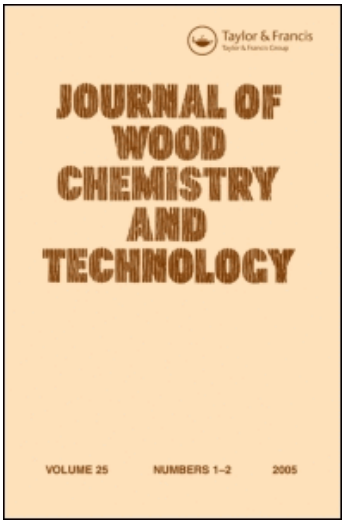

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EXTRACTION AND CHARACTERIZATION OF HEMICELLULOSES AND CELLULOSE FROM OIL PALM TRUNK AND EMPTY FRUIT BUNCH FIBRES

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ABSTRACT

The cell walls of oil palm trunk fibre and empty fruit bunch (EFB) fibre were initially extracted with 5% NaOH at boiling for 2 h, which removed 17.3% and 15.2% hemicelluloses, respectively. Further extraction of the delignified palm trunk and EFB fibre was conducted with 10% NaOH at 20°C for 16 h and 24% KOH-2% H_3BO_3 at 20°C for 2 h. This resulted in the release of 11.9%, 13.5%, 12.7% and 14.9% residual hemicelluloses, respectively. The cellulose content, isolated by 24% KOH-2% H_3BO_3 from the two fibre samples, was found to be 41.3-41.7%, most of which was relatively free of associated lignin and hemicelluloses. The hemicelluloses, extracted with 5% NaOH from the lignified palm trunk fibre and EFB fibre, contained relatively high amounts of xylose, and minor arabinose and rhamnose than the hemicelluloses, extracted with 10% NaOH and 24% KOH-2% H_3BO_3 from the delignified fibres. While the hemicelluloses, extracted with 10% NaOH and 24% KOH-2% H_3BO_3 from the delignified palm trunk and EFB fibre, contained slightly more galactose, glucose, and mannose than the hemicelluloses, extracted with 5% NaOH from the lignified fibres. Further studies implied that the hemicelluloses, extracted with 5% NaOH from the lignified fibres, were more linear and acidic and had a large molecular size (weight-average, 17,400-22,900), together with comparatively high associated lignins (12.0-15.7%). Which were found to be linked to hemicelluloses mainly via syringyl unit. On the other hand,

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the hemicelluloses, extracted with 10% NaOH and 24% KOH-2% H_3BO_3 from the delignified fibres, were more branched but less acidic and had a comparatively small molecular size (weight-average, 6,600-10,800), together with trace amounts of associated lignin (0.3-1.1%). The hemicelluloses in the cell walls of palm EFB had a higher degree of polymerizaton than the hemicelluloses in the cell walls of palm trunk fibre as indicated by the molecular-average weights, ranging from 7,200 to 22,900, and from 6,600 to 17,400, respectively.

INTRODUCTION

Natural fibres, such as coir, banana, sisal, talipot, palmyrah, jute, and pineapple leaf represent a very abundant, inexpensive, and renewable resource for industrial materials. Properties of these natural fibres vary between plant type. For example, coir is a hard and tough multicellular fibre, whereas banana fibre is weak and cylindrical in shape. Pineapple leaf fibre is soft fibre and is known for its high cellulose content.[1] Oil palm trunk fibre and EFB fibre, which are two important type of fibrous materials, obtained from fruit bunch after oil extraction and from the palm trunks periodically during the replanting and pruning, are hard and tough, and show similarity to coir fibres in cellular structure.[1]

EFB and palm trunk fibres are mainly composed of cellulose (41-42%), hemicelluloses (30-31%), and lignin (14-16%). They could potentially represents a very abundant, inexpensive, and renewable resource for paper production. Economically viable products derived from the palm fibres are being eagerly sought and a number of technically feasible products are reconstituted board and ruminant feed.[2,3] There has also been some success in using EFB fibre as a potential reinforcement in phenol-formaldehyde resin.[4] The mechanical performance of phenol-formaldehyde resin is greatly improved by the incorporation of these fibres. However, to date, there has been no systematic or extensive study of the chemical composition of these fibres. In this paper, we report on the chemical constituents of the oil palm trunk fibre and EFB fibre. The effect of an alkali extraction on the sugar composition and the molecular distribution of the

hemicelluloses isolated from the lignified and delignified fibres is reported, via 5% NaOH, 10% NaOH, and 24% KOH-2% H_3BO_3 extraction routes, respectively. The emphasis is on the lignin components associated with the isolated hemicelluloses and cellulose fractions, since the presence of lignin is the principal constituent that must be removed or modified during pulping.

