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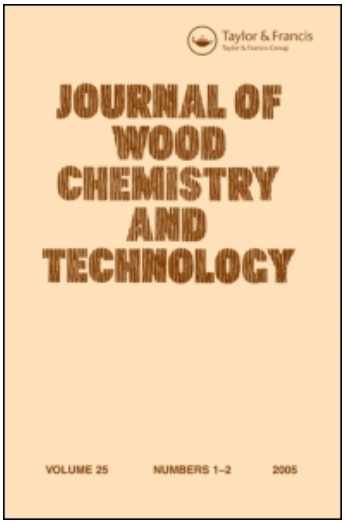

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AUTOHYDROLYSIS OF TROPICAL HARDWOODS

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ABSTRACT

Eight tropical hardwoods (Malaysian) were subjected to autohydrolysis at 195°C for 10 - 100 min, followed by extraction with 90% dioxane. A linear relationship was obtained between the % of water soluble extract, after autohydrolysis, and the % of hemicellulose present in the respective woods. Comparison of the different woods for their response to autohydrolysis was made, based on the % of maximum extractable lignin obtained. It was found that the effectiveness of autohydrolysis was not related to the density of the wood, or to the taxonomic type, but to a certain extent to the content of lignin present in the wood.

INTRODUCTION

Interest in autohydrolysis or the steam treatment, at high temperature and pressure, of lignocelluloses, extends into many diverse areas. Steam-exploded wood, as in the Masonite process[1], continues to be considered as a potential pulping method[2-4], usually with some modifications to avoid extensive fiber deterioration and for non-wood materials. Alternatively, the steaming process is also utilized for the production of feed for ruminants[5-7], because of the higher digestibility of treated lignocellulose, and as an effective pretreatment for increased enzymatic susceptibility of the cellulose in hardwoods and agricultural residues[8-10]. Autohydrolysis followed by solvent extraction, can effect the separation of lignocellulosic components, which are potential feedstocks for chemicals, energy and food[11-13]. Other studies focussed on the characterization of the exploded fiber[14], the water-soluble hemicellulose fraction[15] and the extracted lignins[16-18], from

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which a reaction mechanism was postulated. Steam-treated sawdusts have been used recently as casing material for the cultivation of Agaricus bisporus[19,20] and as substrates for Lentinus edodes[21].

An inherent limitation of autohydrolysis is that the effectiveness of the treatment is very much dependent on the type of wood treated. Generally, softwoods respond poorly to autohydrolysis, as is illustrated by the results of Shimizu et al.[8], which showed a wide range of susceptibility of enzymatic hydrolysis of the different autohydrolyzed wood.

In the present study, the response to autohydrolysis, as measured by the amount of extractable lignin after treatment, of eight tropical hardwoods, of different chemical compositions, was investigated. The chemical and physical properties of the wood that are associated with the effectiveness of the autohydrolysis treatment was also considered.

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RESULTS AND DISCUSSION

Autohydrolyzed Residue (R) and Extracted Autohydrolyzed Residue (ER)

The data tabulated in Table 1, show that after autohydrolysis, about 10 - 30% of each of the different tropical hardwoods became soluble on hot water extraction. This soluble fraction increased with treatment times. Subsequent extraction of the remaining R with 90% dioxane removed another wood component, namely lignin. The overall yields of ER for the different tropical hardwoods were 53 - 81%. The general behaviour of these tropical hardwoods to autohydrolysis and extraction is similar to that observed for other hardwoods[12].

Researchers have shown that the hot water soluble extract contained mainly hemicellulose, their monomeric sugars and degradation products, with small amounts of low molecular weight lignin[15,22,23]. An interesting correlation is shown in Figure 1, between the % water soluble extract (= 100% - % $R_{minimum}$) and the % hemicellulose present in wood (= % Holocellulose - % α-cellulose, found in Table 2). The experimental points approximate a linear relationship in which the amount of water extract equals the hemicellulose present in the respective

TABLE 1

Percentage Yields of Autohydrolyzed Residue (% R) and Extracted Autohydrolyzed Residue (% ER).

Vernacular Name (Malaysian)	Species	Time of Autohydrolysis (min)[a]							
		% R (Based on EFWM)				% ER (Based on EFWM)			
		20	40	60	100	20	40	60	100
Light Hardwoods									
Jelutong	*Dyera costulata*	77	72	72	73	73	63	63	63
Light Red Meranti	*Shorea* spp.	90	85	85	83	81	78	75	72
Ramin	*Gonystylus bancanus*	80	79	78	78	71	64	62	63
Medium Hardwoods									
Kapur	*Dryobalanops aromatica*	78	77	77	78	69	67	66	65
Rubber Wood	*Hevea Brasiliensis*	71	70	70	72	62	54	53	56
Heavy Hardwoods									
Balau	*Shorea* spp.	80	75	82	78	66	60	65	63
Chengal	*Balanocarpus heimii*	83	79	73	84	63	62	57	68
Merbau	*Intsia palembanica*	81	80	80	79	75	74	73	73

[a] Time of autohydrolysis is time at 195°C and does not include preheating time of 8 min.

