, of course, generates a lot of residual processing wastes in the form of slab and sawdust. The slab wastes generated by the sawmill industry consist of bark and wood. The percentage of the bark was found to be about 10~20% of the stem depending on the species and growing conditions (Fengel and Wagener 1984). In another study it was found that the percentage of bark on sengon stems was 6.26% (Chin *et al.* 2013). It is assumed that the portion of the bark on the slab is higher than that of the stem. This large amount of wastes is widely used as firewood by the people surrounding community forests such as those in Wonosobo, Temanggung, Magelang, and Yogyakarta. In Yogyakarta, especially the Godean area, people use sengon wood as energy for the production of bricks and tiles. From field observations, one of the roof tile business owners stated that the consumption of sengon firewood in each industry reached 20~30 m³/year.

Although it has been widely used as fuel, research on the properties of sengon as energy wood is still limited, especially when it is in the form of slab waste. Previously,

the effects of bark, species, tree age, and tree position on energy characteristics have been observed in sengon and other species (Kumar *et al.* 2010; Kumar *et al.* 2011; Chin *et al.* 2013; Nasser and Arif 2014). Therefore, this study aimed to explore the characteristics of the slab waste fuelwood generated from sawmills located in two sengon producing centers, namely Sleman and Wonosobo Regencies.

Sleman Regency had the potential for sengon logs to reach 3,662 m³ spread over 11 sub-districts in 14 villages (Dinas Kehutanan Provinsi D.I.Yogyakarta 2011a). Meanwhile, community forests in Wonosobo in 2011 covered an area of about 18,982 ha, which was dominated by sengon plants with the potential for sengon production reaching 200,000 m³ per year (Kabupaten Wonosobo 2011). The importance of this research is to provide information on the influence of the site of the waste and plant parts on the calorific value produced in order to increase the economic value of the material as well as to estimate the potential biomass energy produced by sengon slab wastes as a substitute for fossil fuels such as kerosene.

Materials and Methods

Field Sampling

Samples were taken from the slab wastes of industrial center sengon sawmills. The collection was carried out in Kepil and Kaliwiro Sub-districts for Wonosobo Regency and in the Sub-districts of Tempel, Kalasan, and Cangkringan for Sleman Regency (Figure 1). In Wonoboso sawmills, the

materials were divided into large-diameter (more than 15 cm) and small-diameter (less than 8 cm) logs.

Sample Preparation

The slab wastes were collected from freshly sawn logs to prevent mixture with previous sawing wastes (Figures 2 and 3). Then, the obtained slabs were air-dried to ease the bark separation. After that, the bark was carefully separated

from the wood. A huge variation was observed in bark thickness from Sleman samples. The bark thickness of slabs from Cangkringan, Tempel, and Kalasan was about 0.47 cm, 0.13 cm, and 0.09 cm, respectively. From each part, 2 g specimens were taken for moisture content, specific gravity, ash content, and volatile matter content tests and 1 g specimens were taken for calorific value test.

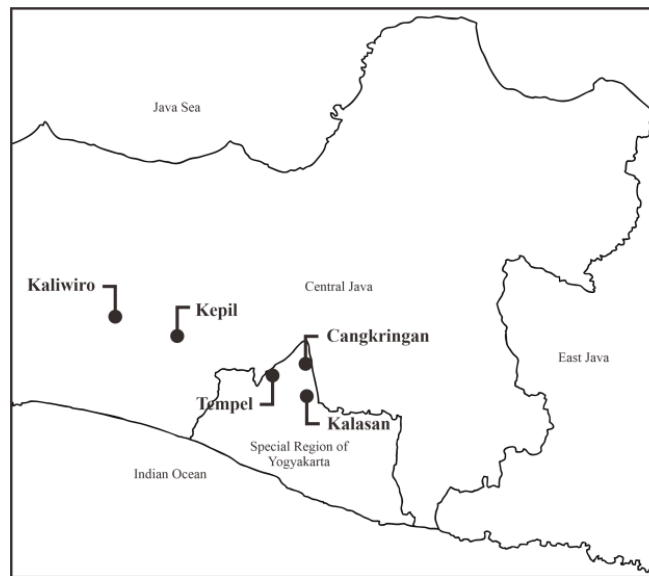


Figure 1. Geographic distribution of sampling sites.