EXPERIMENTAL

Fractional extraction of Hemicelluloses and Cellulose

Oil palm trunk fibre and EFB fibre were obtained from Forest Research Institute of Malaysia. The fibres were firstly cleaned and dried. The air-dried fibres were then ground and passed through a 0.7 mm screen, and further dried at 60°C for 16 h. The dried samples were extracted with toluene-methanol (2:1, v/v) for 6 h in a Soxhlet apparatus. After further drying in an oven for 16 h at 60°C, the extractive free residues were subject to extraction with 95% ethanol for 4 h (in a Soxhlet apparatus), and then with water at boiling for 2 h. Soluble hemicelluloses were further extracted with 5% NaOH at boiling for 2 h.

After treatment, the respective mixtures were screened using a 20 μm nylon cloth to remove the 5% NaOH insoluble materials. The filtrates were neutralized to pH 5.5 with 20% HCl, concentrated using a rotary evaporator under reduced pressure at 40°C, and then mixed with 3 vols ethanol. Precipitated hemicelluloses were filtered, washed with 70% ethanol, and air-dried. The 5% NaOH soluble alkali lignin was obtained by reprecipitation at pH 1.5 with 20% HCl from the supernatant solution. Residual lignins were removed by using sodium chlorite in acidic solution (pH 4.2-4.7 adjusted by 10% acetic acid) at 70°C for 2 h. Residual hemicelluloses were further extracted with 10% NaOH for 16 h at 20°C, and 24% KOH-2% H_3BO_3 at 20°C for 2 h from the delignified residues, respectively. Soluble hemicelluloses and residual lignin were recovered by the two step precipitation method reported.

All fibre residues from both oil palm trunk fibre and EFB fibre were extensively washed with water until the eluant was neutral, and then dried in an oven at 60°C for 16 h. After correction for ash content, the dry masses were taken to be α-cellulose, respectively. A simplified schematic of methodology is presented in Figure 1.

Characterization of Extracted Hemicelluloses and Cellulose

The neutral sugar composition of the isolated hemicelluloses and cellulose was determined by GC analysis of respective alditol acetates.[5] Alkaline nitrobenzene oxidation of the lignins associated with the isolated hemicelluloses and cellulose was performed at 170°C for 3 h. Methods of uronic acid analysis and determination of phenolic acids and aldehydes in the nitrobenzene oxidation mixtures with HPLC have been described in previous papers.[6-10] FT-IR spectra were obtained on an FT-IR spectrophotometer (Nicolet, 750) using a KBr disc containing 1% finely ground samples.

The molecular-average weights of the polysaccharides were determined by gel permeation chromatography using a PL aquagel-OH 50 column calibrated with PL pullulan polysaccharide and operated at 40°C, eluted with 0.02 M NaCl in 0.005 M sodium phosphate buffer, pH 7.5, at a flow rate of 0.3 mL min^{-1}. The samples were dissolved with 0.02 M NaCl in 0.005 M sodium phosphate buffer, pH 7.5, at a sample concentration of 0.1%. 200 μL of this solution was injected.

RESULTS AND DISCUSSION

Yield of Hemicelluloses and Cellulose

Table 1 shows the yields of hemicelluloses, cellulose, and lignin, extracted by 5% NaOH, 10% NaOH, and 24% KOH-2% H_3BO_3, respectively, from oil palm trunk

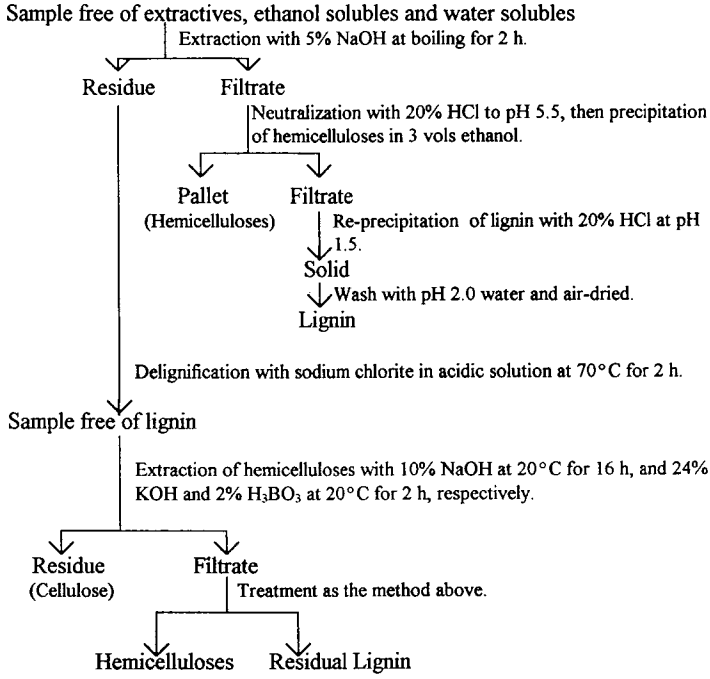

FIGURE 1. Scheme for isolation of hemicelluloses and lignin from oil palm.

