

## Physicochemical Properties of Hydrothermally Treated Hemicellulose from Oil Palm Frond

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Hemicelluloses from oil palm frond (OPF) were extracted using 3 M potassium hydroxide (KOH) for 4 h at 40 °C with stirring at 400 rpm to obtain hemicelluloses A and B. The total yield of the hemicellulose isolated from OPF was 33% (dry weight). Both hemicelluloses A and B were then subjected to hydrothermal treatment at 121 °C and  $1.03 \times 10^5$  Pa for 10, 30, and 50 min. Physicochemical characterizations of hydrothermally treated hemicelluloses, such as Klason lignin content and reducing sugar content, were performed to study the effect of autohydrolysis processing on OPF-derived hemicelluloses. It was shown that Klason lignin content in hemicellulose A was higher than that in hemicellulose B and decreased after hydrothermal treatment. Hydrothermal treatment enhanced the solubility of hemicelluloses, which reflects their higher reducing sugar content. Monosaccharide analysis using HPLC showed that xylose was the predominant monosaccharide for both hemicelluloses A and B.

**KEYWORDS:** Hemicellulose; OPF; Klason lignin; monosaccharides

### INTRODUCTION

Agricultural waste byproducts from oil palm trees, such as empty fruit bunch (EFB), oil palm trunk (OPT), and oil palm frond (OPF), are rich in celluloses and hemicelluloses. Fractionation of these agricultural wastes into their main components may be of interest to obtain separate streams useable for different product applications. Among these enormous amounts of agricultural residues, only a minor quantity is reserved for animal feed or household fuel, and a major portion of the oil palm tree is burned, creating environmental pollution.

Hardwood xylans can be extracted directly from lignified wood with aqueous potassium hydroxide. The yields obtained vary widely for different types of wood, probably reflecting differences in the structure of the cell wall (1). Different extraction procedures also influence the yield of hemicelluloses. The structure of the alkali-extracted xylan is thought to be quite similar to that of the native polysaccharide, except that under alkaline conditions the *O*-acetyl groups are removed (2).

The best pretreatment options for lignocellulosic materials are those in which physical and chemical modifications are combined (3). In this regard, high-pressure steaming, with or without rapid decompression (explosion), has been claimed as one of the most successful pretreatment methods for fractionating wood into its three major components and enhancing the susceptibility of cellulose to enzymatic attack (4).

In this study, mild hydrothermal treatments using an autoclave at 121 °C and  $1.03 \times 10^5$  Pa with different treatment times were applied. A low-temperature process was chosen as more advantageous for the protection of oil palm frond against carbohydrate degradation and production of furfural and hydroxymethylfurfural (HMF) under drastic conditions.

### MATERIALS AND METHODS

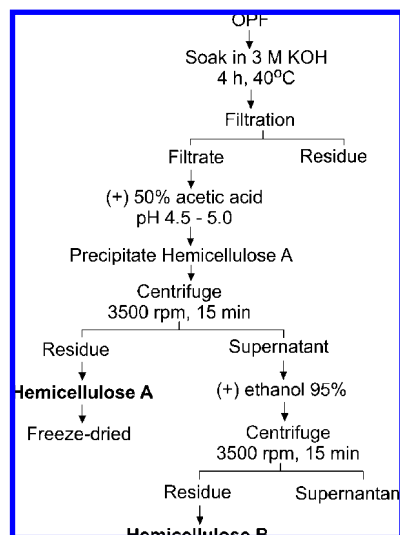
**Materials.** OPF samples used in this study were kindly supplied by Malaysian Palm Oil Berhad (MPOB), Bangi, Selangor. The samples were already chipped into small pieces and were kept at room temperature for further analysis. Moisture content for untreated OPF was  $8.56 \pm 0.02\%$ .

