STEAM EXPLOSION TREATMENT OF TWO MALAYSIAN HARDWOODS

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HALIMAHTON MANSOR, SUDO, K. & ISHIHARA, M. 1990. Steam-explosion treatment of two Malaysian hardwoods. Steam explosion under various steam pressures and reaction times was found to enhance the enzymatic susceptibility of *Acacia mangium* and *Hevea brasiliensis* (rubberwood) in spite of the presence of lignin. The pretreatment also caused the degradation of hemicellulose and rendered it water-soluble. Depending on the starting material, 9 to 17% water solubles containing mainly hemicellulose with xylose contents up to 97% after acid hydrolysis could be recovered from the exploded material.

Key words: *Acacia mangium* - rubberwood - steam-explosion - enzymatic saccharification - lignin - cellulose - sugars

Introduction

Steam explosion is one of the most promising pretreatments for increasing the susceptibility of wood cellulose and hemicellulose toward enzymatic hydrolysis (Shimizu *et al.* 1983), and in the conversion of woody biomass into useful products (Dietrich *et al.* 1978, Puls *et al.* 1983, Bender *et al.* 1970). This process was originally developed by Mason in 1925 (Schultz *et al.* 1983), which is a combination of chemical degradation of wood components and mechanical deformation of wood. During the process the wood is permeated by saturated steam and develops high internal pressures. When the reactor is opened, a sharp reduction in pressure occurs causing the defibration of the wood. With this pretreatment, and an additional alkaline extraction or dioxane treatment, wood can be nearly separated into the three main constituents, that is, cellulose, hemicellulose and lignin, and this can lead to the total use of wood as a source of chemicals, energy and food.

In this paper, studies on steam explosion of *Acacia mangium* and *Hevea brasiliensis* (rubberwood) are reported, focussing on the chemical analysis and characterisation of the steam exploded wood. These species were chosen due to their availability, in addition to *A. mangium* being an important plantation species in Malaysia while rubberwood has become an important timber with wide applications. The aim of this work was to investigate the feasibility of steam explosion pretreatment technique on these Malaysian hardwoods.

Materials and methods

Equipment

The apparatus for steam explosion consists of a reactor, a collecting chamber and a steam generator, all of which are made of stainless steel. The steam generator can produce pressures of up to 40 *kg* cm^2 (Nitto Koatsu Corporation, Japan).

Steam explosion treatment

Samples of wood which had been air and oven dried (40°*C*), were cut into approximately matchstick size chips. About 300 *g* of the chips were then loaded into the steam explosion reactor. The reactor was then sealed and steam was gradually applied until the required pressure was obtained. The pressure was maintained for the required reaction time. The pressure was then released rapidly and the steam exploded wood was collected, weighed and analysed.

Steam explosion of the wood chips was carried out at various pressures and retention times. The steaming process has been described by various workers (Shultz *et al.* 1983 & References).

Extraction of steam exploded wood

About 100 *g* of the steam exploded wood was extracted with distilled water (300 *ml*) at 70°*C* for 2 *h*. The mixture was filtered and the solution reduced to a small volume, freeze dried and weighed. The extracts were then analysed by GPC and HPLC. The water extracted wood was then extracted with 90% dioxane (300 *ml*) for 4 *h* at 70°*C*. The dioxane extracts were evaporated to dryness under reduced pressure and weighed.

Acid hydrolysis of water soluble extracts

This reaction was carried out by the method of Paice *et al.* (1982). Trifluoroacetic acid solution (2 M, 1.6 *ml*) was added to the extracts (5 *mg*) and the mixture was then kept at room temperature for 48 *h*. This was followed by heating the mixture in air at 90°*C* for 2 *h*. The acid was removed under reduced pressure and the resultant mixture dissolved in distilled water for HPLC analysis.

Determination of Klason lignin

The determination was carried out according to TAPPI T222 in TAPPI Testing Procedures (Anonymous 1978).