TABLE 1.

Yield of hemicelluloses, cellulose and lignin extracted by alkali extraction from oil palm trunk fibre and EFB fibre.

	5% NaOH Solubles[a]		10% NaOH Solubles[b]		24% KOH Solubles[c]		Cellulose	
	Hemi-celluloses	Lignin	Hemi-celluloses	Lignin	Hemi-celluloses	Lignin	Residue of 10% NaOH Extraction	Residue of 24% KOH Extraction
Trunk	17.3	6.6	11.9	0.7	13.5	0.3	43.5	41.7
EFB	15.2	6.8	12.7	2.0	14.9	0.9	43.2	41.3

[a]Extraction with 5% NaOH at boiling for 2 h from the sample free of extractives, ethanol solubles and water solubles.
[b]Extraction with 10% NaOH at 20°C for 16 h from 5% NaOH extracted and delignified sample.
[c]Extraction with 24% KOH and 2% H_3BO_3 at 20°C for 2 h from 5% NaOH extracted and delignified sample.

and EFB fibre. Treatment of the lignified palm trunk fibre with 5% NaOH yielded a slightly higher amount of hemicelluloses (17.3%) than obtained from lignified EFB fibre (15.2%). However, extraction with 10% NaOH and 24% KOH-2% H_3BO_3 of the delignified EFB fibre yielded a slightly higher hemicellulosic content (12.7%, 14.9%) than the yield obtained from the delignified palm trunk fibre (11.9%, 13.5%). This is probably due to the less solubilized hemicelluloses during the previous treatment of lignified EFB fibre with 5% NaOH.

The cellulose content of the two fibres is comparatively high (41.3-43.5%). The higher yield, obtained by the 10% NaOH extraction method is presumed due to the incomplete extraction of hemicelluloses. Thus, it appears that extraction with 24% KOH-2% H_3BO_3 is more efficient in the isolation of hemicelluloses and for preparation of pure cellulose. The total content of holocellulose in the trunk fibre and EFB fibre was found to be 72.5-72.7% and 71.1-71.4%, respectively. The current results were partially consistent with the studies of oil palm fibres by Sreekala and co-workers.[1] Sreekala et al. reported that treatment of oil palm EFB fibre with 1% NaOH resulted in a 20% solubles. However, a much higher yield of cellulose (65%), obtained by Sreekala et al.[1] from the palm EFB fibre is undoubtedly due to the higher content of associated hemicelluloses in the preparation of cellulose. Muthurajah and Bin[11] reported that oil palm empty bunch waste contained 71.5% holocellulose and 42.7% cellulose. Similar results have been reported by Akamatsu et al.[12] They indicate that the refined EFB vascular strands contained 70.0% holocellulose and 17.2% Klason lignin. The reported chemical composition results from this study of oil palm trunk and EFB fibre resemble those of the grasses and cereal straws in their polysaccharide composition except for the higher lignin and lower ash contents.

Composition of Neutral Sugars and Uronic Acids

Sugar and uronic acid composition of the isolated hemicellulosic fractions and cellulose preparations from the trunk and EFB fibre are provided in Table 2.

TABLE 2.

The content of neutral sugars (relative % dry weight) and uronic acid (% dry weight) in the extracted hemicelluloses and cellulose fractions.

Sample	Fractions	Neutral Sugars							Uronic
		Rha	Dib	Ara	Xyl	Man	Glc	Gal	Acids
Trunk	5% NaOH Soluble hemicelluloses	1.26	0.21	1.22	92.92	0.24	2.72	1.41	4.95
	10% NaOH soluble hemicelluloses	0.88	T	1.11	87.59	0.75	5.63	4.04	4.87
	24% KOH soluble hemicelluloses	0.70	T	1.00	88.20	0.60	3.73	7.77	4.50
	Cellulose (residue of the 10% NaOH extraction)	N	N	N	2.04	1.42	96.54	N	-
	Cellulose (residue of the 24% KOH extraction)	N	N	N	1.05	1.01	97.94	N	-
EFB	5% NaOH Soluble hemicelluloses	1.24	T	3.59	90.42	0.41	2.04	2.30	5.50
	10% NaOH soluble hemicelluloses	0.50	0.36	2.22	88.59	0.79	5.74	1.79	4.38
	24% KOH soluble hemicelluloses	0.61	0.41	2.29	83.68	0.81	4.12	8.09	4.12
	Cellulose (residue of the 10% NaOH extraction)	N	N	N	3.50	1.02	95.48	N	-
	Cellulose (residue of the 24% KOH extraction)	N	N	N	1.80	0.61	97.59	N	-

T = trace; N = not detectable.