Figure 2. Slab wastes from a sengon sawmill in Wonosobo Sleman.



Figure 3. Slab wastes from a sengon sawmill in Wonosobo.

Determination of Density (g/cm³)

Volumes of oven-dried samples were determined by water displacement method (ASTM D 2395-02, 2006). The densities of the samples (d) were determined using eqn. (1),

$$D = W_{OD}/V_{OD} \dots\dots\dots (1),$$

where W_{OD} is the oven-dry mass of wood and V_{OD} is the oven-dry volume of wood.

Determination of Calorific Value (cal/g)

The one-gram wood specimens were burned in an oxygen bomb calorimeter (Parr Instrument Company Inc, no. 1341 series 3403) for determining the calorific value. The testing referred to ASTM 5865-04.

Proximate Analysis

The air-dry weights (W_A) of the samples were recorded. These specimen blocks were oven-dried at $(103 \pm 2)^\circ\text{C}$ until they achieved constant mass (W_o). The moisture content (MC) was determined using eqn. (2),

$$MC (\%) = [(W_A - W_o) / (W_o)] \times 100 \dots\dots\dots (2).$$

The ash and volatile matter contents were determined according to ASTM D1102-84 and ASTM D3175-02, using a muffle furnace. The fixed carbon content (FCC) was estimated using eqn. (3),

$$FCC (\%) = [100 - (\% \text{ ash content} + \% \text{ volatile matter content})] \dots\dots\dots (3).$$

The testing for each characteristic was repeated three times.

Fuel Value Index

The fuel value index (FVI) was calculated using eqn. (4) (Purohit and Nautiyal 1987),

$$FVI = CV \times D / AC \dots\dots\dots (4),$$

where CV is the calorific value (kJ/g), AC is the ash content (g/g), and D is the density (g/cm³) of biomass.

Estimation of Sawmill Recovery

Recovery data was obtained through secondary data and direct observation in March 2011. The data were provided by the Industry and Trade Service of Sleman Regency and the Forestry Service of the Special Region of Yogyakarta. For primary data collection, several sawmills were selected in each of these areas. The selected sawmills consumed a minimum of 250 m³ of sengon raw material per month. Recovery calculation was performed with eqn. (5),

$$\text{Recovery } (\%) = (\text{Output} / \text{Input}) \times 100 \dots\dots\dots (5),$$

where input is the volume of round logs before conversion with Smalian's formula (m³) and output is the volume of lumber obtained after conversion (m³).

Estimation of Potential Slab Waste Energy

Potential annual energy estimation was carried out after calculating the wood consumption of the sengon processing industry, the waste potential, and the dry weight of the slab wastes. The wood consumption can be seen from the secondary data from the Forestry Service of Yogyakarta Special Region and the Forestry Service of Wonosobo Regency in 2011.

Based on the calculation of the recovery data, the potential for sengon sawmill wastes could be estimated. The waste potential was estimated with eqn. (6),

$$\text{Waste potential (m}^3\text{)} = WC - (WC \times R) \dots\dots\dots (6),$$

where WC is the wood consumption (m³) and R is the sawn recovery (%).

Biomass in energy production refers to living or recently dead biological material that can be used as a fuel source. This dry biomass can be expressed in units of kilograms or tons. The content of biomass in wood can be calculated using eqn. 7 (Brown 1997),

$$\text{Dry weight} = D_o \times V_o \dots\dots\dots (7),$$

where D_o is the oven-dry density (gr/cm³) and V_o is the oven-dry volume (cm³).

The potential energy estimation from slab wastes from sengon sawmills can be calculated using eqn. 7 eqn. 8 (Brown 1997),

$$\text{Estimated Energi (cal)} = DW \times CV \dots\dots\dots (8),$$

where DW is the dry weight (kg) and CV is the calorific value (kcal/kg).

Results and Discussion

Based on the proximate analysis, technically, a good fuelwood is to have a high level of fixed carbon content while other parameters are at low levels. Proximate measurements for sengon slabs from two sites are presented in Table 1. The moisture content was slightly wetter in the bark, while the moisture content in the wood was still in the range of air-dry moisture content (13~18%). The bark part showed higher values in fixed carbon and ash contents but lower in volatile matter content than did the wood part. In general, the samples from Wonosobo gave higher values in fixed carbon content but smaller in moisture, volatile matter, and ash contents than the samples in Sleman. The difference between large- and small-diameter logs can be seen in the Kepil sample. It was measured that big logs gave lower fixed carbon content values, but their ash and volatile matter content values were larger compared to those of small-diameter logs.

