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Fractionation of oil palm frond hemicelluloses by water or alkaline impregnation and steam explosion

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ABSTRACT

Steam explosion of oil palm frond has been carried out under different temperatures between 180 and 210 °C for 4 min (severity of 2.96–3.84) after impregnation of the frond chips with water or KOH solution. The effects of impregnation and steam explosion conditions of oil palm fronds on the water soluble fraction and insoluble fraction were investigated. The maximum yield of hemicelluloses in water soluble fractions recovered was 23.49% and 25.33% for water and KOH impregnation, treated with steam explosion at temperature of 210 °C (severity of 3.84) with a fractionation efficiency of 77.30% and 83.32%, respectively. Under this condition, the water insoluble fractions contained celluloses at 60.83% and 64.80% for water and KOH impregnation, respectively. The steam explosion temperature of 210 °C for 4 min ($\log R_o$ 3.84) was found to be the best condition in the extraction of hemicelluloses from OPF for both types of impregnation.

1. Introduction

Oil palm tree (*Elaeis guineensis Jacq.*) is one of the most important commercial crops for the production of palm oil in Malaysia and each hectare of oil palm plantation was reported to produce 10.88 tons of oil palm fronds (OPF) as a by-product (Kelly-Yong, Lee, Mohamed, & Bhatia, 2007). Currently OPF are left to rot in the field for soil conservation. Utilization of the OPF particularly on the fractionation of hemicelluloses for industrial purposes could provide an additional income for the palm oil producers and contributes to the socio-economic development in a society.

Hemicellulose is a complex carbohydrate structure that consists of different polymers like pentoses (xylose and arabinose), hexoses (mannose, glucose and galactose), and sugar acids. Recent studies demonstrated that hemicelluloses have been used for the production of xylooligosaccharides (Bian et al., 2014; Sabiha-Hanim, Mohd Noor, & Rosma, 2011), xylitol (Ping, Ling, Song, & Ge, 2013) and furfural (Sánchez, Serrano, Andres, & Labidi, 2013), films formation (Egüés, Eceiza, & Labidi, 2013) hydrogel (Sun, Wang, Jing, & Mohanathas, 2013) and ester derivatives (Belmokaddem, Pinel, Huber, Petit-Conil, & Perez, 2011).

In recent years, interest in the isolation of hemicelluloses from biomass has greatly increased (Rabetafika, Bchir, Blecker, Paquot, & Wathelet, 2014). Hemicelluloses are relatively tightly bound in the plant cell wall network to lignin and cellulose through hydrogen and covalent bonds respectively; it is difficult to separate them without significant modification of their structure (Sun, Sun, Sun, & Su, 2004). Highly branched hemicelluloses are easily water soluble. However, more uniform hemicelluloses with a low degree of side-chain substitution are tightly bound to cellulose and thus are less water soluble (Lawther, Sun, & Banks, 1995). Removal of hemicelluloses in a pure form from wood involves hydrolysis of ester and ether bonds which link the hemicelluloses to lignin (Sjöström, 1993).

There are several pretreatment technologies that have been used for the removal of hemicelluloses from biomass such as steam explosion, liquid hot-water extraction, alkaline extraction, dilute acid steam explosion and ammonia fibre explosion (Mosier et al., 2005). Steam explosion is the most commonly used pretreatment of biomass which uses both physical and chemical methods to break the structure of the lignocellulosic material through a hydrothermal treatment. In this process, the biomass is treated with high pressure steam at high temperature for a short period of time, followed by immediate depressurization which destroys the fibrils structure of the biomass. Among the advantage of this steam explosion pretreatment includes low energy requirement without any recycling or environmental costs as compared to mechanical comminution (Sun & Cheng, 2002).

In previous work the effectiveness of autohydrolysis process on hemicelluloses fractionation of OPF using conventional autoclave