Hemicellulosic fractions: Xylose was found to be the predominant component sugar in all six hemicellulosic fractions, comprising 83.68-92.92% of the total sugars. Glucose, galactose, arabinose, rhamnose, and mannose appeared as minor constituents. Ribose was present in trace amounts. The content of xylose and uronic acids was higher in the 5% NaOH soluble hemicelluloses (from lignified fibre) than in the hemicelluloses extracted with 10% NaOH and 24% KOH-2% H_3BO_3 (from delignified fibre). This indicated that extraction by 5% NaOH from lignified palm trunk and EFB fibre resulted the liberation of slightly more linear and

acidic hemicellulosic fractions, while the extractions with 10% NaOH or 24% KOH-2% H_3BO_3 from the delignified samples produced hemicellulosic fractions which were relatively less acidic but more branched. The opposite trend is true of hemicellulosic preparations obtained from straw and grass, suggesting that xylans in oil palm trunk and EFB fibre are more readily released during the alkali pre-treatment process.[7]

The higher content of arabinose and rhamnose in the 5% NaOH soluble hemicelluloses as compared to the hemicellulosic fractions extracted by 10% NaOH and 24% KOH-2% H_3BO_3 (from the delignified fibres) suggested that arabinose and rhamnose (probably as a side chain in hemicelluloses) are bound to ferulic acid or directly to lignin and are easily liberated,[10] whereas mannose, glucose, and galactose, presumably in the main chain of hemicelluloses, are prevented from the extraction prior to delignification. Similarly, the higher glucose content and much lower galactose content in hemicelluloses extracted with 10% KOH (from both trunk and EFB fibre) than those found in hemicelluloses extracted with 24% KOH-2% H_3BO_3, implied that 10% sodium hydroxide is more effective in liberating glucose rich hemicelluloses and 24% KOH-2% H_3BO_3 is more effective when applied to hemicelluloses containing more galactose.

There was no significant difference in the sugar composition between the corresponding hemicellulosic fractions extracted from the palm trunk and EFB fibre, suggesting that the hemicelluloses in the cell walls of trunk and EFB fibre may have similar structures. The similar results were obtained from the leaf cell walls of oil palm by Jarvis.[13] Who indicated that the carbohydrate in the leaf cell walls was comprised of moderately crystalline cellulose and acetylated arabinoxylans as the major polysaccharides, as in the Gramineae. Further studies by ^{13}C-NMR spectroscopy demonstrated that the major monosaccharide residues present in the oil palm trunk are glucose and xylose, indicating that cellulose and

xylans were the predominant polysaccharides in the cell walls of palm trunks. This observation implied that the oil palm appears closer to the Gramineae in chemical composition than to other monocotyledons.[2] Xylan can be used as a raw material for food and pharmaceutical industries for xylose or xylitol production.[14] Cellulose can be used as a raw material for paper production.

Cellulose fractions: Cellulose preparations consisted of 95.48-97.94% glucose and minor amounts of other sugars such as xylose (1.05-3.50%) and mannose (0.61-1.42%). The significant presence of xylose (2.04-3.50%) and mannose (1.02-1.42%) other than glucose in the cellulose preparations, when isolated by a 10% NaOH extraction as compared to a 24% KOH-2% H_3BO_3 extraction could be due to the more incomplete extraction of hemicelluloses by the 10% NaOH route.[15] The resistance to extraction of the residual hemicelluloses when using 24% KOH-2% H_3BO_3 indicated that the hemicelluloses are very strongly associated to the surface of cellulose.

Composition of Phenolic Acids and Aldehydes

The presence of associated lignin in the hemicellulosic preparations from straw, grass, and wood was studied in detail.[9,16-24] To further verify the presence of associated lignin in isolated hemicelluloses and cellulose from oil palm trunk and EFB fibre, alkaline nitrobenzene oxidation of the six isolated hemicellulosic fractions and four cellulose preparations was performed at 170°C for 3 h. This method provided an estimate of the amount of associated lignin and an indication of its composition. Table 3 gives the results of nitrobenzene oxidation of residual lignin in the isolated hemicelluloses and cellulose.

