SUBCRITICAL WATER EXTRACTION OF MONOSACCHARIDES FROM OIL PALM FRONDS HEMICELLULOSES

(Pengekstrakan Air Subgenting Daripada Monosakarida Dari Hemiselulosa Pelepah Kelapa Sawit)

R., Norsyabilah, S. Sabiha Hanim*, M. H., Nor Suhaila, A. Noraishah, A.K., Siti Kartina

Faculty of Applied Sciences,
Universiti Teknologi MARA, 40450 Shah Alam, Selangor D.E. , Malaysia

**Corresponding author: sabihahanim@salam.uitm.edu.my*

Abstract

Oil palm plantations in Malaysia generate more than 36 million tones of pruned and felled oil palm fronds (OPF) and are generally considered as waste. The composition of monosaccharide in oil palm frond can be extracted using hydrothermal treatment for useful applications. The objectives of this study were to quantify the yield of monosaccharides at various reaction conditions; temperature 170 °C to 200 °C, pressure from 500 psi to 800 psi, reaction time from 5 to 15 min using subcritical water extraction and to determine the composition of oil palm frond hemicelluloses at optimum condition. The monosaccharides composition of oil palm frond hemicellulose were analysed using High Performance Liquid Chromatography (HPLC). The highest yield of monosaccharides can be extracted from OPF at temperature of 190 $^{\circ}$C, pressure of 600 psi and 10 min of contact time which is xylose the most abundant composition (11.79 %) followed with arabinose (2.82 %), glucose (0.61 %) and mannose (0.66 %).

Keywords: oil palm fronds; monosaccharide; subcritical water extraction; HPLC

Abstrak

Ladang kelapa sawit di Malaysia telah menghasilkan lebih daripada 36 juta tan buah sawit yang masak dan juga pelepah sawit di mana ianya di kategorikan sebagai sisa-sisa tanaman kelapa sawit. Kandungan monosakarida yang terdapat dalam pelepah kelapa sawit ini boleh diekstrak dengan menggunakan hidrotermal proses untuk pelbagai aplikasi yang berguna. Objektif-objektif kajian ini adalah untuk menetukan hasil monosakarida pada keadaan yang berbeza dari segi suhu 170 °C hingga 200 °C, tekanan pengekstrakkan 500 psi hingga 800 psi dan masa 5 hingga 15 min dengan menggunakan kaedah pengekstrakkan "subcritical water extraction" dan untuk mengkaji komponen-komponen monosakarida yang terdapat dalam hemiselulosa pelepah kelapa sawit dalam keadaan yang optimum. Komponen dalam monosakarida dianalisis dengan menggunakan Kromatografi Cecair Berprestasi Tinggi (HPLC). Hasil pengektrakan monosakarida pelepah kelapa sawit yang tertinggi adalah pada suhu 190 $^{\circ}$C, tekanan 600 psi dan masa10 min di mana kandungan xilosa adalah yang paling banyak (11.7902 %) diikuti dengan arabinosa (2.8202 %), glukosa (0.6076 %) dan mannosa (0.6618 %).

Kata kunci: pelepah kelapa sawit; monosakarida; "subcritical water extraction"; HPLC

Introduction

Nowadays, agriculture waste from Oil palm tree reached an abundant of waste because of the oil palm tree is a most important commercial crop in Malaysia. The most generated oil palm biomass is oil palm fronds, which is produce 83 million tonnes per year, and it also can be obtained daily during replanting or pruning season for harvesting empty fruit bunch [1]. Currently, there are lots of studies focusing on the oil palm by-product such as oil palm fronds because it consists of high carbohydrate, which is simple sugar and less component of heavy metal [2]. Simple sugar might be produced as recycling nutrient with appropriate method or treatment. Hemicellulose is the second abundant in biomass component, and they are containing several types of monosaccharide as known as simple sugars units with different structure. An enrichment component of the hardwood is a carbohydrate.

Monosaccharide and oligosaccharides which are produced by the carbohydrate decomposition and it can be converted into such as biofuel, additive food or valuable product [3]. Solubilized monosaccharide can be converted to others polymer [4]. Subcritical water extraction (SWE) is an extractant as known as uncatalyzed hydrothermal treatment for hemicelluloses oil palm fronds extraction. The principle of SWE can maintain in a liquid phase at the high temperature with suitable pressure during the extraction process within the range that was given. It also can call as an environmental process because no chemical added instead of deionised water. Hydrothermal treatment is an effective process, especially in hydrolysis of hardwood processes and minor effect to softwood [5]. Monosaccharides can be separated and quantified by chromatographic methods [6].

Materials and Methods

Oil palm fronds were collected from local oil palm plantation in Selangor area. The raw materials were washed with deionised water to remove the impurities like sand or other small particle and then were dried in oven at 40 °C for 24 hours. The samples were cut, ground and sieved to achieve fine fibres with a size of <0.5 mm. The samples were then stored at room temperature.