Determination of holocellulose of the untreated wood

The holocellulose content was determined by the acid chlorite method (Browning 1967).

Enzymatic hydrolysis

The steam exploded wood (200 *mg* moisture free basis) was placed in an L-shaped glass tube. To it was added commercial cellulase (50 *mg*, "Meicelase-P", derived from *Trichoderma viride*) and a buffer solution of pH 5.0 (10 *ml*). The mixture was placed in a water bath at 40°*C* for 48 *h*, with continuous agitation. It was filtered into a G-4 filter glass, washed with distilled water, and dried at 105°*C* for 12 *h* before weighing. The filtrate was made up to 100 *ml* with distilled water and analysed by HPLC.

Analysis by HPLC

Liquid chromatograph (Dionex 200i, USA) with ion exchange column (Dionex AG-7 and AS-7, USA) and a pulsed amperometric detector were used for analysing 0.5 *ml* solutions of enzymatic hydrolysates. Distilled water was used as an eluant with a flow rate of 1.0 $ml\ min^{-1}$. To obtain adequate sensitivity of the electrochemical detection, 0.3 N sodium hydroxide solution was added to the column eluant with a flow rate of 1.0 $ml\ min^{-1}$.

Analysis by GPC

Gel permeation chromatograph (Shimadzu, LC-3A) with two connected columns (Shodex Ionpak KS-802, Showa Denko K.K., Japan; length 30 *mm* × diameter 8 *mm*) were used for analysing 100 μl solutions of water extracts. Distilled water was used for the elution, at a flow rate of 0.8 $ml\ min^{-1}$. The eluant was monitored by refractive index.

Results and discussion

The high pressure steaming brings about both physical and chemical changes accelerating the depolymerisation of both the hemicellulose and lignin, and modifying the cellulose into a readily accessible form. This process opens up the fibres and renders the hemicellulose soluble in water, and the lignin soluble in dioxane (also soluble in methanol and aqueous sodium hydroxide). Table 1 shows the results for the enzymatic saccharification and the chemical composition of the steam exploded wood. The yields for the residues ranged from 79 to 99%.

Table 1. Enzymatic susceptibility and chemical composition of steam exploded wood of Malaysian trees

Species	Condition		Yield	Susceptibility	Water extract	K.L.	S.L.
	Pressure (*kg cm*^{2})	Time (*min*)	(%)	(%)[a]	(%)[b]	(%)	(%)
Acacia mangium	25	6	98.9	53.3	10.2	29.8	14.3
	25	10	85.7	97.6	9.3	38.2	35.7
	30	2	97.7	78.1	13.0	33.3	20.1
	30	4	82.6	74.6	12.2	36.1	41.9
	30	6	82.0	79.8	10.5	39.7	49.6
Rubberwood	20	10	81.8	88.5	10.4	32.0	11.0
	25	6	99.1	85.6	16.8	34.2	19.0
	25	10	78.7	69.0	11.5	42.5	43.1
	30	6	84.4	85.1	16.5	36.4	39.8

Note: [a] Based on the residual polysaccharides in the fibre material; [b] Based on oven dried steam exploded fibre; K.L. Klason lignin, based on the residue; S.L. Soluble lignin, content of extractable lignin with 90% dioxane, based on the residue

Lignin remains in the wood tissue though it is depolymerised by steaming (Lora & Wayman 1978, Wayman & Lora 1979). As a result, the relative amount of polysaccharides in the steam exploded wood (steamed under the drastic conditions) is reduced. The Klason lignin content of the residual cellulosic materials ranged from 30 to 43%, indicating that the lignin was retained mostly in the residues after the pretreatment. A significant portion of the lignin could be extracted with 90% dioxane. However, removal of lignin from residual polysaccharides does not increase the enzymatic susceptibility of the material (Shimizu *et al.* 1983, Puls *et al.* 1983).