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was evaluated (Sabiha-Hanim et al., 2011): a significant amount of hemicelluloses (11.46–14.94%) was produced in autohydrolysate with the different autohydrolytic treatment conditions (severity of 1.92–2.52). Anis (2000) reported that steam explosion of OPF at severity factor of 3.30–3.84 (190–210 °C for 3–8 min) had a good recovery of hemicellulose and that the main steaming product was hemicelluloses. However severity factor of 3.90 (210 °C for 5 min) had given more undesired compounds such as furfurals and acetic acids in the water extracts. Therefore the steaming temperature used for this study was carried out at temperature range of 180–210 °C for 4 min (severity factor of 2.96–3.84) to minimise the formation of undesired compound. In the present study, steam explosion with water or KOH impregnation under different temperatures followed by water extraction was employed to separate the water soluble fraction containing hemicelluloses and the insoluble fraction (oil palm fronds residue). This method would increase the yield of hemicelluloses in water soluble fractions compared to the conventional autoclave. The effects of different impregnation and steam explosion treatment conditions on water soluble fraction and insoluble fraction were investigated. The molecular weight, monosaccharide content, Fourier transform infrared (FT-IR), Klason lignin, acetic acid and furfural were determined in the water soluble fractions under different treatment conditions while cellulose, hemicelluloses and Klason lignin remaining in the steam exploded fronds (water or KOH impregnation) after water extraction were determined.

2. Materials and methods

2.1. Materials

Chipped and dried OPF samples were kindly supplied by the Malaysian Palm Oil Board (MPOB), Bangi, Selangor and stored at room temperature. The moisture content of the OPF was 7.79% upon receipt. The size and length of samples were around 0.5 mm and 3–8 mm, respectively and contained 44.0% cellulose, 30.4% hemicellulose, 15.4% Klason lignin, 4.1% ethanol-toluene extractive, 3.2% ash and 2.9% others (Sabiha-Hanim et al., 2011). The chemicals used in this study were of analytical grade unless otherwise stated.

2.2. Steam explosion treatment

Impregnation of dried OPF was achieved by soaking 100 g of dry fronds in 1.0 L water or 0.5% KOH solution for 24 h. After soaking, the excess solution was filtered off. Impregnated OPF was then steam exploded in a reactor steam explosion apparatus (Nitto Koatsu Corporation, Japan) with maximum operating pressure of 25.17 kg/cm^2. Steam explosion treatment was carried out at the Forestry and Forest Products Research Institute, Tsukuba, Japan. The water or KOH impregnation OPF were steamed at different temperatures from 180 to 210 °C during 4 min (corresponding to severity factors of 2.96–3.84), before a sharp decompression. The severity factor was calculated by the following equation (Overend and Chornet, 1987):(1)$\log R_o = \log\{t \exp\left[(T-100)/14.75\right]\}$where t is residence time in minutes and T is the reaction temperature in °C.

Following that, the exploded OPF was collected in a container, vacuum filtered and dried at 40 °C until a constant weight was obtained. The steam exploded fronds obtained from water and KOH impregnation were designated as SEF_w and SEF_k respectively.

2.3. Water extraction

An amount of 10 g dried SEF_w and SEF_k were then extracted with water at 70 °C for 2 h at a solid liquid ratio of 1:10 (%w/v), and filtered (Halimahton, Sudo, & Ishihara, 1990). Then, it was centrifuged at 3500 rpm for 15 min using a Kubota 5100. The water soluble fraction was filtered and freeze-dried (Labconco FreeZone, USA). The water insoluble fraction was dried at 40 °C for 3 h and the weight was recorded. The water soluble fraction obtained from SEF_w and SEF_k was designated as WS_w and WS_k respectively, meanwhile the insoluble fraction obtained from water and KOH impregnation of steam exploded fronds was designated as WI_w and WI_k respectively.

2.4. Analytical methods

Reducing sugars were quantified by the Nelson–Somogyi method (Chaplin & Kennedy, 1986) and expressed as xylose equivalents. Total sugar content was measured according to the phenol–sulphuric acid method (Dubois, Gilles, Hamilton, Rebers, & Smith, 1956) and expressed as glucose equivalents.

The monosaccharide (glucose, xylose and arabinose) contents were determined by high-performance liquid chromatography (HPLC; Waters 2690, U.S.A). HPLC analyses were performed with a Sugar-Pak I column (6.5 mm × 300 mm, Waters, U.S.A) with 0.1 mM CaEDTA as the mobile phase at a flow of 0.6 mL/min and a column temperature of 90 °C. The eluted monosaccharides were detected by a refractive-index detector (Waters 2410) at 37 °C.

Molecular weight of hemicelluloses was determined using a Shodex Ionpak KS 804 column (8 mm × 30 mm, Showa Denko K.K, Japan). The exclusion molecular-weight limit of the column used was 4×10^5 g/mol. The chromatographic system was equipped with a binary HPLC pump (Waters 1525) and a refractive-index detector (Waters 2414), set at 37 °C. Deionized water was used as an eluent at a flow rate of 1.0 mL/min, with a column temperature of 80 °C and an injection volume of 100 μL. The 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 5×10^3 to 8×10^5 g/mol.