**Extraction of Hemicelluloses.** The procedure of Anis (5) with some modifications was used for alkaline extraction of hemicelluloses (Figure 1). Approximately 50 g samples were soaked in 3 M potassium hydroxide (KOH) with stirring at 400 rpm in a 40 °C water bath (CerTomat WR). The ratio of solid to liquid used was 1:10. After 4 h of extraction, the crude hemicelluloses were vacuum filtered using Whatman filter paper no. 4 through a Büchner funnel. The extracted fibers were rinsed with distilled water to remove residual alkali-soluble material and then kept for Klason lignin analysis. The filtrate was acidified with 50% (v/v) acetic acid until the pH reached 4.7–5.0 and allowed to stand for 24 h at 4 °C. The mixture was centrifuged (Kubota 5100, Japan) at 3000g for 15 min. The precipitate obtained was identified as hemicellulose A (HA) and was further washed with 50 mL of 95% (v/v) ethanol (technical grade) to remove residual acid from the samples. HA then was dried at 25 °C for 24 h in a vacuum oven (1450 D, ShelLab) to evaporate the ethanol. The supernatant (from the first precipitation to get HA) was then mixed with 4 volumes of 95% ethanol and was kept for 24 h at 4 °C. The mixture was centrifuged

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**Figure 1.** Flow chart for alkaline extraction of hemicelluloses using 3 M KOH at 40 °C for 4 h with stirring at 400 rpm.

(Kubota 5100) at 3000g for 15 min. The precipitate obtained was identified as hemicellulose B (HB). HB was further washed with 50 mL of 95% (v/v) ethanol and dried at 25 °C for 24 h in a vacuum oven (1450 D, ShelLab) to evaporate the ethanol. Both HA and HB were freeze-dried (LABCONCON) prior to analysis.

**Hydrothermal Treatment.** HA and HB from alkaline extraction of OPF samples were subjected to hydrothermal treatment using an autoclave (Hirayama HA 240) at 121 °C and  $1.03 \times 10^5$  Pa for 10, 30, and 50 min. Different treatment times were chosen to study the reducing sugar profiles obtained as a result of the autohydrolysis process. A preliminary study was carried out using different ratios of sample to water (1:5, 1:8, and 1:10). The ratio of 1:10 was chosen for further experiments on the basis of the higher solubility and reducing sugar obtained. Approximately 100 mL of distilled water was added to 10 g samples, which were then subjected to hydrothermal treatment using an autoclave. Time zero was taken when the temperature reached 121 °C. Samples were heated for 10, 30, and 50 min before cooling. After achieving ambient pressure, samples were taken from the autoclave and freeze-dried for further analysis.

**Determination of Klason Lignin Content.** Chemical analysis of untreated OPF, OPF fiber after alkaline extraction, HA, HB, and solid residue of hydrothermally treated hemicelluloses A and B was performed in duplicate according to a modification of TAPPI T222 for acid-insoluble lignin (6).

Approximately 2 mL of 72%  $\text{H}_2\text{SO}_4$  (v/v) was added to 0.2 g of dried samples in a 250 mL Erlenmeyer flask. The mixtures were gently stirred for 60 min at room temperature. The mixtures were added to approximately 56 mL of distilled water and treated in an autoclave at 121 °C,  $1.03 \times 10^5$  Pa, for 60 min. Preweighed glass microfiber filters were used to filter off the lignin. After filtration, the residues were washed with hot water until reaching neutral pH and dried at 105 °C overnight. The samples were stabilized in a desiccator and weighed. The weight loss was defined as percent of Klason lignin.

**Reducing Sugar Analysis.** Reducing sugar content of HA and HB was determined using the method of Bruner (7) with some modifications. A mixture of samples and 3,5-dinitrosalicylic acid (DNS) reagent was homogenized and put in a water bath (100 °C) for 5 min. The mixtures were then cooled immediately using ice cubes. Samples were analyzed using a UV spectrophotometer at 540 nm.