The results of measurement of density, calorific value, and FVI are presented in Table 2. The bark had higher values than the wood in density. A reverse trend was observed in the calorific value and FVI parameters. The samples from Sleman gave higher density values, especially in the bark part, than the Wonosobo samples. On the other hand, the calorific values of the bark of the Sleman samples showed lower levels than the Wonosobo samples. For the FVI, the wood samples in Sleman showed lower values than those in Wonosobo. Large-size logs (Wonosobo samples) showed higher values in density and calorific values than of small logs.

The specific gravity value range of sengon wood was found to be 0.24~0.49, the calorific value 4,664 cal/g, and the ash content 0.6% (Martawijaya *et al.* 2005). Research on sengon wood from Malaysia (Chin *et al.* 2013) showed specific gravity of 0.50, calorific value of 4,294 cal/g (high heating value), and ash content of 1.46%. The highest calorific value was observed in a Wonosobo sample (Kepil/big log, 4,749 cal/g), and so was the highest FVI value (Kepil/small log, 18.74). This variation in calorific value or FVI is thought to be due to the influence of the chemical properties of the material that were not measured in this study, such as the extractive and lignin contents. Previous studies have shown a significant correlation between calorific value and extractive content as well as between calorific value and moisture content in sengon wood (Chin *et al.* 2013). In other species, the contents of lignin, ash, and extractives were found to affect the calorific value (White 1987; Fuwape 1991; Nasser and Arif 2014). While the high values of density, lignin content, and extractive content in the bark would increase the calorific value, the comparatively high value of ash content and moisture content might decrease the calorific value and FVI levels. The average FVI of wood samples from Wonosobo shows a value of > 10, implying that slabs from the regency are more profitable as a fuel (Kataki and Konwer 2001) than those from Sleman. Although their FVI values were relatively low, in the future, sengon wood wastes will still be the main choice as biomass fuel due to their abundance.

Samples with large diameters in Wonosobo showed higher densities and calorific values than small-diameter logs. It is assumed that the large-diameter logs were from older wood or from the bottom parts of the trees as characterized by low percentages of juvenile wood and high extractive contents. A study on Eucalyptus hybrids showed that the calorific values of mature trees were higher than those of lower-age trees, but the ash content values were much higher in lower-age trees compared to mature trees (Kumar *et al.* 2010). The calorific values were found to decrease along the stem length towards the tree-top in *A. auriculiformis* and *C. equisetifolia* (Kumar *et al.* 2011). Furthermore, it was noticed that the ash content values in general were found to be higher in the top portions of the trees, and, similarly, they were found significantly higher in the case of *A. auriculiformis*. Thus, further research on the effects of age and position in the sengon tree is important. It was also noticed that some samples showed comparatively high ash content values. This has necessitated a study on the relation with toxic metals in sengon wood. Research on South African fuelwood showed that the calorific value should not be the only factor to be taken into account when evaluating fuelwood; negative environmental impact should also be considered (Manalula and Meincken 2009).

Table 1. Proximate analysis of of slab waste from sengon sawmills (average of three replications with standard deviation in parentheses)

Location	Parts	Moisture content (%)	Volatile matters content (%)	Fixed carbon content (%)	Ash content (%)
Sleman					
Kalasan	Wood	17.28 (0.66)	88.94 (0.31)	10.23 (0.35)	0.83 (0.05)
	Bark	20.03 (0.45)	83.94 (1.26)	11.47 (1.33)	4.59 (0.22)
Cangkringan	Wood	16.79 (1.08)	88.50 (0.99)	10.68 (0.87)	0.82 (0.05)
	Bark	19.50 (0.38)	83.58 (1.04)	12.65 (1.19)	3.77 (0.13)
Tempel	Wood	15.07 (0.23)	88.37 (0.55)	10.81 (0.59)	0.81 (0.03)
	Bark	19.82 (0.46)	84.64 (0.75)	12.21 (1.69)	3.40 (0.21)
Wonosobo					
Kepil	Big log	16.32 (0.25)	82.89 (0.55)	16.50 (0.45)	0.60 (0.11)
	Small log	13.90 (0.78)	85.65 (0.74)	13.96 (0.77)	0.30 (0.09)
	Bark	17.59 (0.45)	75.84 (2.38)	20.62 (2.32)	3.53 (0.07)
Kaliwiro	Big log	15.65 (0.26)	83.17 (0.80)	16.14 (0.79)	0.68 (0.60)
	Small log	15.82 (0.56)	83.71 (0.52)	15.98 (0.54)	0.38 (0.10)
	Bark	17.37 (0.55)	76.90 (0.65)	19.18 (0.73)	3.91 (0.18)

