THE EFFECT OF LIGNIN COMPOSITION ON DELIGNIFICATION RATE OF SOME TROPICAL HARDWOODS

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ABSTRACT

The effect of lignin composition on delignification rate and pulp properties of albizia (*Paraserianthes falcataria* L. Nielsen), gmelina (*Gmelina arborea* Linn.), yellow meranti (*Shorea acuminatissima* Sym.), and kapur (*Dryobalanops aromatica* Gaertn.) woods was determined. The lignin characterization showed that the syringyl-guaiacyl ratio of albizia, gmelina, kapur, and yellow meranti woods are 2.03, 2.02, 1.87, and 1.30, respectively. It means that the lignin structure of the above mentioned woods are predominated by syringyl units. To assess the influence of lignin structure on delignification rate and pulp properties, these wood samples were then subjected to the kraft pulping process under the following conditions: wood-to-liquor ration = 1:4, cooking temperature = 170 °C, time to cooking temperature = 90 minutes, cooking time = 90 minutes, total active alkali = 16 %, sulfidity = 22.5 %. From the present investigation it can be explained that the delignification rate of hardwood containing syringyl-rich lignin was higher than that of hardwood containing syringyl-poor lignin. The physical properties of pulp from hardwood containing syringyl-rich lignin are also higher than that of hardwood containing syringyl-poor lignin.

Keywords : tropical hardwoods, lignin composition, syringyl-guaiacyl ratio, delignification rate, pulp properties

The process of delignification followed two pseudo first order rate kinetics in terms of lignin concentration. A faster rate of delignification was ollowed by a slower process. The rate of delignification of the initial faster process was directly proportional to the molar ratio of syringyl to guaiacyl units of lignin (Singh *et al*., 1982). Syafii & Yoshimoto (1991) reported that in one-hour chlorite treatment the rate delignification of hardwoods species such as ulin (*Eusideroxylon zwageri*), bangkirai (*Shorea laevis*), merawan (*Hopea pierrei*), and tekaliu (*Homalium foetida*) which containing guaiacyl-rich lignin was much slower than that of hardwoods containing syringyl-rich lignin.

Although the tropical hardwoods constitute a vast source of cellulose fibers, their limited use in pulp and paper industry on the one hand, could be described as due to their heterogenity. On the other hand, it may be due to the fact that practically little is known about the chemical composition of lignins of domestic tropical hardwoods and their reactions during pulping processes. Lignin is considered to be a polymeric natural products arising from an enzyme initiated dehydrogenative polymerisation of three types of primary precursors, namely (i) guaiacyl alcohol (ii) syringyl alcohol (iii) *p*-coumaryl alcohol. The constitutional model of lignin is composed of many reactive groups such as ether of various types, primary and secondary alcoholic hydroxyl groups, phenolic hydroxyl groups, carbonyl groups, methoxyl groups, aromatic sites of phenyl propanoid structure (Lewis & Sarkanen, 1998).

It is well known that chemically the lignins vary from species to species even in the same genus and their composition is also highly influenced by the climatic conditions of the place where the tree is growing. As stated by Higuchi (1985) that the softwood lignin is predominated by monomeric guaiacyl units which are connected by both ether and carbon-carbon linkages, while the hardwood lignin is composed of approximately equal amount of guaiacyl and syringyl units and connected by linkages similar to those of softwood lignin. As a result of this inherent variation in lignin composition, the pulping characteristics are bound to be highly species dependent. Therefore, in order to increase or rationalize the use of tropical hardwoods fiber in pulp and papermaking, a detailed investigation on the chemical composition of lignin and their influences during kraft pulping and their pulp properties was undertaken.

METHODS

Material

Four samples of wood species, namely albizia (*Paraserianthes falcataria* L. Nielsen), gmelina (*Gmelina arborea* Linn.), kapur (*Dryobalanops aromatica* Gaertn..), and yellow meranti (*Shorea acuminatissima* Sym.) woods were used in this experiment. The albizia and gmelina woods were taken from Bogor and Sumedang, respectively, while the kapur and yellow meranti woods from Berau (East Kalimantan). The result of pre-investigation showed that the wood samples used in this experiment having a basic density of 310 kg/m^3, 480 kg/m^3, 570 kg/m^3, and 620 kg/m^3 respectively.