**FTIR Spectrum Analysis.** The infrared spectra of untreated and hydrothermally treated hemicelluloses were obtained from potassium bromide (KBr) pellets of the samples using a Perkin-Elmer System 2000 spectrophotometer in the frequency range of 4000–400  $\text{cm}^{-1}$ . The pressed-disk technique was employed for disk preparation, where  $950 \pm 0.1$  mg of dried KBr and  $5 \pm 0.1$  mg of sample were used. The KBr and sample mixtures were intimately mixed using a pestle and

mortar before being placed in a special die and compressed into a small disk. After the disk had been removed from the die, it was placed in a suitable holder in the spectrometer and scanned directly.

**Monosaccharide Analysis (HPLC).** Samples were hydrolyzed with some modifications prior to analysis. A monosaccharide profile for each sample was determined using HPLC with a refractive index detector. A Sugar-Pak I column (6.5 mm  $\times$  300 mm, Waters) was used with 0.001 M CaEDTA as a solvent at a flow rate of 0.5 mL/min. Samples were neutralized and filtered through SEP  $\text{C}_{18}$  followed by 0.45  $\mu\text{m}$  PTFE membrane before being used for direct HPLC determination of monosaccharides.

**Molecular Weight Distribution.** Molecular weights of HA, HB, and hydrothermally treated hemicelluloses were determined using a Shodex Ionpak column KS-804 (Showa Denko K.K, Japan, 30 mm  $\times$  8 mm). The exclusion molecular weight limit of the column used was  $4 \times 10^5$  g/mol. The chromatographic system was equipped with a Waters 1525 Binary HPLC Pump. A differential refractive index detector (Waters 2414) was used. Deionized distilled water was used as the eluent, and the injection volume was 100  $\mu\text{L}$ . The analysis was performed at a flow rate of 1 mL/min and at temperatures of 80 °C for the column and 35 °C for the RI detector. Samples in freeze-dried form were dissolved in deionized distilled water and were filtered through a 0.45  $\mu\text{m}$  membrane filter (Minisart, Sartorius) before being injected into the column. Molecular weights were estimated by comparing sample peak retention times to a standard curve composed of the logarithmic average molecular weight of the pullulan standards (Shodex pullulan standards P-82, Showa Denko). The molecular weight markers of pullulan used were in the range of 5000–800000 g/mol.

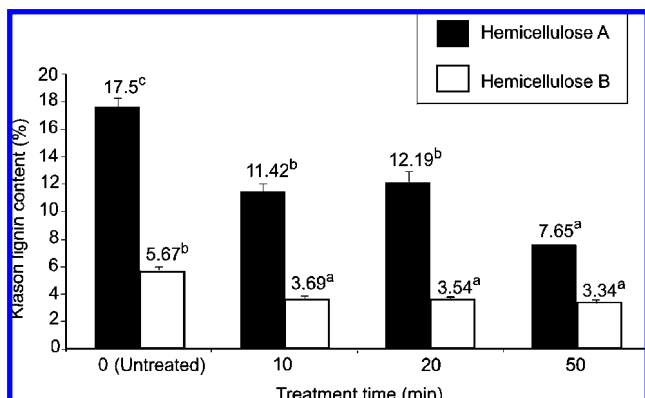
**Statistical Analysis.** One-way ANOVA was used to analyze the experimental data, and Duncan's multiple-range test was applied to determine the significant difference ( $P < 0.05$ ) of the samples. Significant correlations among some physicochemical properties of OPF-derived hemicellulose were also observed using SPSS 11.5 for Windows.