Hemicellulosic fractions: The hemicelluloses, extracted with 5% NaOH from the lignified trunk and EFB fibre, produced syringaldehyde as a major component; 62.90% and 61.40% of the total phenolic monomers, respectively. Small amounts

TABLE 3.

Content (% hemicellulose/cellulose sample, w/w) of phenolic acids and aldehydes from the nitrobenzene oxidation of residual lignin in various isolated hemicelluloses and cellulose fractions.

Sample	Fractions	Phenolic Acids and Aldehydes								
		PHBA	PHBAL	VA	SYA	VAN	SYAL	PCA	FA	Total
Trunk	5% NaOH Soluble hemicelluloses	0.028	0.16	0.061	0.16	0.98	2.56	0.11	0.0082	4.07
	10% NaOH soluble hemicelluloses	0.0087	0.0089	0.045	0.018	0.044	0.14	0.0066	0.0035	0.27
	24% KOH soluble hemicelluloses	0.0078	0.012	0.0074	0.016	0.038	0.12	0.0079	0.0039	0.21
	Cellulose (residue of the 10% NaOH extraction)	0.016	0.089	0.014	0.011	0.041	0.037	0.0063	T	0.21
	Cellulose (residue of the 24% KOH extraction)	0.015	0.057	0.015	0.012	0.042	0.035	0.0062	T	0.18
EFB	5% NaOH Soluble hemicelluloses	0.039	0.18	0.089	0.23	1.44	3.50	0.21	0.013	5.70
	10% NaOH soluble hemicelluloses	0.011	0.025	0.051	0.017	0.22	0.039	0.0066	0.0054	0.38
	24% KOH soluble hemicelluloses	0.010	0.016	0.031	0.0096	0.086	0.021	0.0042	N	0.18
	Cellulose (residue of the 10% NaOH extraction)	0.010	0.014	0.012	0.0046	0.041	0.021	0.014	N	0.12
	Cellulose (residue of the 24% KOH extraction)	0.010	0.0096	0.0075	0.0076	0.033	0.010	0.018	N	0.10

PHBA, p-Hydroxybenzoic acid; PHBAL, p-Hydroxybenzaldehyde; VA, Vanillic acid; SYA, Syringic acid; VAN, Vanillin; SYAL, Syringaldehyde; PCA, p-Coumaric acid; FA, Ferulic acid; T=trace; N=not detectable.

of benzaldehydes and phenolic acids such as vanillin, *p*-hydroxybenaldehyde, syringic acid and *p*-coumaric acid, and traces of *p*-hydroxybenzoic acid, vanillic acid and ferulic acid were also identified in the nitrobenzene oxidation products.

Interestingly, as shown in Table 3, syringaldehyde was found to be a major component of phenolic monomers in the nitrobenzene oxidation mixtures of residual lignin from the hemicelluloses when extracted with 10% NaOH and 24%

KOH-2% H_3BO_3 from palm trunk fibre. Hemicelluloses, extracted with 10% NaOH and 24% KOH-2% H_3BO_3 from EFB fibre, where found to contain vanillin as major product of nitrobenzene oxidation representing 57.90% and 47.78% of the total phenolic monomers, respectively. This observation implies that the hemicelluloses, extracted with either 5% NaOH from lignified palm trunk and EFB fibre or by 10% NaOH and 24% KOH-2% H_3BO_3 from delignified palm trunk fibre, are mainly linked to lignin via syringyl units, while in the hemicelluloses, extracted by the same method from delignified EFB fibre, are associated to lignin mainly via guaiacyl units. It is due to the lignin-hemicellulose complex in the cell walls of palm trunk and EFB fibre that the content of phenolic acids and aldehydes in the nitrobenzene oxidation products from the hemicelluloses extracted directly from the lignified fibres (with 5% NaOH), is 15-32 times that of the hemicelluloses extracted (with 10% NaOH and 24% KOH-2% H_3BO_3) from the delignified trunk and EFB fibre. The relatively high content of *p*-coumaric acid as compared to ferulic acid in the nitrobenzene oxidation mixtures (from all ten polysaccharide preparations) suggested that a majority of *p*-coumaric acids is linked to hemicelluloses, whereas the most of the ferulic acids are linked to lignin in the cell walls of both palm trunk and EFB fibre. An alternative explanation is that they are oxidized into vanillin under the nitrobenzene oxidation conditions given (170°C, 3 h).

Cellulose fractions: Table 3 also shows the phenolic composition of residual lignin from cellulose preparations obtained by nitrobenzene oxidation. The major compounds were found to be *p*-hydroxybenzaldehyde, vanillin, and syringaldehyde. The low phenolic monomers content in the nitrobenzene oxidation products from cellulose preparations (ranging between 0.10% and 0.21%) implies that these cellulose preparations are relatively free of lignin.