A part of the steam exploded fibre was hydrolysed with a commercial cellulase, yielding a hydrolysate comprising mainly glucose and xylose (Table 2). The extent of enzymatic susceptibility of the residual polysaccharides varied from 53 to 98% depending on the steaming condition and the species. The residual polysaccharides of the steam exploded wood was highly susceptible to enzymatic attack compared to the corresponding untreated wood (Table 3). Based on the percentage of enzymatic susceptibility, the most efficient operating conditions were 25 *kg cm*^{2} (10 *min*) for *A. mangium*, and 20 *kg cm*^{2} (10 *min*) for rubberwood. Under these respective reaction conditions, the level of enzymatic digestibility of the steam exploded materials was at its maximum.

Table 2. Composition of reducing sugars in the enzymatic hydrolysates of steam exploded wood of Malaysian trees

Species	Condition		Reducing sugars (ppm)				
	Pressure (*kg cm*$^{-2}$)	Time (*min*)	Arabinose	Galactose	Glucose	Xylose	Mannose
Acacia mangium	25	6	-	-	1311.9	166.9	67.0
	25	10	-	-	1418.4	72.8	-
	30	2	-	-	721.2	22.9	22.9
	30	4	-	-	1137.1	57.7	-
	30	6	-	-	1135.0	-	-
Rubberwood	20	10	-	-	592.8	-	-
	25	6	-	-	1243.4	-	-
	25	10	-	-	1106.9	-	-
	30	6	-	-	1543.0	-	-

Table 3. Enzymatic saccharification and chemical composition of the untreated wood

Species	Moisture content (%)	Susceptibility (%)[a]	Hot-water solubles (%)[b]		K.L. (%)	Holocellulose (%)[c]
Acacia mangium	6.2	7.8	4.3[d]	4.0[e]	28.18	63.5
Rubberwood	5.5	22.4	6.7	6.3	19.53	66.3

Note: [a] Based on the residual polysaccharides in untreated woodmeal; [b] Based on oven-dried untreated woodmeal; [c] Based on extractive-free woodmeal; [d] Based on difference in weight of the sample before and after the extraction; [e] The weight of the water extract after evaporation under reduced pressure

During the steaming process, xylan which is the main hardwood hemicellulose is hydrolysed to xylose and xylooligomers (Conner 1984, Sudo *et al.* 1986). The reaction is accelerated in acidic medium brought about by acetic acid liberated from the acetyl group of xylan. Furthermore, xylose is converted to furfural on dehydration in acidic medium at high temperature. The dehydration reaction of xylose takes place more easily than the hydrolysis of xylan. Hence, under the more drastic conditions the amounts of xylose and xylooligosaccharides in the steam exploded wood are reduced and cellulose is also partially decomposed. The GPC analysis of the water extracts of the steam exploded wood showed predominantly xylose and xylooligomers (Figure 1). Table 4 shows the main sugar components in the water extracts after acid hydrolysis with trifluoroacetic acid. Depending on the starting material, 9 to 17% water extracts consisting mainly of hemicelluloses with xylose contents up to 97% can be recovered by aqueous extraction of the steam-exploded wood and acid hydrolysis of the extract. Glucose seems to be the other major sugar present in the extract. As can be seen in Table 4, steam explosion of *A. mangium* resulted in the production of the highest percentage of xylose in the water extract while rubberwood generally gave xylose and glucose in about equal amounts.

Table 4. Sugar compositions in the water extracts after steam explosion and acid hydrolysis

Species	Condition		Water extract	Reducing sugars (%)[a]				
	Pressure (*kg cm*^{2})	Time (*min*)	(%)	Glc	Xyl	Gal	Ara	Fruc
Acacia mangium	25	6	10.2	1.3	93.3	3.4	2.0	-
	25	10	9.3	11.7	88.3	-	-	-
	30	2	13.0	-	97.2	2.8	-	-
	30	4	12.2	11.5	86.0	2.5	-	-
	30	6	10.5	40.7	59.3	-	-	-
Rubberwood	20	10	10.4	55.6	41.3	1.2	1.9	-
	25	6	16.8	60.2	39.8	-	-	-
	25	10	11.5	53.0	47.0	-	-	-
	30	6	16.5	52.0	48.0	-	-	-