## RESULTS AND DISCUSSION

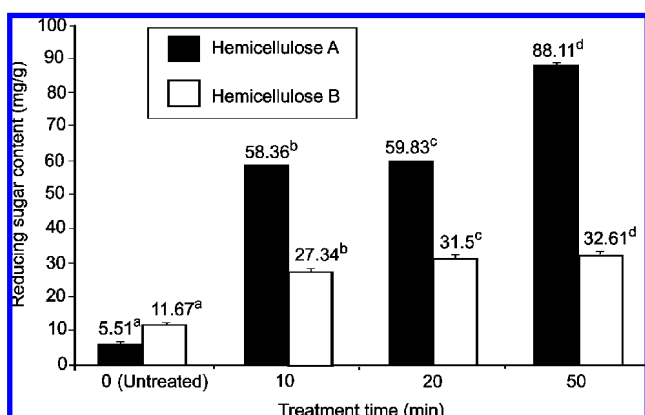
**Yield of Hemicellulose.** The total yield of the hemicellulose isolated from OPF was 33.1% (dry weight) of OPF fiber. However, the yield of HA (26.2%) was significantly higher than that of HB (6.9%). According to Nacos et al. (8) the first precipitation using acetic acid usually precipitates hemicellulose with higher molecular weight, whereas the next precipitation using ethanol precipitates hemicellulose with lower molecular weight.

Hemicellulose has a limited solubility in cold alkaline solutions, but warm alkaline solutions lead to hemicellulose degradation (9). During the extraction process, hydroxyl ions in KOH solution will cause swelling of cellulose and disruption of hydrogen bonds between cellulose and hemicelluloses. This tends to increase hydrophilicity and hence solubility of the polymers (10). Extraction of hemicelluloses also involves hydrolysis of ester linkages of hemicelluloses. According to Xiao et al. (10), in particular, all of the ester-linked substances of the hemicelluloses can be cleaved by alkali except for the cleavage of  $\alpha$ -ether bonds between lignin and hemicelluloses.

**Klason Lignin Content.** The lignin content in hemicellulosic samples was measured by acid-insoluble lignin (Klason lignin), which is the material left after acid hydrolysis of samples, because acid hydrolysis mainly degrades polysaccharides to monosaccharides (11). **Figure 2** shows that Klason lignin content in fiber after alkaline extraction was higher than in untreated OPF. This was due to the removal of substantial hemicellulose fraction in OPF samples by the action of KOH. Generally, Klason lignin content in HA was significantly higher than that in HB, either for untreated or hydrothermally treated hemicelluloses (**Figure 2**). After hydrothermal treatment, Klason



**Figure 2.** Klason lignin content in HA, HB, and hydrothermally treated hemicelluloses. Values are means, and error bars indicate the standard deviations. Letters (a–c) represent statistical comparisons made between different samples (HA and HB) at different treatment times. Means with the same letters for each sample are not significantly different ( $P > 0.05$ ).

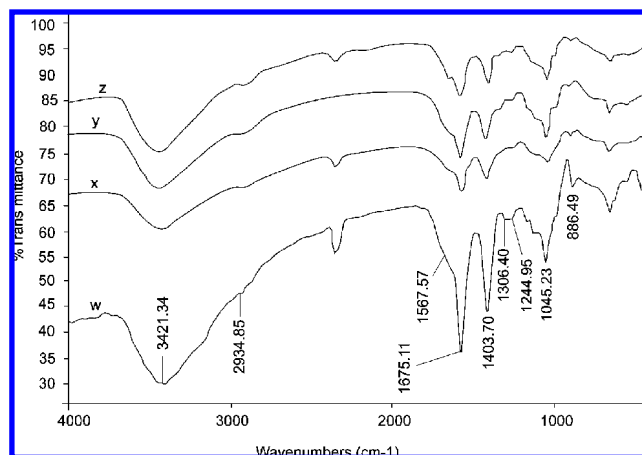


**Figure 3.** Total reducing sugar content in HA, HB, and hydrothermally treated hemicelluloses. Values are means, and error bars indicate the standard deviations. Letters (a–d) represent statistical comparisons made between different samples (HA and HB) at different treatment times. Means with different letters for each sample are significantly different ( $P < 0.05$ ).