Methods

Sample Preparation

A Willey mill has been used to prepare woodmeal that pass through a 40-mesh screen and retain on a 60-mesh screen. The woodmeal was then air-dried to about 15% of moisture content. Extraction of the woodmeal with alcohol-benzene (1:2 v/v) has been

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carried out in order to prepare an extractive-free woodmeal sample, which is then used to determine the Klason lignin content and lignin composition by nitrobenzene oxidation procedure.

After bark removal the wood sample was converted to chips at the size of about 2.5 cm x 2.5 cm x 0.25 cm, followed by air drying to about 15% of moisture content. The air-dried wood chips is then used for determination of delignification rate in the pulping process. Prior to pulping, the moisture content of wood chips should be determined exactly to calculate the need of cooking liquor in the pulping process.

Characterization of Lignin

The most common method for the quantitative determination of lignin in wood is based on gravimetry (Klason lignin). In this study the Klason lignin content was determined according to the procedure described by Dence (1992). The wood sample is first treated with 72 % sulfuric acid and subsequently heated with dilute acid to hydrolyze the polysaccharides to soluble fragments, after which the solid residue (Klason lignin) is washed, collected, dried, and weighed. To determine the lignin composition, the procedure of alkaline nitrobenzene oxidation reported by Syafii & Yoshimoto (1991) was applied. Approximately 50 mg of alcohol-benzene extracted wood meals was oxidized with 0.24 ml of nitrobenzene and 4 ml of 2N KOH in a stainless steel tube for 2 hours at 160^0 C. At the end of oxidation period, the stainless steel tube was immediately cooled down in running water to stop the reaction, and the solution was filtered. The oxidation products which still remaining in the residue was washed with a small amount of 0.1N KOH solution. After removing nitrogenous compounds from alkaline solution with chloroform, the pH of this alkaline solution was adjusted to 2.5 with 1N HCl solution. Finally, the solution was extracted with 30 ml of chloroform. This extraction was repeated four times. The extract was then quantitatively analyzed by gas chromatography under the following conditions: BPX5 0.5 column, N_2 carrier gas, 0.4 ml per minute flow rate, temperature of 200 ^{0}C, FID detector, 300 ^{0}C temperature injection, detector temperature of 350 ^{0}C.

Lignin composition was quantitatively determined by calculating the peak area of vanillin (guaiacaldehyde) and syringaldehyde from gas chromatogram. The total aldehyde as well as the syringyl-guaiacyl ratio were also determined. All of this parameters were calculated based on the Klason lignin content of wood samples.

Pulping Process

To study delignification rate, wood chips was pulped by using conventional kraft process in the laboratory digester. The kraft pulping process are applied because it is not only the dominant alkaline pulping technique for wood raw material but also the most important pulping process altogether. In this experiment the kraft pulping process is applied according to the methods conducted by Gomide *et al.* (1997) with some modifications. The pulping was carried out in a rotating digester and electrically heated. In applying this technique, 3 different cooks were carried out using different cooking times. Each cook was 30 minutes longer than the previous one (cooking times = 0, 30, 60, and 90 minutes). The cooking conditions were: chips = 150 grams, wood-to-liquor ratio = 1 : 4, maximum cooking temperature = 170 ^{0}C, time to maximum temperature = 90 minutes, total active alkali = 16 %, based on oven-dry chips, sulfidity = 22.5 %. All cooks were carried out in duplicates.

Determination of Delignification Rate

The pulp yield and the kappa number of pulp are parameters that can be used to determine the delignification rate during pulping process. The determination of pulp yield and kappa number were applied according to the Tappi T 236 cm-85 (TAPPI Testing Methods, 1989).

Determination of Physical Properties

This procedure describes the testing of pulp handsheet for their strength and other physical properties. Information derived from handsheet testing indicates pulp quality and is a measure of the potential contribution of the pulp to the strength of the finished paper products. The physical properties of pulp was carried out according to the Tappi T 220 om-88 (TAPPI Testing Methods, 1989).