Note: [a] Based on the total solubilised sugars; Glc - glucose; Xyl - xylose; Gal - galactose; Ara - arabinose; Fruc - fructose

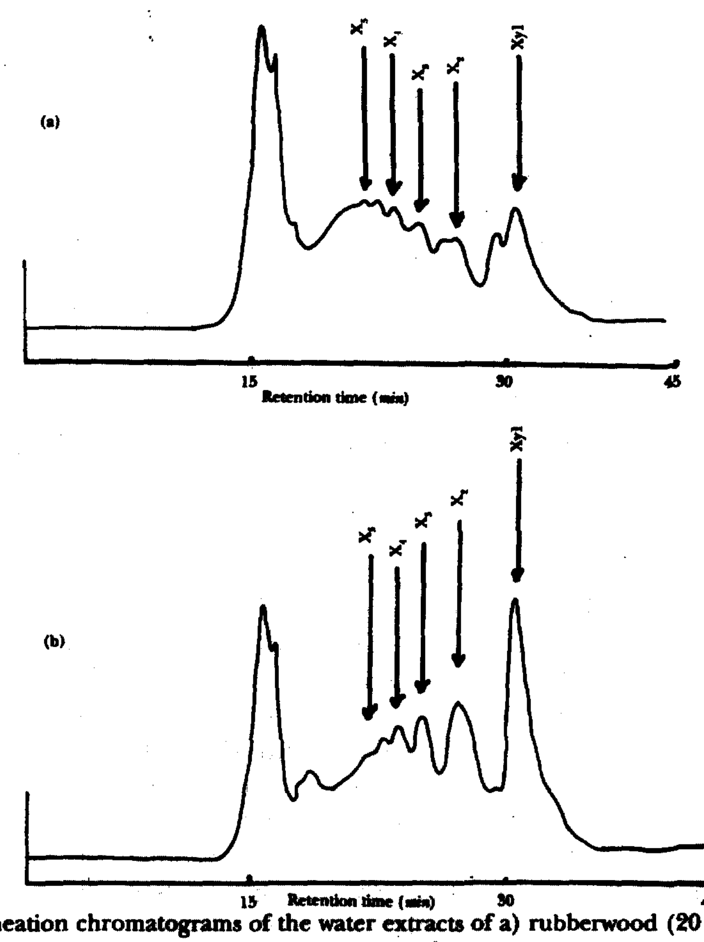

Figure 1. Gel-permeation chromatograms of the water extracts of a) rubberwood (20 *kg cm*^{1}, 10 *min*) and b) *A. mangium* (25 *kg cm*^{1}, 10 *min*)

For *A. mangium*, there was an increase of glucose and a decrease of xylose in the acid hydrolysate with increasing steam pressure and reaction time (Table 4). However, such changes were not observed for steam exploded rubberwood.

The two wood species in this study showed quite a marked difference in enzymatic susceptibility under the same reaction conditions. This is quite expected since factors such as chemical components including ash, hot water extract, holocellulose, ethanol-benzene extract and lignin, as well as basic density and morphological properties, differ from one species to another. The differences in susceptibility observed for these steamed hardwoods seem to be related partly to the differences in the chemical structure of the lignins.

Conclusion

Steam explosion was shown to be an excellent pretreatment method for enhancing the enzymatic hydrolysis of *A. mangium* and rubberwood. Since the steam-exploded materials gave very high enzymatic susceptibility they can be a significant source of fermentation substrates for the production of ethanol. Selective extraction of these substrates to their major components of cellulose, hemicellulose and lignin is also made possible by this pretreatment. Hydrolysis of the hemicellulose produces mainly xylose which can be converted to xylitol which is known to be a diabetic and noncariogenic sweetener. These preliminary results also demonstrate that the steaming process will have to be optimised for each substrate since the different species behaved differently under identical steaming conditions.

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