Furfural was determined using a UV–vis spectrophotometer at 280 nm (Aguilar, Ramirez, Garrote, & Vazquez, 2002) with furfuraldehyde (RandM, U.S.A) as a standard in the range of 0 to 0.09 μg/mL. Acetic acid concentration was determined using HPLC (Waters 2690) with the ROA–Organic acid column (300 mm × 7.8 mm, Rezex Phenomenex, U.S.A). Elution took place at 40 °C with 0.005 N H_2SO_4 at 0.5 mL/min with peak detection using a UV detector (Waters 2487) at 210 nm. Acetic acid (ChemAR, Systerm, Malaysia) in the range of 0–10 mg/mL was used as a standard.

The pH of WS_w and WS_k was determined using a pH meter Cyberscan 500 (Eutech Cybernetics, Singapore) in a triplicate analysis. The Klason lignin was measured following TAPPI T222 OM-88. FT-IR spectra were obtained on an FT-IR spectrophotometer (Perkin Elmer System 2000) using a KBr disc containing 1% finely ground samples. The OPF residues were analysed for cellulose, hemicelluloses and lignin according to Han and Rowell (1996).

2.5. Statistical analysis

The results were expressed as mean ± SD (standard deviation). One way ANOVA was used to analyse the experimental data and Duncan's multiple range test was applied to determine the significantly different ($p < 0.05$) samples using Statistical Package for Social Science, Version 10 (SPSS Inc., Illinois USA).

Table 1
Steam explosion conditions and the recovery yield (%) of steam exploded fronds.

Temperature (°C)	Severity factor ($\log R_o$)	Steam exploded fronds[1]	
		SEF_w	SEF_k
180	2.96	88.20 ± 0.72^{c}	87.70 ± 0.42^{a}
190	3.25	88.00 ± 0.98^{c}	86.90 ± 0.46^{a}
200	3.55	86.70 ± 1.12^{bc}	86.25 ± 0.62^{a}
210	3.84	84.20 ± 0.71^{a}	86.10 ± 0.35^{a}

Data is presented as means ± standard deviations ($n = 3$). Mean values followed by different lower case superscripts in a row are significantly different ($p < 0.05$).
[1] Represents the steam exploded fronds obtained from water impregnation (SEF_w) and KOH impregnation (SEF_k).

3. Results and discussion

3.1. Steam explosion treatment

The dried fronds were soaked in water or KOH solution for 24 h to moisten the fronds. According to Glasser and Wright (1998), the addition of water or solution to very dry wood could increase the moisture contents to 50–55% moisture level that is suitable for steam explosion treatment. In this study it was found that 51.2% and 50.5% moisture were obtained after soaked fronds in water and 0.5% KOH, respectively for 24 h.

Table 1 shows the effect of steam explosion on the recovery yield of steam exploded frond soaked in water and KOH solution. The yields are expressed as weight percent of the dried OPF. The recovery yield of the SEF_w and SEF_k were ranged from 84.2% to 88.2% and 86.1% to 87.7%, respectively which was comparable to those obtained at similar severity for cotton gin waste which ranged from 88.2% to 97.6% (Jeoh & Agblevor, 2001).

As shown in Table 1, the losses incurred in this study for SEF_w and SEF_k ranged from 11.8% to 15.8% and 12.3% to 13.9%, respectively at 180–210 °C ($\log R_o$ 2.96–3.84). In comparison, a total loss of 16.9–24.4% at $\log R_o$ 3.70–4.54 was reported for red oak by Ibrahim and Glasser (1999) while in cotton gin waste the loss was 2.4–12.8% at $\log R_o$ 2.79–3.91 (Jeoh & Agblevor, 2001). The fibre losses are higher at high severities and lower at low severities. This indicates that different sources of raw material for steam explosion result in different values of losses despite having similar severities ranges. In addition, the yield of SEF_k was slightly lower than the yield of SEF_w, indicating that soaking the OPF in 0.5% KOH solution could contribute to the loss of cellulose and hemicelluloses.

3.2. Water extraction of steam exploded fronds

Table 2 shows the yield of WS_w, WS_k, WI_w and WI_k obtained after extraction with water of the fronds steam exploded at different temperatures. The yields are expressed as dry weight percent of OPF. The yield of both WS_w and WS_k was found to increase with the increment of the severity treatment from 14.47% to 26.50% and 10.64% to 15.75%, respectively. The yield of WS_k was significantly lower than WS_w indicating that soaking of OPF in 0.5% KOH solution prior steam explosion treatment may have an influence on the water soluble yield. The highest yield of WS_w and WS_k was obtained at the steaming temperature of 210 °C ($\log R_o$ 3.84).