RESULTS AND DISCUSSION

Extractives Content

To asses the normality of extractives content in the wood samples, ethanol-benzene extract yield was determined (Table 1). The total amount of ethanol-benzene extractives obtained from the wood of albizia, gmelina, yellow meranti and kapur are 8.14 , 9.15 , 13.6, and 15.65 % based on oven-dry wood sample respectively. The acetone extracts obtained from this experiment is relatively higher than those of the average of extractives content in the tropical hardwoods. Tsoumis (1991) stated that the content of extractives varies from less than one percent to more than ten percent depends on the family, species, and tissue. The acetone extract obtained from the heartwood of gonzalo alves (*Astronium fraxinifolium*), rasamala (*Altingia excelsa*), ulin (*Eusideroxylon zwageri*), and sonokeling (*Dalbergia latifolia*) was reported reach to 3.34 , 2.64 , 8.18 , and 8.23 % respectively (Syafii *et al.*, 1985; Syafii & Yoshimoto, 1993; Syafii, 2000).

Table 1. The ethanol-benzene extractives content obatined from four species of tropical hardwoods

No.	Wood samples	Content (% based on oven-dry wood)
1.	Albizia	8.14
2.	Gmelina	9.15
3.	Yellow meranti	13.60
4.	Kapur	15.65

It is interesting to note that the ethanol-benzene extractives content has a correlation with the specific gravity of wood samples in which the higher specific gravity show the higher of extractives content. It could be understood since the extractives content is one of the factors which influence the specific gravity of wood. Tsoumis (1991) stated that extractives are compounds of varying chemical composition that are not part of the wood substances, but are deposited within cell walls and cavities. Higher amount of extractives is a cause for the higher density of wood and the removal of extractives results in reduction of density.

Lignin Characteristics

The Klason lignin content of four wood species is resumed in Table 2. The lignin content of the tropical hardwoods tested in this experiment is in the range of 22.40 to 30.72 %. The Klason lignin content of albizia wood is the lowest whereas the lignin content of kapur wood is the highest.

Table 2. The lignin composition of wood samples (indicated by S/G ratio) calculated from nitrobenzene oxidation products *)

Wood samples	Klason lignin (%)	Guaiacyl (G) (%)	Syringyl (S) (%)	Total aldehyde (%)	S/G Ratio (molar)
Albizia	22.40	7.00	14.22	21.22	2.03
Gmelina	25.50	8.07	16.30	24.37	2.02
Yellow meranti	30.00	9.56	17.87	27.43	1.87
kapur	30.72	11.94	15.51	27.45	1.30

*) Based on the Klason lignin content.

In order to get more detailed information on the lignin characteristics, the structural composition of lignin of all the four species was determined by analysing the alkaline nitrobenzene oxidation products on a gas chromatogram. Table 2 represented the oxidation products of lignin of the four species. The total aldehyde yields of four wood samples are in the range of 21.22 to 27.45 % on the basis of Klason lignin content. Table 2 also showed that the S/G ratio all the four wood samples are greater than one. It means that the amount of syringaldehyde content of the wood samples are higher than that of guaiacyl content. The values of S/G ratio both in yellow meranti and kapur woods are relatively lower than those of albizia and gmelina woods. It is indicating thereby that the lignin of yellow meranti and kapur woods contain a large amount of guaiacyl units, suggesting that the lignin macromolecules of these woods have more sites for internal condensation.

These results show that the amount of syringyl units in the lignin of tropical hardwoods investigated follow the order of albizia wood > gmelina wood > yellow meranti wood > kapur wood. These results are of great importance in contemplating and assessing the delignification characteristics of these woods, since S/G ratio should have a correlation with delignification rate. In other words, lignin containing higer amount of syringyl units should have less number of site available for possible internal condensation during delignification process. As stated by Fengel and Wegener (1984) that as in the case of sulfite pulping, the alkaline pulping reactions with lignin are also nucleophilic reactions which are contributing to the degradation and dissolution of lignin, and condensations of lignin units to fragments with increased molecular weight and reduced solubility.

Rate of Delignification

To assess the influence of lignin structure on delignification rate and pulp properties, these wood samples were then subjected to the kraft pulping process. The kappa number of pulp is usually used to determine the delignification rate during pulping process. The yield and the kappa number of pulp produced from four species of tropical hardwoods were presented in Table 3.

Table 3 showed that at 60 and 90 minutes cooking times the pulp yield of albizia and gmelina woods are much higher than that of yellow meranti and kapur woods. The results also showed that at the same cooking times the kappa number of pulp of albizia and gmelina are lower than that of yellow meranti and kapur woods. The low kappa number means that the delignification rate of these woods are faster than that of yellow meranti and kapur woods. The slow rate of delignification of yellow meranti and kapur woods might be due to the physical and chemical factors.