Extraction of hemicelluloses

SWE was carried out at Block G laboratory, UiTM Shah Alam. SWE was performed using an accelerated solvent system ASE 200 from Dionex Corporation. In the extraction process, the subcritical water extractions were focused on three parameters, which were extraction temperature (180, 190 and 200 °C), pressure (500, 600 and 700 psi) and extraction time (5, 10 and 15 min). The oil palm fronds chips (2.0 g) were added in the extraction cell. Approximately, 60 mL of water was filled in the cell and heated at those parameters. The extracts were collected, centrifuged at 8000 rpm for 15 min and then the liquid extract was filtered with 0.45 µm cellulose acetate membrane filter (Minisart, Sartorius, Germany). The extracts were freeze-dried prior to analyse using high performance liquid chromatography (HPLC).

Quantification of monosaccharide sugars using HPLC

Monosaccharide compositions were determined by HPLC (Agilent, USA). Deionized water was used as a mobile phase at flow rate of 0.5 mL/min, temperature 80 °C and 35 °C for column Bio-rad Aminex HPX 87H (7.8 mm x 300 mm) and refractive index detector, respectively. Freeze dried hemicelluloses was dissolved in deionized water and filtered through a 0.45 µm cellulose acetate membrane filter (Minisart, Sartorious, Germany) before injecting (20 µL) into the column. The mixture of xylose, glucose, arabinose, and mannose were used as a standard.

Statistical Analysis

The data were determined by the Duncan multiple range test from one-way analysis of variance (ANOVA), and the significance of the differences between means was determined, where $p < 0.05$ of sample was considered statistically significant. The SPSS (Statistical Package for Social Science) statistical computer package was used to analyze the experimental data (SPSS, Inc., Chicago, IL, USA) [6].

Results and Discussion

Effect of temperature on monosaccharide yield

Temperature is an important factor that influenced the extraction process on monosaccharide [7]. SWE extraction process was carried out at different temperature, which were 180 °C, 190 °C and 200 °C, while the pressure and extraction time were fixed at 600 psi and 10 min, respectively.

Clearly, xylose is the most of highest composition (11.79 %) followed with arabinose (2.82 %) and the minor quantity were glucose (0.61 %) and mannose (0.66 %) at temperature of 190 °C. The same finding was reported from the previous study which xylose was found to be the main constituent in the extracts of flax shives using PLPW at extraction temperature of 180 °C [8]. Based on the previous studies, extraction temperature of 190 °C was selected as an optimum temperature due to high total sugar content. It showed that the trend of the total monosaccharide yield was proportionally increased when the temperature was increased [9]. Statistical analysis showed that significant differences existence between temperature of 180 °C and 200 °C ($P<0.05$) but there was no significant difference between temperature of 190 °C and 200 °C ($P>0.05$). Therefore, 190 °C was selected as the optimum point of extracting temperature in the response surface methodology (RSM) experiment. Different agricultural wastes had different structure and they also had different responses to experimental condition [10].

Table 1. Design matrix and the yield of monosaccharides obtained

Treatment Condition			**Percent yield of monosaccharides (%)**			
Temperature (^{O}C)	Pressure (psi)	Time (min)	Xylose	Glucose	Mannose	Arabinose
180	500	10	11.79	1.77	0.94	1.79
190	500	10	10.67	1.60	0.86	1.79
200	500	10	7.14	3.32	0.57	1.99
190	600	10	11.79	0.61	0.66	2.83
190	700	10	2.49	1.27	2.46	8.16
190	600	5	4.16	0.17	2.25	3.29
190	600	15	10.67	1.60	0.87	1.79

Effect of pressure on monosaccharide yield

To investigate the effect of pressure on the monosaccharide yield, the experiment was conducted at constant temperature (190 $^{\circ}$C) and time (10 min) with the pressure between 500, 600 and 700 psi. The result showed that the percent yield of monosaccharides increased proportionally with pressure between arabinose and mannose at different condition compared to xylose and glucose. It was reported that steam pressure could help to optimise and obtain an intermediate hemicelluloses product for high-value utilization induced by modification of remarkable structural in the treatment process [11].The highest total monosaccharide was obtained at 600 psi. According to previous study, the yield of monosaccharide was increased between 500 to 600 psi and decreased when pressure higher than 600 psi [9]. The statistical analysis showed that there were significant differences ($P<0.05$) between 500, 600 and 700 psi of pressure. Therefore, 600 psi was selected as the optimum point of extracting contact time in the response surface methodology (RSM) experiment.

Effect of contact time on monosaccharide yield

Another factor that influences the extraction efficiency and selectivity of fluid is contact time. The results showed that the yield of xylose, arabinose, glucose and mannose was high at 10 min. Similar results were observed from the previous study [8]. The total yield of monosaccharide composition was increased when increasing time from 5 to 10 min and decrease slightly after 10 min. Statistical analysis showed that significant differences existence between 5 and 10 min ($P<0.05$) but there was no significant difference between 10 min and 15 min ($P>0.05$). Longer time can be affected the structure of monosaccharide [12]. Furthermore longer reaction time of the extraction process can cause more decomposition of monosaccharide content [13]. Therefore, 10 min was selected as the optimum point of extracting contact time in the response surface methodology (RSM) experiment.

Conclusion

In conclusion, the highest monosaccharide's composition can be extracted from OPF using subcritical water extraction at temperature of 190 $^{\circ}$C, pressure of 600 psi and 10 min of contact time which is xylose the most abundant composition (11.79 %) followed with arabinose (2.82 %), glucose (0.61%) and mannose (0.66 %).

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