Molecular Weight Distribution

Table 4 shows the weight-average (M_w) and number-average (M_n) molecular

TABLE 4.

Weight-average (M_w) and number-average (M_n) molecular weights and polydispersity (M_w/M_n) of hemicellulosic fractions extracted from oil palm trunk fibre and EFB fibre.

Sample	Hemicellulosic Fractions	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
Trunk	5% NaOH Soluble Hemicelluloses	17,400	4,800	3.6
	10% NaOH Soluble Hemicelluloses	10,200	5,700	1.8
	24% KOH Soluble Hemicelluloses	6,600	3,200	2.0
EFB	5% NaOH Soluble Hemicelluloses	22,900	7,800	3.0
	10% NaOH Soluble Hemicelluloses	10,800	6,600	1.6
	24% KOH Soluble Hemicelluloses	7,200	5,100	1.4

weights, and the polydispersity (M_w/M_n) of the six hemicellulosic fractions. The hemicelluloses, extracted from the lignified palm trunk and EFB fibre with a low alkali concentration (5% NaOH), had a much higher degree of polymerization, with molecular-average weights ranging from 17,400 to 22,900. This range is approximately three times higher than the hemicelluloses, isolated with a high alkali concentration (24% KOH-2% H_3BO_3). Increasing the alkali concentration from 5% to 10% NaOH resulted in a decrease of molecular-average weight from 17,400 to 10,200, and from 22,900 to 10,800, respectively. This phenomenon implied that extraction of hemicelluloses from palm trunk and EFB fibre with high alkali concentration might result in some degradation as in the case of 24% KOH-2% H_3BO_3 hemicellulose extraction. Additionally, the three hemicellulosic fractions (Table 4), extracted from the EFB fibre, exhibited higher molecular-average weights than the corresponding three hemicellulosic fractions extracted from the palm trunk fibre. This indicates that the hemicelluloses in the cell walls of EFB fibre had a large molecular size than those found in the cell walls of palm trunk fibre.

The GPC molecular weight distribution of the hemicelluloses, extracted with 5% NaOH from the palm EFB fibre, is illustrated in Figure 2. The elution maximum

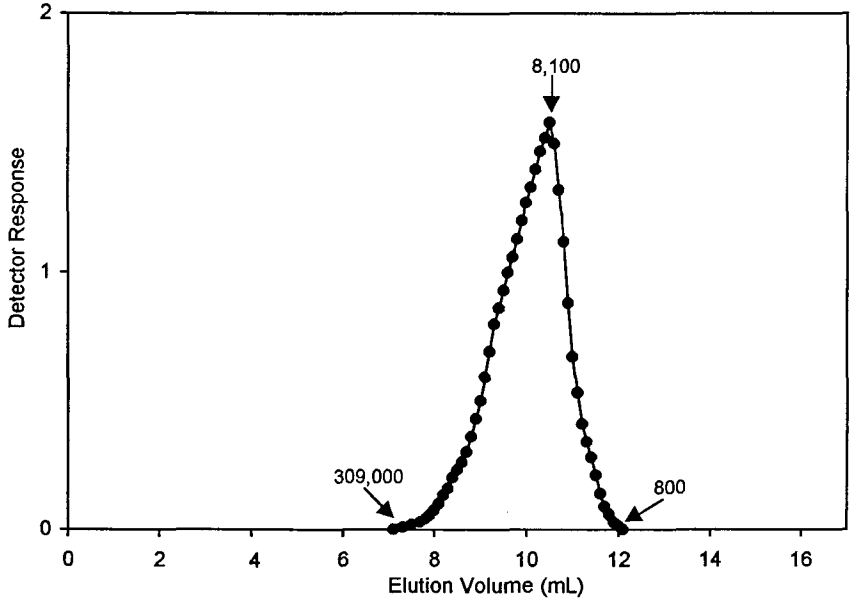

FIGURE 2. GPC molecular weight distribution of hemicelluloses extracted with 5% NaOH from oil palm EFB fibre.

corresponded to a polysaccharide molecular weight of 8,100. The elution profile of the hemicelluloses showed a wide polymolecularity, ranging from oligosaccharides up to polysaccharides with a molecular weight over 300,000.