The physical factor is usually related to the wood density. Determination of specific gravity of the wood samples showed that the specific gravity of albizia, gmelina, yellow meranti and kapur woods are 0.31, 0.48, 0.57, and 0.62, respectively. Yellow meranti and kapur woods having higher specific gravity are more difficult to be delignified compared to the albizia and gmelina woods. From this results, it can be stated that the delignification rate of wood samples might be correlated with the specific gravity. Specific gravity is a measure of the weight of wood substances contained in a unit of volume of wood. Cell walls of all wood species should have the same specific gravity. Therefore, variation in specific gravity of wood species reflects differences in

Table 3. Yield and kappa number of pulp produced from four species of tropical hardwoods

Wood Samples	Cooking time at maximum temperature (minutes)							
	0		30		60		90	
	Yield (%)	Kappa Number	Yield (%)	Kappa Number	Yield (%)	Kappa Number	Yield (%)	Kappa Number
Albizia	42.75	33.79	48.55	31.65	49.15	28.05	49.98	22.71
Gmelina	49.25	33.35	44.40	30.85	53.90	25.85	49.15	20.70
Yellow meranti	43.60	42.85	39.80	35.75	34.48	31.33	31.55	30.75
Kapur	44.65	40.85	42.07	36.85	39.70	32.39	40.20	30.60

thickness of cell wall. A wood species with a high specific gravity posseses a thick cell wall, and consequently the cell lumen of this wood is small (Tsoumis, 1991). In this experiment, the wood samples of yellow meranti and kapur woods which have high specific gravity are difficult to be delignified. These results might be explained by the limited impregnation of cooking chemicals into the cell wall.

The chemical factor which affects the slow rate of delignification of yellow meranti and kapur woods is usually related to their lignin chemical structure. The results of this experiment showed that the rate of delignification increases with the increase in S/G of lignin of the wood samples. The same results were also found by previous investigators (Singh *et al.*, 1982; Syafii & Yoshimoto, 1991). These results means that the delignification of hardwood containing syringyl-rich lignin faster than that of hardwood containing syringyl-poor lignin. As previously described, the syringyl content in the lignin of yellow meranti and kapur woods are low, and consequently these two wood samples gave low rate of delignification. Therefore from this experiment, it can be suggested that the lignin structure of the wood samples is correlated with the rate of delignification by kraft pulping process.

Pulp Properties

The following data describes the strength and other physical properties of un-bleached pulp handsheets. The pulp handsheets was prepared by beating pulp at 45° SR with the grammature of 60 gram/m^2. The physical properties examined in this experiment are density, tear index, tensile index, burst index, and breaking length. This physical properties is listed in Table 4.

The physical characterization of unbleached pulp showed that the physical properties of yellow meranti wood is comparable to the kapur wood. The pulp properties of albizia has also showed the same phenomena in which it is comparable to the gmelina wood. However, the pulp properties of yellow meranti and kapur woods are much lower than those of albizia and gmelina woods. This low properties might be due to the low S/G ratio of these woods. As described before that the hardwood containing syringyl-rich lignin (high S/G ratio) showed the higher rate of delignification compared to those of hardwood containing syringyl-poor lignin (low S/G ratio), and as the consequence, it produces higher kappa number pulp. Casey (1980) stated that the high kappa number pulp correlates with high residual lignin. Therefore the physical properties of this pulp is lower than that of low kappa number pulp which contain low residual lignin.

Table 4. The physical properties of unbleached kraft pulp produced from four species of tropical hardwoods

Properties	Pulp-sheet samples			
	Albizia	Gmelina	Yellow Meranti	Kapur
Density, g/cm^3	0.68	0.57	0.28	0.28
Tear index, mN.m^2/g	5.09	4.29	0.33	0.24
Tensile index, N.m/g	102.7	90.9	65.6	52.5
Burst index, kN/g	6.37	5.75	3.02	2.23
Breaking length, km	5.55	4.67	0.36	0.26

CONCLUSION

The syringyl-guaiacyl ratio of albizia, gmelina, yellow meranti, and kapur woods were 2.03, 2.02, 1.87, and 1.30 respectively. It means that the lignin structure of the above mentioned wood samples are predominated by syringyl units.

The delignification rate of hardwood containing syringyl-rich lignin was higher than that of hardwood containing syringyl-poor lignin. The physical properties of pulp from hardwood containing syringyl-rich lignin were also higher than that of hardwood containing syringyl-poor lignin.

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