EFWM = Extractive-free wood meal

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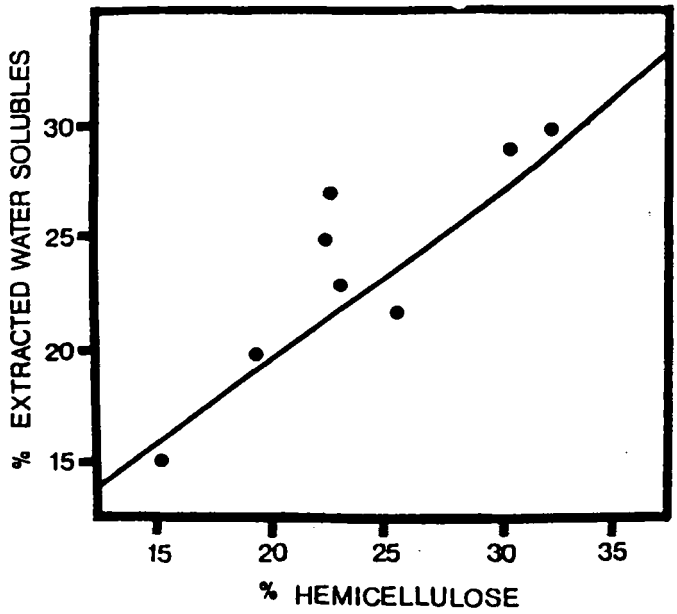

FIGURE 1. Relationship between % Extracted Water Solubles and % Hemicellulose in Wood (% based on EFWM)

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wood. In the case of the 90% dioxane extract, it is known that it contains modified depolymerized lignin, leaving in the ER, the insoluble residual lignin[17].

Residual Lignin in Extracted Residue (ER)

The residual lignin present in the ER of the respective tropical hardwoods for different autohydrolysis times, shown in Figure 2, decreased to a minimum, corresponding to maximum lignin extractability, before increasing for longer autohydrolysis times. This delignification trend was observed for all the tropical hardwoods studied, except in the case of Ramin, which required longer treatment times to complete the pattern. Such curves, also obtained for temperate hardwoods[12], were postulated to be due to the consecutive reactions of depolymerization, resulting in extractable lignin, and condensation/repolymerization, which formed insoluble lignin.

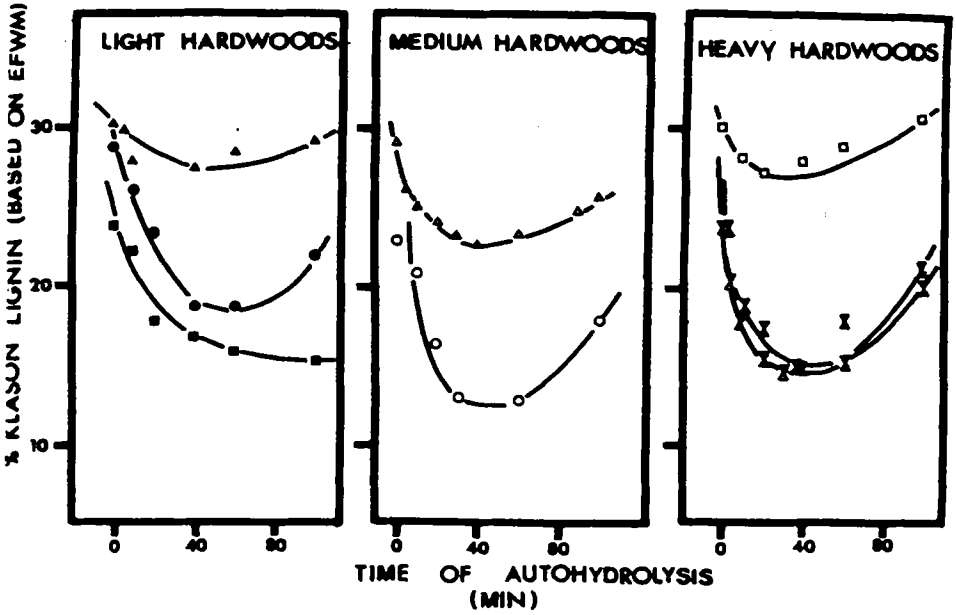

FIGURE 2. LIGNIN REMAINING IN EXTRACTED AUTOHYDROLYZED RESIDUE (ER) FOR DIFFERENT AUTOHYDROLYSIS TIMES
LIGHT RED MERANTI ▲ , JELUTONG ● , RAMIN ■ , KAPUR △ , RUBBER WOOD O , MERBAU □ , BALAU ⧗ , CHENGAL ⧖ .

To compare the response to autohydrolysis of the woods, the % maximum delignification for each wood was calculated, as shown in Table 3. It ranged from 15 - 52%. From the results, it is seen that the extent of delignification was not related to wood density, shown by the vast difference in response for the three categories of timber. (Classified[24] as Light Hardwoods 250-450 kg/m^3; Medium Hardwoods 451-650 kg/m^3; Heavy Hardwoods 651-850 kg/m^3).