Sawmilling is the process of converting logs into lumber by using a variety of machines. The measurement of recovery (yield or conversion efficiency) showed the range of 45~71% (Table 3). Previous research on sengon wood sawing in a flat-sawn pattern (diameter of 24~50 cm) obtained a recovery of 45% with a productivity of 0.66 m³/hour (Rachman 1991). The recovery in Wonosobo site showed a smaller variation in value than that in Sleman site. This might be due to the various types and conditions of bandmills used, worker experiences (years), and sizes of logs converted.

Wood biomass is an important resource for generating energy with both environmental and economic benefits. The

estimation of potential energy showed a large difference between Sleman and Wonosobo sites (Table 4). This can be seen from the potential area and larger volume of timber in Wonosobo Regency. Although the average density of slab wastes was higher for the Sleman samples when compared to the Wonosobo samples (0.59 vs 0.38 g/cm³), the slab wastes in Wonosobo produced 11 times greater energy (1,521 × 10¹⁴ cal) than those in Sleman (1,374 × 10¹³ cal). Furthermore, if we assume that fuel wood substitutes domestic heating oil (kerosene), then the amount will equal to about 1.52 million litres in Sleman or 16.8 million litres in Wonosobo.

Table 2. Density, calorific, and fuelwood value index of slab waste from sengon sawmills (average of three replications with standard deviation in parentheses).

Sawn industry	Parts	Density (g/cm ³)	Calorific value (cal/g)	Fuelwood Value Index
Sleman				
Kalasan	Wood	0.23	4,546	5.34
	Bark	0.94	4,089	3.52
Cangkringan	Wood	0.34	4,720	8.16
	Bark	0.84	4,215	3.94
Tempel	Wood	0.31	4,697	7.46
	Bark	0.89	4,274	4.69
	Average	0.59 (0.33)	4,423 (266)	5.51 (2.06)
Wonosobo				
Kepil	Big log	0.30	4,749	10.22
	Small log	0.25	4,645	18.74
	Bark	0.52	4,524	2.71
Kaliwiro	Big log	0.36	4,690	15.65
	Small log	0.26	4,581	15.82
	Bark	0.59	4,474	2.90
	Average	0.38 (0.11)	4,637 (88)	11.00 (6.34)

Remark : big log = diameter >15 cm, small = log diameter < 8 cm

Table 3. Recovery assesment of sengon sawmills in Wonosobo and Sleman Regencies

No	Name of sawn industry	Input/month (m ³)	Output/month (m ³)	Recovery (%)
Wonosobo - Kepil				
1	Mitra Abadi	270.0	159.30	59.0
2	Rizquan Abadi	500.0	300.0	60.0
3	Eka Abadi	350.0	201.25	57.5
Wonosobo - Kaliwiro				
1	Karunia Abadi	380.0	228.0	60.0
2	Maju Makmur	400.0	246.0	61.5
3	Kambium Prima	600.0	360.0	60.0
Average				59.70
Sleman				
1	CV Sinar Albasia**	985.15	616.43	62.57
2	Remaja Sejahtera*	233.0	125.0	53.64
3	PT Citra Raharja Utama*	2450.0	1740.0	71.02
4	PT Perwira Karya**	211.40	91.98	45.31
5	UD Sengkati Bersaudara	270.0	157.0	58.0

Remark: * Source = Dinas Perindustrian dan Perdagangan Kabupaten Sleman (2011), ** Source = Dinas Kehutanan D.I.Yogyakarta (2011a).