Table 2
The yield (%) of water soluble fraction and water insoluble fraction obtained after water extraction of steam exploded fronds.

Severity factor ($\log R_o$)	Water soluble fraction[1]		Water insoluble fraction[2]	
	WS_w	WS_k	WI_w	WI_k
2.96	14.47 ± 0.34^{bc}	10.64 ± 0.89^{a}	73.73 ± 1.30^{c}	77.06 ± 1.80^{c}
3.25	15.50 ± 0.71^{bc}	11.49 ± 0.67^{a}	72.50 ± 1.60^{c}	75.41 ± 1.50^{bc}
3.55	20.00 ± 0.51^{d}	12.88 ± 0.92^{ab}	66.70 ± 1.80^{b}	73.37 ± 1.60^{b}
3.84	26.50 ± 0.30^{e}	15.75 ± 0.60^{c}	57.70 ± 1.50^{a}	70.35 ± 1.60^{a}

Data is presented as means ± standard deviations ($n = 3$). Yield values followed by different lower case superscripts in a column are significantly different ($p < 0.05$).
[1] Represents the water soluble fraction obtained from water impregnation of steam exploded fronds (WS_w) and KOH impregnation of steam exploded fronds (WS_k).
[2] Represents the water insoluble fraction obtained from water impregnation of steam exploded fronds (WI_w) and KOH impregnation of steam exploded fronds (WI_k).

As the severity factor increased from 2.96 to 3.84, the yield of WI_w correspondingly decreased to 57.70%. Similarly, the yield of WI_k decreased to 70.35%. This phenomenon indicates that treatment at high severity factor has a major influence on the yield of the water insoluble fraction as demonstrated by Emmel, Mathias, Wypych, & Ramos (2003). The result also shows that the yield of WI_w was lower than WI_k.

3.3. Composition of water soluble fractions

Table 3 represents the fractionation efficiency and chemical composition of the water soluble fraction at different severities of treatment. The maximum hemicelluloses yield of 23.49% and 25.33% with a fractionation efficiency of 77% and 83% were achieved at temperature of 210 °C (severity factor of 3.84) for both WS_w and WS_k, respectively. During the steam explosion process, glycosidic bonds in hemicelluloses and cellulose were hydrolyzed to some extent and the hemicelluloses-lignin bonds were cleaved due to autohydrolysis pressure. This allowed the hemicelluloses to be depolymerised, partially degraded and solubilised in hot water (Chen & Liu, 2007).

An increase in severity treatment from $\log R_o$ 2.96 to 3.84 resulted in decrease concentration of glucose and arabinose in the WS_w from 8.01% to 6.84% and 9.73% to 7.74%, respectively, while xylose concentration increased from 4.40% to 12.89%. This indicates that the hemicellulose was hydrolysed, which led to sugar monomers. An increase in severity treatment from $\log R_o$ 2.96 to 3.84 resulted in an increase of xylose concentration in the WS_k from 0.69% to 1.33%, while arabinose and glucose concentration decreased from 3.68% to 1.78% and 1.40% to 1.03%, respectively. This significant increase in xylose content and substantial decrease in glucose content with the increase of severity from $\log R_o$ 2.96 to 3.84 suggest the presence of glucose in the OPF walls. Glucose is probably present in the side chains of hemicellulose and easily released at low temperature, while xylose is present in the main chains of hemicellulose, and is favourably extracted at a relatively high severity of treatment. This observation implies that the hemicellulose extracted was mainly composed of xylan structure. It was also observed that glucose was not detected in the WS_k at a temperature of 210 °C. This could possibly be due to glucose degradation during soaking with KOH and steaming at high temperature.

Arabinose was easily solubilized during the steam explosion treatment. The presence of a noticeable amount of arabinose implied that the water-soluble fraction consisted of side chain arabinose. In general, the ratio of arabinose to xylose (Ara/Xyl) is indicative of the degree of linearity or branching of hemicelluloses (Chaikumpollert, Methacanon, & Suchiva, 2004). The Ara/Xyl ratio for both WS_w and WS_k were in the range of 0.60–2.21 and 1.34–5.33, respectively. The Ara/Xyl ratio of WS_w was lower than WS_k indicating that WS_w seemed to be more linear than WS_k.