From the view point of taxonomy, the eight tropical hardwoods belong to the following five botanical classes[25]: Jelutong (Apocynaceae); Light Red Meranti, Kapur, Balau and Chengal (Dipterocarpaceae); Ramin (Thymelaeaceae); Rubber Wood (Euphorbiaceae) and Merbau (Leguminosae). From the % delignification obtained, there is no clear pattern between effectiveness of autohydrolysis and taxonomic type.

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TABLE 2

Chemical Composition of Tropical Hardwoods

Wood	% Extractives[a]	% Lignin[b]	% Holocellulose[b]	% α-cellulose[b]	% Hemicellulose[b]	% Pentosan[b]
Light Hardwoods						
Jelutong	11.0	29.4	72.5	42.2	30.3	15.3
Light Red Meranti	7.3	34.6	68.3	53.1	15.2	9.9
Ramin	5.6	29.7	77.9	52.5	25.4	17.3
Medium Hardwoods						
Kapur	10.1	33.9	68.7	45.3	23.4	13.9
Rubber Wood	4.5	23.1	73.4	40.6	32.8	16.0
Heavy Hardwoods						
Balau	16.6	30.2	73.6	50.7	22.9	13.5
Chengal	31.3	30.4	71.2	48.0	23.2	14.8
Merbau	19.6	31.9	61.1	41.6	19.5	17.4

[a]% based on wood meal

[b]% based on extractive-free wood meal

Correlating the chemical composition of the woods (Table 2), with the % maximum delignification, the results show the lignin content of the wood affects its response to autohydrolysis. Five of the woods studied, with lignin contents of 30% or lower (namely Jelutong, Ramin, Rubber Wood, Balau and Chengal) had higher lignin extractability after autohydrolysis and extraction, of 37 - 52%, than the other three woods with higher lignin contents (namely Merbau, Kapur and Light Red Meranti). However, the correlation between lignin content and % maximum delignification is not linear. Ultimately the chemical structure of the lignin is probably the most important factor. Other wood components, such as hemicellulose show some correlation, but was not very distinct. For example, the two woods, Light Red Meranti and Merbau, had lower hemicellulose content than the other

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TABLE 3

Percentage Delignification Calculated from the Amount of Maximum Lignin Extracted After Autohydrolysis at 195°C

Wood	Time at Max. Lignin Extracted[a] (min)	Max. Lignin Extracted (% based on EFWM)[b]	Max. Delign. (% based on KL)[c]
Light Hardwoods			
Jelutong	60	10.9	37.1
Light Red Meranti	50	7.1	20.5
Ramin	100	14.2	47.8
Medium Hardwoods			
Kapur	40	11.4	33.6
Rubber Wood	48	10.8	46.7
Heavy Hardwoods			
Balau	45	15.2	50.3
Chengal	40	15.9	52.3
Merbau	30	4.9	15.4

[a]Minimum point for each wood in Figure 2.

[b]Max. lignin extracted = Original Klason lignin present - Lignin remaining in ER at minimum point (All data are % based on EFWM; EFWM = extractive-free wood meal)

[c]Max. Delignification = $\frac{\%\text{ Max. lignin extracted}}{\%\text{ Original Klason Lignin}}$

woods, and had low % maximum delignification as well. Although, Kapur does not fit this trend.

In summary, the lignin content of the wood appears to govern, to some extent, the response of the wood to autohydrolysis treatment. It should be noted, that in addition, the chemical structure of the lignin, in terms of types of linkages and phenylpropane units present, will certainly influence the effectiveness of autohydrolysis treatment.

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EXPERIMENTAL

The following tropical hardwoods were subjected to autohydrolysis and extraction : Jelutong, Light Red Meranti, Ramin, Kapur, Rubber Wood, Balau, Chengal and Merbau.

About 5 g of each of these woods was put in 30 ml pressure vessels, equipped with pressure gauge, thermocouple and safety valve. Water, to obtain a 1:1 wood:water ratio, was added and mixed well. The pressure vessel was then immersed in a silicone oil bath, set at 195°C, for periods ranging from 10 - 100 min., not including the preheating time of 8 min. At the completion of treatment, the pressure vessel and contents were rapidly cooled by immersion in an ice-bath. The contents were washed with hot water, filtered, air-dried and weighed. This autohydrolyzed residue (R) was then batch extracted with 90% dioxane at 70°C for 1 h each time, for 3 times.The air-dried extracted autohydrolyzed residue (ER) was weighed and the Klason lignin content determined.

The chemical composition of the different woods was analyzed according to the following procedures : % extractives - Tappi Standard T12 m-59, in which the solvents hexane and chloroform were substituted for benzene in the soxhlet extraction; % lignin - Tappi Standard T13 m-54, for determination of Klason lignin; % pentosan - Tappi Standard T19 m-50, the gravimetric determination of furfural formed from the conversion of pentosan using hydrochloric acid; and % holocellulose and α-cellulose, by the chlorite method of Ericksson[26].

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