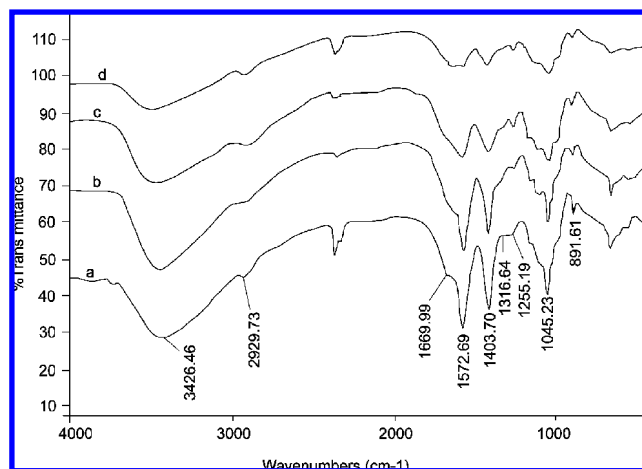
lignin content decreased. This may be related to chemical breakdown during the autohydrolysis process (12). However, the different hydrothermal treatment times of HB did not affect the Klason lignin content, because there were no significant differences ( $P > 0.05$ ) between any hydrothermally treated samples.

**Reducing Sugar Content.** Figure 3 shows that the total reducing sugar in untreated hemicellulose was lower than in hydrothermally treated samples. Reducing sugar content in HA was lower than in HB. However, after hydrothermal treatment, reducing sugar content in HA increased to above that of HB. These results suggest that hydrothermal treatment enhanced the degradation of hemicelluloses. During hydrothermal treatment, the hemicellulose–lignin bonds are cleaved, allowing the hemicelluloses to become water-soluble, where the solubilized materials are mainly monomeric and oligomeric sugars (13).

**FTIR Spectra.** As shown in Figures 4 and 5, all spectral profiles and relative intensities of most bands appeared to be rather similar, indicating a similar structure for all hemicellulosic samples. All of the spectra had a band at  $890\text{ cm}^{-1}$ , corresponding to the C-1 group frequency or ring frequency, which is characteristic of  $\beta$ -glucosidic linkages between the sugar units (14). This suggested that the xylose residues forming the



**Figure 4.** FTIR spectra of HA (w), HA<sub>10</sub> (x), HA<sub>30</sub> (y), and HA<sub>50</sub> (z).



**Figure 5.** FTIR spectra of HB (a), HB<sub>10</sub> (b), HB<sub>30</sub> (c), and HB<sub>50</sub> (d).

backbone of the macromolecule are linked by  $\beta$ -form bonds. After hydrothermal treatment, the band decreased, indicating that cleavage of the linkage occurred during the treatment (15). The wavenumber characteristic of typical xylans is  $1045\text{ cm}^{-1}$ , which is assigned to C–O and C–C stretching and the glycosidic (C–O–C) contributions (16). Several bands at 1255, 1403, and  $1316\text{ cm}^{-1}$  showed lignin content in hemicelluloses (17). Meanwhile, the absorbance at  $1572\text{ cm}^{-1}$  in all spectra of hemicelluloses originated from aromatic skeletal vibrations in associated lignin (16). Interestingly, in the spectra of HA and HB, the intensities of 1255, 1403, 1316, and  $1572\text{ cm}^{-1}$  were stronger than those in hydrothermally treated hemicelluloses, which corresponded to the result obtained by the analysis of Klason lignin content. A strong band due to hydrogen-bonded hydroxyl groups appeared at  $3430\text{ cm}^{-1}$  and the symmetric C–H vibration band appeared at  $2920\text{ cm}^{-1}$ , which showed the  $\text{CH}_3$  group (18).