FT-IR Spectra

The FT-IR spectra of the three hemicelluloses, extracted with 5% NaOH, 10% NaOH, and 24% KOH-2% H_3BO_3 from the palm trunk fibre, are shown in Figure 3. The spectral profiles and relative intensities of the band were very similar, indicating similar structures of the hemicelluloses. The band at 1630 cm^{-1} is principally associated with the C=O stretch of carboxylic anions (salt) for uronic acids in hemicelluloses.[25] The prominent absorption at 1043 cm^{-1} is attributed to

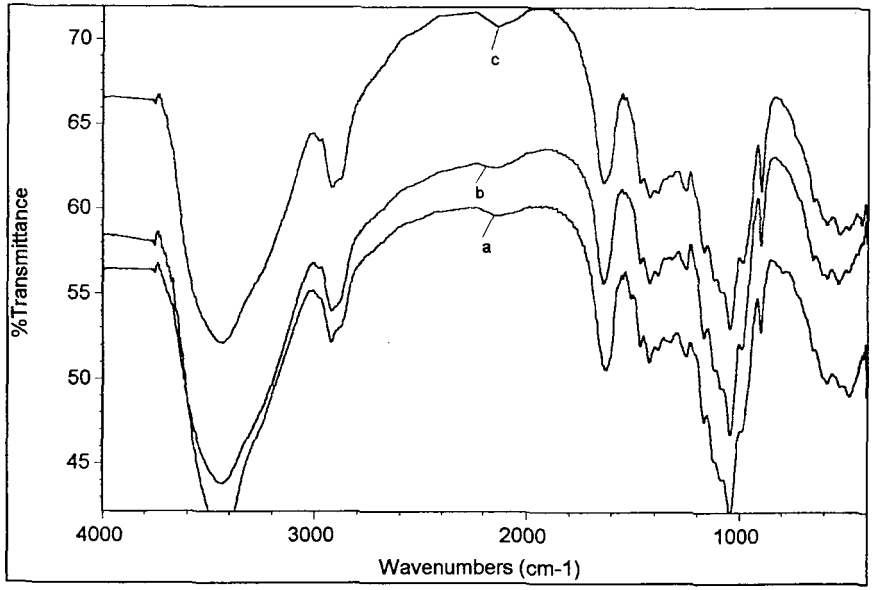

FIGURE 3. FT-IR spectra of hemicellulosic fractions extracted with (a) 5% NaOH, (b) 10% NaOH, and (c) 24% KOH-2% H_3BO_3 from oil palm trunk fibre.

the C-OH bending. The small sharp band at 897 cm^{-1} , which corresponds to the glycosidic C_1-H deformation with ring vibration contribution and OH bending, is characteristic of β-glycosidic linkages between the sugar units.[26] The presence of the arabinosyl side-chains is documented by the low-intensity absorption at 1170 cm^{-1} , which represents C-O, C-O-C stretching and C-OH bending.[27] The low intensity of the band at 990 cm^{-1} indicates the presence of arabinosyl units which have been reported to be attached only at positions 3 of xylopranosyl constituents. The bands in the region of 1125-1000 cm^{-1} are typical of xylans. Two small bands at 1125 and 1075 cm^{-1} indicate the C-O, C-C, stretching, and ring vibration and C-OH bending in xylans, respectively.[28] The occurrence of a small band at 1507 cm^{-1} in the hemicelluloses (spectrum a), extracted with 5% NaOH from lignified palm trunk fibre, corresponds to the aromatic skeleton vibrations in lignin. This further

indicates the presence of associated lignin in the hemicelluloses. The band intensity at 1341 cm^{-1} , which represents the syringyl ring breathing with C-O stretching in lignin molecules, is comparatively higher in spectrum a than in spectra b and c. This indicates a comparatively higher amount of lignin associated in the hemicelluloses when extracted with 5% NaOH from the lignified palm trunk fibre, than when extracted with 10% NaOH or 24% KOH-2% H_3BO_3 from the delignified palm trunk fibre. These results support with the data and conclusions resulting from alkaline nitrobenzene oxidation.

Figure 4 shows the FT-IR spectra of two hemicellulosic fractions, extracted with 5% NaOH from the lignified palm EFB fibre (spectrum a) and 10% NaOH from the delignified palm EFB fibre (spectrum b). As previous discussed, the absorbances at 1630, 1470, 1421, 1388, 1255, 1169, 1125, 1075, 1044, 990, and 897 cm^{-1} are associated with hemicelluloses. The lignin-related absorbance appears at 1507 cm^{-1} in the hemicelluloses extracted with 5% NaOH from the lignified palm EFB fibre, and completely disappears in the hemicelluloses, extracted with 10% NaOH from the delignified palm EFB fibre. This indicates that the hemicelluloses extracted with 10% NaOH from the delignified fibre, are relatively free of lignin. Additional evidence for the presence of associated lignin in the hemicelluloses comes from the absorbance at 1340 cm^{-1} . This absorbance can be assigned to the syringyl ring breaching with CO stretching.