The results showed that the Klason lignin in the water soluble fractions increased with the severity of treatment for both types of impregnation. Both WS_w and WS_k contained relatively low amounts of Klason lignin, ranging between 1.58% and 4.12%. These low concentrations of Klason lignin indicated that steam explosion at elevated temperatures and low acidity was more dramatic in terms of cleavage of lignin carbohydrate bonds than mild acidolysis due to the higher temperature. In comparison, the Klason lignin content in the WS_k was lower than that of WS_w. This suggests that

Table 3
Chemical composition of the water soluble fractions obtained after water extraction of steam exploded fronds.

Severity factor ($\log R_o$)	2.96	3.25	3.55	3.84
WS_w[1]				
Fractionation efficiency (%)[3]	50.66	55.16	64.47	77.30
Hemicellulose (%)	15.40 ± 0.13^{a}	16.77 ± 1.60^{b}	19.60 ± 0.73^{c}	23.49 ± 1.70^{d}
pH	3.70 ± 0.02^{b}	3.67 ± 0.02^{ab}	3.65 ± 0.02^{ab}	3.60 ± 0.03^{a}
Total sugars (%)	38.49 ± 2.26^{a}	44.74 ± 2.05^{b}	55.82 ± 1.68^{c}	64.47 ± 1.54^{d}
Monosaccharides (%)				
Glucose	8.01 ± 0.17^{d}	7.67 ± 0.20^{c}	7.32 ± 0.11^{b}	6.84 ± 0.17^{a}
Xylose (Xyl)	4.40 ± 0.29^{a}	5.15 ± 0.12^{b}	7.04 ± 0.09^{c}	12.89 ± 0.30^{d}
Arabinose (Ara)	9.73 ± 0.18^{d}	9.21 ± 0.19^{c}	8.81 ± 0.33^{b}	7.74 ± 0.20^{a}
Ara:Xyl	2.21	1.79	1.25	0.60
Acetic acid (g/L)	0.56 ± 0.01^{b}	0.83 ± 0.03^{c}	1.06 ± 0.05^{d}	1.35 ± 0.04^{e}
Furfural (g/L)	0.18 ± 0.01^{a}	0.39 ± 0.02^{b}	0.56 ± 0.03^{c}	0.73 ± 0.03^{d}
Klason lignin (%)	2.25 ± 0.20^{a}	3.07 ± 0.30^{b}	3.35 ± 0.26^{b}	4.12 ± 0.26^{c}
WS_k[2]				
Fractionation efficiency (%) 3	55.36	62.11	70.26	83.32
Hemicellulose (%)	16.83 ± 0.90^{a}	18.88 ± 0.83^{b}	21.36 ± 0.80^{c}	25.33 ± 1.00^{d}
pH	5.71 ± 0.01^{e}	5.44 ± 0.01^{d}	5.15 ± 0.03^{c}	5.08 ± 0.03^{c}
Total sugars (%)	23.78 ± 1.46^{a}	26.65 ± 2.40^{ab}	29.99 ± 1.80^{b}	38.87 ± 1.20^{c}
Monosaccharides (%)				
Glucose	1.40 ± 0.14^{c}	1.19 ± 0.13^{b}	1.03 ± 0.13^{a}	ND[4]
Xylose (Xyl)	0.69 ± 0.19^{a}	0.95 ± 0.15^{b}	1.20 ± 0.17^{c}	1.33 ± 0.12^{d}
Arabinose (Ara)	3.68 ± 0.30^{d}	3.06 ± 0.12^{c}	2.35 ± 0.16^{b}	1.78 ± 0.07^{a}
Ara:Xyl	5.33	3.22	1.96	1.34
Acetic acid (g/L)	0.34 ± 0.02^{a}	0.52 ± 0.04^{b}	0.97 ± 0.03^{cd}	1.28 ± 0.06^{e}
Furfural (g/L)	0.16 ± 0.01^{a}	0.33 ± 0.01^{b}	0.50 ± 0.03^{c}	0.67 ± 0.04^{d}
Klason lignin (%)	1.58 ± 0.14^{a}	1.67 ± 0.15^{a}	1.83 ± 0.13^{a}	2.04 ± 0.15^{a}

Data is presented as means ± standard deviations ($n = 3$). Mean values followed by different lower case superscripts in a row are significantly different ($p < 0.05$).
Values are expressed as weight% of dried water soluble fraction.
[1] Represents the water soluble fraction obtained from water impregnation of steam exploded fronds.
[2] Represents the water soluble fraction obtained from KOH impregnation from steam exploded fronds.
[3] Calculated as the hemicelluloses concentration in the water soluble fraction divided by the original hemicelluloses in dried oil palm frond.
[4] ND, not detected.

when the OPF was soaked in KOH the Klason lignin was partially solubilised and dissolved in the aqueous phase. Additionally, this observation shows that more condensation and repolymerization reactions between the degradation products of hemicellulose and lignin took place during steam explosion resulting in the increase of Klason lignin in the WS_w.