To safely use wood biomass for energy, the available wood biomass should be estimated from an economic perspective. A previous study on some small- and medium-scale enterprises in the food and beverage industry in Wonosobo showed that the fuel cost of using wood pellets was smaller than the fuel cost of using other fuels, such as firewood, gas, and sawdust (Sylviani *et al.* 2013). Despite some weaknesses that exist in the use of wood or bark materials, using them as substitutes for fossil materials such as kerosene in a year can save up to about Rp102.5 billion for Wonosobo and Rp 9.2 billion for Sleman (Table 4). The

assumption is that kerosene sold for Rp 6,071/L (in 2011) with a calorific value of 10,986 cal/g and specific gravity of 0.82 (Staffel 2011). Another scheme is that the enormous amount of sengon wood wastes is converted into briquettes (Saputro & Widayat 2016) and carbonized into charcoal, rocket stove fuel (Wibowo 2020), as well as wood activated charcoal on solid propellants for rocket fuel (Manistatho *et al.* 2021). It will be more advantageous for megawatt electricities as charcoal has a higher calorific value than that of wood itself.

Table 4. Energy estimation of slab waste potential from sengon sawmills per year

No	Characteristics	Equation	Sleman	Wonosobo
1	Wood consumption (m ³)		12,406*	213,715 **
2	Recovery (%)		57.75	59.70
3	Waste potential (m ³)	WC-(WC × Recovery)	5,247.738	86,127.145
4	Density (g/cm ³)		0.592	0.383
5	Dry weight(kg)	density × waste potential	3,106,660	32,986,641
6	Calorific value (kcal/kg)		4,424	4,610
7	Energy estimation (cal)	dry weight × calorific value	1.374×10 ¹³	1.521 × 10 ¹⁴
8	Kerosene equivalent (L) ^a	energy estimation/(10.986 × 0.82)	1,525,222	16,884,016
9	Economical value (Rp) ^b	(× Rp 6,071)	9,259,627,552	102,502,861

Remark: * Source= Dinas Kehutanan Provinsi D.I.Yogyakarta (2011b); ** Source = Kabupaten Wonosobo (2011), WC = wood consumption; a = kerosene's calorific value of 10,986 cal/g and specific gravity of 0,82; kerosene price (2011) = Rp 6,071.

Conclusions

The understanding of fuel properties is very important in the utilization of any material as fuel. The energy properties of slab wastes generated by sawmills in Sleman and Wonosobo Regencies were determined. Besides the sawmill location, the stem part (wood and bark) and log size factors were also indicated to affect the energy

characteristics of the slabs. The highest calorific value (Kepil/big log, 4,749 cal/g) and FVI (Kepil/small log, 18.74) were observed in the Wonosobo samples. The sawmill recovery value ranged from 45 to 71%. Based on secondary data, the wood consumption in Wonosobo was considerably higher than that in Sleman. It was calculated that the estimated potential energy produced by sawmill slab wastes in Sleman and Wonosobo reached 1,374 × 10¹³

calories (equivalent to 1,525,222 L of kerosene) and 1.521×10^{14} calories (equivalent to 16,884,016 L of kerosene) a year, respectively. In addition, the effect of log diameter on calorific value have been observed in this experiment. Due to huge variations of log diameter in sawmill from both sites, therefore, the relationship between the two should be determined in the future works.

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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.

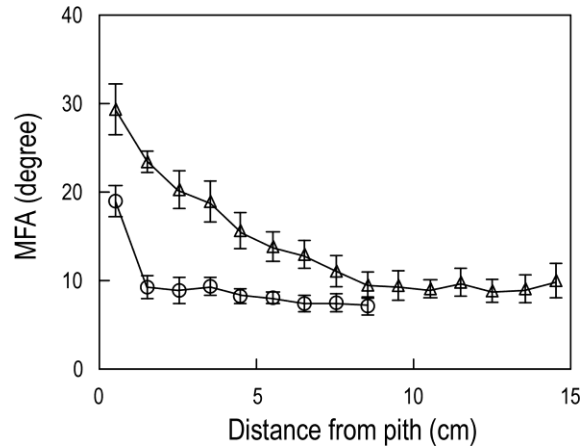


Figure 3. Radial variation of microfibril angle of the S2 layer in tracheid. Open circle, *Agathis* sp.; open triangle, *Pinus insularis*; Bars indicate the standard deviation. (Source: Ishiguri *et al.* 2010)