**Monosaccharide Composition.** Generally, the extracted hemicelluloses consisted of two fractions: water-soluble and water-insoluble. Here, HA can be considered as the water-insoluble fraction, whereas HB is the water-soluble hemicellulose. In this study, hemicelluloses A and B were hydrolyzed using 72%  $\text{H}_2\text{SO}_4$  to release constituent sugars before being analyzed with HPLC. As shown in Table 1, hydrolysis of hemicelluloses using 72%  $\text{H}_2\text{SO}_4$  released three major sugar components: xylose, glucose, and arabinose. However, the compositions of these three sugar components were different between HA and HB. The different monosaccharide compositions between HA and HB are due to their different chemical structures. However, on the basis of the sugar composition alone,

**Table 1.** Monosaccharide Compositions and Ratios of Xylose to Arabinose of HA, HB, and Hydrothermally Treated Hemicelluloses, Hydrolyzed with 72% H<sub>2</sub>SO<sub>4</sub><sup>a</sup>

sample	monosaccharide components (mg/g)			ratio Xyl/Ara
	glucose	xylose	arabinose	
HA	116.23 b ± 1.77	802.07 d ± 1.30	61.82 a ± 2.59	12.97
HA <sub>10</sub>	98.48 a ± 1.92	590.50 a ± 1.88	62.85 a ± 1.45	9.40
HA <sub>30</sub>	136.37 c ± 3.35	602.99 b ± 2.53	82.93 b ± 3.78	7.27
HA <sub>50</sub>	205.15 d ± 2.61	615.90 c ± 1.79	97.95 c ± 2.77	6.29
HB	50.38 b ± 7.09	693.30 c ± 6.60	102.21 a ± 5.19	6.78
HB <sub>10</sub>	20.04 a ± 4.06	516.03 a ± 3.75	102.37 a ± 4.35	5.04
HB <sub>30</sub>	25.73 a ± 2.10	523.27 a ± 2.54	106.87 ab ± 6.07	4.90
HB <sub>50</sub>	26.93 a ± 1.55	538.43 b ± 2.25	112.40 b ± 1.70	4.79

<sup>a</sup> Letters (a–d) represent statistical comparisons made between each sample and monosaccharide at different treatment times. Means with different letters are significantly different ( $P < 0.05$ ).

it is difficult to draw conclusions about the branching patterns of the hemicelluloses (19).

The results revealed that xylose was the predominant monosaccharide for both HA and HB, ranging from 590.50 to 802.07 mg/g for HA and from 516.03 to 693.30 mg/g for HB. The next most abundant sugar for HA was glucose (98.48–205.15 mg/g), followed by arabinose (61.82–97.95 mg/g). For HB, the second most abundant sugar was arabinose (102.21–112.40 mg/g), followed by glucose (20.04–50.38 mg/g). This result suggested that the hemicelluloses from OPF are composed mainly of arabinoxylan. Revanappa et al. (20) also reported that hemicellulose A in Indian wheat varieties contained predominantly xylose, with a moderate amount of glucose along with a small amount of arabinose, and suggested that the fraction may be a mixture of xylan with small amounts of arabinoxylan-type polysaccharides. This observation is also similar to those made for rice straw and wheat straw (21). Thomsen et al. (22) also reported that the highest fraction of sugar released from wheat straw treated by hydrothermal treatment is xylan.

Although arabinoxylans from various cereals or various plant tissues share the same basic chemical structure, they differ in the manner of substitution of the xylan backbone. The main differences are found in the ratio of xylose to arabinose (Xyl/Ara), in the relative proportions and sequence of the various linkages between these two sugars, and in the presence of other substituents (23). According to Wedig et al. (24), xylose to arabinose ratios are indicative of the degree of linearity or branching of hemicelluloses. A high xylose to arabinose ratio indicates a high degree of polymerization with little bonding with other monosaccharide constituents. A low xylose to arabinose ratio suggests a short-chain polymer with a large amount of branching with other monosaccharides.

From **Table 1**, the xylose to arabinose ratios of HA and HB were approximately 12.97 and 6.78, respectively, which indicated that HB was more highly branched than HA. This observation corresponded well with the previous reports: the lower the arabinose content, indicating a lower degree of branching of the xylan chains, the lower the solubility of the polymer (25). Bendahaou et al. (26) also reported that water-soluble hemicelluloses are more highly branched than water-insoluble hemicelluloses.