The acetic acid concentration was also found to increase for both WS_w and WS_k when the severity of treatment increased due to the hemicelluloses depolymerisation (Sun et al., 2005; Carvalheiro, Esteves, Parajo, Pereira, & Girio, 2004). The acetic acid concentration increased as the temperature increase which reflects on the increased extent of the acetyl group removal from hemicellulose (Vazquez, Alonso, Dominguez, & Parajó, 2006). Acetic acid concentrations obtained from the WS_w and WS_k ranged from 0.56 to 1.35 g/l, and 0.34 to 1.28 g/l respectively. These acetic acid concentrations were lower than those usually reported for the hydrothermal treatment of xylan-rich material. In the present study the maximum concentration of acetic acid (1.35 g/l) in WS_w was obtained at 210 °C ($\log R_o$ 3.84). The maximal acetic acid concentration obtained by Carvalheiro et al. (2004) was 2.19 g/l after 20 min of treatment at 190 °C ($\log R_o$ 3.95) while Garrote, Dominguez, and Parajo (2002) reported that the steam explosion of corncob at 216 °C produced 3.70 g/l acetic acid. As shown in Table 3, the acetic acid concentrations in the WS_w were higher than the WS_k at different severity. This suggests that soaking of OPF in water prior to steam explosion which initial pH was 4.07 (data not shown) led to increase in acetic acid.

In addition, the higher steaming temperature with longer period of treatment will increase the furfural content in the hydrolysates. Therefore, mild severity in the treatment step is desirable to limit sugar dehydration to furfural compounds which is toxic to micro-organisms. Furfural was generated as a degradation product from a pentose like xylose. Table 3 shows the furfural concentrations of the WS_w and WS_k ranged from 0.18 to 0.73 g/l and 0.16 to 0.67 g/l respectively. Garrote, Dominguez, and Parajo (1999) reported that at steaming temperature of 175 °C for 18.2 min ($\log R_o$ 3.47), the concentration of furfural was 0.157 g/l, while Carvalheiro et al. (2004) found that the furfural concentration were in the range of 0.52–0.74 g/l from steam explosion treatment at 150 °C for 120 min ($\log R_o$ 3.55) to 190 °C for 5 min ($\log R_o$ 3.35). In the present study, the furfural content was very low, indicating that hydrolytic reactions largely predominated over degradation reactions such as dehydration. In any case, the acetic acid and furfural could not be quantitatively recovered in water soluble fraction because they were partially lost to the atmosphere after explosive decompression (Emmel et al., 2003). Furthermore the water extract in this study were freeze-dried prior to analyses, hence this step also contributes to the losses of acetic acids and furfural to the atmosphere (Nabarlatz, Ebringerova, & Montane, 2007).

3.4. Weight average molecular weight

Table 4 shows the molecular weight and polydispersity of hemicelluloses in water soluble fractions. The gel permeation chromatography (GPC) revealed that the M_w of hemicelluloses in the WS_w and WS_k ranged from 27,445 to 30,021, and from 23,017 to 25,869 g/mol, respectively, indicating that the long chain hemicelluloses were degraded under the steam explosion conditions used. The GPC spectra for WS_w and WS_k is shown in Fig. 1.

Increased severity factor from 2.96 to 3.84, led to a decrease of degraded hemicelluloses molecular weights by 8.6% in the WS_w and 11.0% in the WS_k. Sun et al. (2005) reported that this reduction in chain length of the hemicelluloses resulted partially from the action of heat and steaming temperature produced during steam explosion. The results confirmed again that steam explosion not only attacked the integrity of the cell walls rendering their components more accessible to treatment, but also broke the inter

Table 4
Weight-average (M_w) and number-average (M_n) molecular weight and polydispersity (M_w/M_n) of the water soluble fractions for water-soaked and KOH-soaked fronds steam explosion.