CONCLUSIONS

Considered collectively, these results indicate that treatment of lignified palm trunk and EFB fibre with 5% NaOH solubilized 17.3% and 15.2% hemicelluloses, respectively. These are significant linear and acidic as shown by the comparatively high contents of xylose and uronic acids. While the extractions of the delignified palm trunk and EFB fibre with 10% NaOH and 24% KOH-2% H_3BO_3 yielded

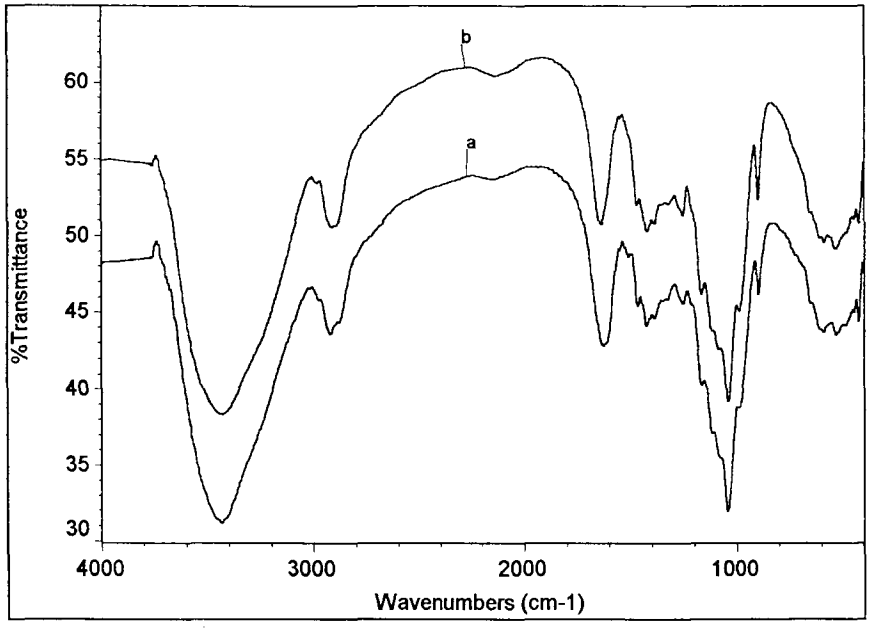

FIGURE 4. FT-IR spectra of hemicellulosic fractions extracted with (a) 5% NaOH and (b) 10% NaOH from oil palm EFB fibre.

11.9-13.5% and 13.5-14.9% hemicelluloses respectively. These are more branched and less acidic as indicated by the comparatively high galactose, glucose, and mannose contents, and low uronic acid content.

Additionally, the hemicelluloses, extracted with 5% NaOH from the lignified palm trunk and EFB fibre, had a large molecular size (weight-average, 17,400-22,900) and contained a comparatively high amounts of associated lignin (12.0-15.7%) as shown by the 4.07-5.70% yield of phenolic acid and aldehydes from the nitrobenzene oxidation. In contrast, the hemicelluloses, extracted with 10% NaOH and 24% KOH -2% H_3BO_3 from the delignified palm trunk fibre and EFB fibre, had a relatively small molecular size (weight-average, 6,600-10,800), and are

relatively free of associated lignin (0.3-1.1%) as shown by the 0.18-0.38% yield of the phenolic monomers from the nitrobenzene oxidation.

Syringaldehyde was found to be the major phenolic monomer in most of the nitrobenzene oxidation mixtures of residual lignin from the isolated hemicellulosic fractions, suggesting that lignin in the cell walls of palm trunk and EFB fibre is associated with hemicelluloses mainly via syringyl units. Further studies showed that the hemicelluloses in the cell walls of palm EFB fibre had a higher degree of polymerization, while the hemicelluloses in the cell walls of palm trunk fibre had a relatively lower degree of polymerization.

Both cell walls of palm trunk and EFB fibre yielded approximate 41-42% cellulose, isolated by 24% KOH-2% H_3BO_3. The cellulose, isolated with 10% NaOH from the palm trunk fibre and EFB fibre, contained relatively high amounts of xylose (2.04-3.50%) and mannose (1.02-1.42%), suggesting that extraction with 10% NaOH might result in incomplete isolation of hemicelluloses from the cell walls of trunk and EFB fibre. It is suggested that an optimum procedure for isolation of a pure cellulose could be extraction with 24% KOH-2% H_3BO_3 at 20°C for 2 h. This procedure resulted in cellulose preparations with relatively free of lignins.

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