**Molecular Weight Distribution.** In general, there are two major fundamental properties of polysaccharides that determine the overall functionality of the macromolecules; one is primary structure and the other is molecular weight and molecular weight distribution. As shown in **Tables 2** and **3**, two major peaks were found for HA and HB, which ranged from 12491 to 457921

**Table 2.** Molecular Weight Distribution of HA and Hydrothermally Treated Hemicellulose A

sample	peak	$M_w$	$M_n$	polydispersity ( $M_w/M_n$ )
HA	I	457921	407323	1.12
	II	91345	88046	1.04
HA <sub>10</sub>	I	407445	371928	1.09
	II	65877	61333	1.07
HA <sub>30</sub>	I	393155	361503	1.09
	II	66367	62881	1.06
HA <sub>50</sub>	I	414239	372014	1.11
	II	77289	73292	1.05

**Table 3.** Molecular Weight Distribution of HB and Hydrothermally Treated Hemicellulose B

sample	peak	$M_w$	$M_n$	polydispersity ( $M_w/M_n$ )
HB	I	350470	316456	1.11
	II	25734	19824	1.30
HB <sub>10</sub>	I	345030	312093	1.11
	II	22073	16796	1.31
HB <sub>30</sub>	I	314610	281956	1.12
	II	12491	8823	1.42
HB <sub>50</sub>	I	320892	291694	1.10
	II	14610	9351	1.56

g/mol. These relatively high molecular weights of HA and HB may indicate that the alkaline treatment under the condition used (temperature of 40 °C, 4 h, 3 M KOH) did not degrade the macromolecular structure of hemicellulose to any noticeable extent.

The reason for the higher molecular weight was probably that more lignin–hemicellulosic complex was coextracted with hemicelluloses. Thus, the molecular weight fractions identified in all hemicellulosic samples do not reflect the true molecular weight distributions of hemicelluloses. This result also relates to Klason lignin content; HB had a lower Klason lignin content as compared to HA. Correlation analysis shows that there was positive correlation (0.802) between molecular weight distribution and Klason lignin content for HB at  $P < 0.01$ . However, there was no significant correlation between molecular weight distribution and Klason lignin content for HA. Xu et al. (27) reported that water-soluble hemicellulose from perennial ryegrass leaves had a lower molecular weight than alkali-soluble hemicelluloses. Sun et al. (28) also reported that water-soluble hemicellulose from sugar cane bagasse showed a much lower molecular weight than alkali-soluble hemicellulose. Garcia et al. (29) also reported that Xilan A extracted from corn cobs had a higher molecular weight than Xilan B did.

Due to partial depolymerization during the delignification process with sodium chlorite, hemicellulosic fractions in this study were directly extracted with potassium hydroxide. Sun et al. (17) reported that molecular weights of hemicellulosic fractions before delignification were higher than those of hemicelluloses after delignification. In addition, a similarly low value of polydispersity of HA and HB indicates that all hemicelluloses solubilized having a more narrow molecular weight distribution. Molecular weight distribution for hydrothermally treated hemicelluloses was expected to decrease as the treatment time increased. However, the result shows that there were no specific trends in molecular weight distribution for both hydrothermally treated hemicelluloses A and B. It should be noted that the molecular weights of polysaccharide polymers vary depending on the method of their estimation. In

addition, depending on solvent quality, chain aggregation may be partially responsible for such a wide variation in the estimates of molecular weight of these hemicelluloses (30). In addition, the extraction protocol employed, including variable factors such as solvents, conditions, sample history, and calibration methods, may influence the molecular weight determination.

This study has elucidated the significance of hydrothermal treatment on the physicochemical properties of both OPF-derived hemicelluloses A and B. Knowledge of the physicochemical and functional properties of hemicelluloses will open up possibilities or new opportunities in food applications. It is hoped that this will be a useful guideline toward utilization of OPF for food or nonfood applications as well as toward achieving zero waste strategies in the palm industry. Nevertheless, to be commercialized, more research and investigation should be done on the chemical structure and functional properties of OPF-derived hemicelluloses.

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