Severity factor ($\log R_o$)	2.96	3.25	3.55	3.84
WS_w[1]				
M_w (g/mol)	30,021 ± 421[d]	29,987 ± 637[cd]	28,354 ± 832[c]	27,445 ± 381[c]
M_n (g/mol)	27,365 ± 720[b]	25,784 ± 662[a]	25,067 ± 427[a]	24,311 ± 651[a]
Polydispersity, P (M_w/M_n)	1.097 ± 0.018[a]	1.163 ± 0.037[a]	1.131 ± 0.029[a]	1.129 ± 0.014[a]
WS_k[1]				
M_w (g/mol)	25,869 ± 1412[b]	25,326 ± 1132[b]	24,287 ± 867[ab]	23,017 ± 1267[a]
M_n(g/mol)	24,165 ± 1015[b]	23,134 ± 327[ab]	22,867 ± 1245[a]	21,785 ± 1231[a]
Polydispersity, P (M_w/M_n)	1.071 ± 0.041[a]	1.095 ± 0.060[a]	1.062 ± 0.025[a]	1.057 ± 0.001[a]

Data is presented as means ± standard deviations ($n = 3$). Mean values followed by different lower case superscripts in a row are significantly different ($p < 0.05$).
[1] Corresponding to the water soluble fractions in Table 3.

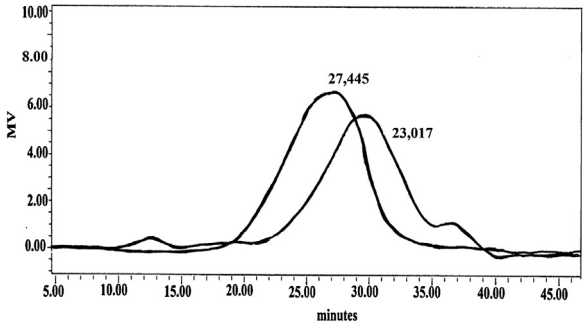

Fig. 1. GPC spectra of WS_w (M_w = 27,445 g/mol) and WS_k (M_w = 23,017 g/mol) at temperature of 210 °C for 4 min (severity of 3.84).

and intra-molecular hemicellulose backbone linkages, resulting in a depolymerization of the hemicellulose macromolecules into fragments soluble in water. As can be seen, low value of the polydispersity was obtained in both WS_w and WS_k. The low polydispersity indicated that hemicellulose solubilised has a narrow molecular weight distribution.

3.5. FT-IR spectra

The FT-IR of WS_w (spectrum 1) and WS_k (spectrum 2) are shown in Fig. 2. Both fractions were obtained at steam explosion of 210 °C for 4 min (severity of 3.84). Obviously, all the two spectra had a specific band maximum in the 1250–1000 cm^{-1}, which was typical of xylans. This region was dominated by ring vibrations overlapped with stretching vibrations of (C—O—H) side groups and the (C—O—C) glycosidic bond vibration (Sun et al., 2005). The prominent absorption at 1048 cm^{-1} was attributed to the C—O, C—C stretching or C—OH bending in hemicellulose (Kacurakova, Belton, Wilson, & Hirsch, 1998). A strong band at 1735 cm^{-1} in the spectrum 1 was attributed either to the acetyl and uronic ester groups of the hemicellulose, or from the ester linkage of carboxylic group of the ferulic acid. The absence of this signal in spectrum 2 indicates that the soaking of OPF in 0.5% KOH solution prior to steam explosion treatment completely cleaved this ester bond from the hemicellulose.

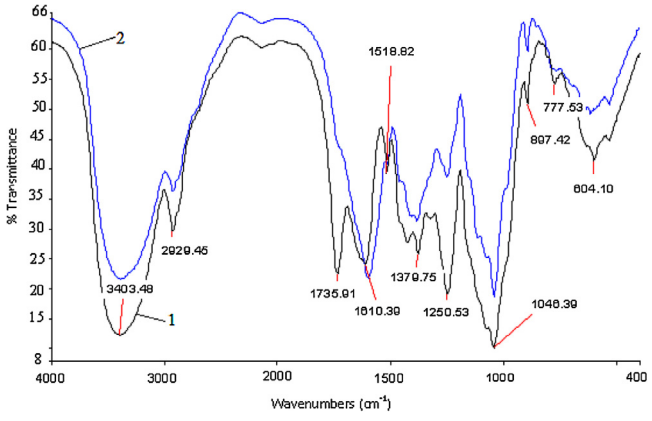

Fig. 2. FT-IR spectra of WS_w (spectrum 1) and WS_k (spectrum 2) at temperature of 210 °C for 4 min (severity of 3.84).

The band at 1610 cm^{-1} was principally associated with absorbed water (Oliveira et al., 2010), and the small band at 1379 cm^{-1} showed low Klason lignin content in water soluble fractions. The lignin-related absorbance at 1518 cm^{-1} was also observed for spectra 1 and 2 and indicated minor quantities of the associated lignin. The small band at 897 cm^{-1} was a characteristic of β-glycosidic linkages between the sugar units (Geng, Sun, Sun, & Lu, 2003). This suggests that the xylose residues forming the backbone of the macromolecule are linked by β form bonds. The absorptions at 1250 and 1048 cm^{-1} are associated with hemicelluloses (Peng, Peng, Xu, & Sun, 2012). All these absorbance bands occurred simultaneously in both spectra 1 and 2. The prominent band around 3403 cm^{-1} represents the hydroxyl stretching vibrations of the hemicellulose and the water involved in hydrogen bonding.

3.6. Composition of water insoluble fraction

The hemicelluloses content in the WI_w and WI_K decreased from 15.00% to 6.91% (w/w) and from 13.57% to 5.07% (w/w) respectively as shown in Table 5. As expected, the content of hemicellulose decreased steadily with the severity of treatments, owing to the higher conversion of hydrolytic degradation reactions (Vazquez et al., 2006). The result also indicates at lower severity, most the hemicelluloses accumulate in the water soluble fraction. However, at higher severity, some hemicelluloses remained in the insoluble fraction hence the content of this hemicelluloses in the water soluble fraction does not reflect the total amount of hemicelluloses extracted from the OPF. This is a common observation made for several raw materials treated in a similar manner (Garrote et al., 2002; Lloyd & Wyman, 2003).

As the steam explosion temperature increased from 180 to 210 °C ($\log R_o$ 2.96–3.84) in WS_k the cellulose content increased up to 64.80% (w/w) and Klason lignin increased from 19.80% to 28.56% (w/w) (Table 5). This suggests that at higher temperature the cellulose and Klason lignin content in the insoluble fraction increases. This was due to the increased release of hemicellulose in the water soluble fraction (Kabel, Bos, Zeevalking, Voragen, & Schols, 2007). The high temperature steam radically modified the plant cell wall structure, yielding a dark brown material from which partially hydrolysed hemicellulose were easily recovered by water extraction. This left behind the solid residue composed of cellulose, residual hemicelluloses and a chemically modified lignin (Ramos, 2003).

Table 5
Chemical composition of the water insoluble fraction obtained after water extraction of steam exploded fronds.

Severity factor ($\log R_o$)	*Water insoluble fraction*[1]					
	WI_w			WI_k		
	Cellulose	Hemicellulose	Klason lignin	Cellulose	Hemicellulose	Klason lignin
2.96	57.76 ± 0.85^{a}	15.00 ± 0.13^{c}	18.30 ± 0.73^{a}	60.20 ± 1.07^{a}	13.57 ± 0.85^{c}	19.80 ± 0.31^{a}
3.25	58.50 ± 0.65^{a}	13.63 ± 1.59^{c}	19.53 ± 0.95^{a}	61.21 ± 2.03^{a}	11.52 ± 0.83^{c}	22.00 ± 1.00^{a}
3.55	59.15 ± 0.35^{ab}	10.08 ± 0.73^{b}	20.47 ± 0.90^{a}	62.16 ± 1.20^{a}	9.04 ± 0.80^{b}	24.77 ± 0.40^{b}
3.84	60.83 ± 0.76^{b}	6.91 ± 1.70^{a}	21.23 ± 0.98^{a}	64.80 ± 1.39^{b}	5.07 ± 0.98^{a}	28.56 ± 0.77^{c}

Data is presented as means ± standard deviations ($n = 3$). Mean values followed by different lower case superscripts in a row are significantly different ($p < 0.05$).
[1] Corresponding to the water insoluble fractions in Table 2.

4. Conclusion

This work shows that the steam explosion is a promising technique for extracting hemicelluloses from OPF. Soaking the OPF in water prior to steam explosion gave a higher yield of water soluble fraction when compared to OPF soaked in KOH solution, however soaking OPF in KOH solution prior to steam explosion gave the higher fractionation efficiency for hemicelluloses extraction. The steam explosion temperature of 210 °C for 4 min ($\log R_o$ 3.84) was found to be the best condition in the extraction of hemicelluloses from OPF for both type of impregnation. Water-soluble fraction containing hemicelluloses will be further treated by enzyme hydrolysis for xylo-oligosaccharides production.

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