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Trace metals content (contaminants) as initial indicator in the quality of heat treated palm oil whole extract

Noor Akhmazillah bt Mohd Fauzi[1], Mohd Roji Sarmidi[2]

[1] Chemical and Bioprocess Department, Faculty of Civil and Environmental Engineering, Universiti Tun Hussein Onn Malaysia (UTHM), 86400 Parit Raja, Batu Pahat, Johor,Malaysia.
[2] Chemical Engineering Pilot Plant, Faculty of Chemical and Natural Resources Engineering, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia.

Abstract
An investigation was carried out on the effect of different sterilization time on the trace metals concentration of palm oil whole extract. Palm fruits were collected, cleaned and sterilized for 0, 20, 40 and 60 minutes. The kernels were then stripped from the sterilized fruits to get the pulp and later the pulp was pressed using small scale expeller. The resulting puree was centrifuge at 4000 rpm for 20 minutes. The palm oil whole extract were then collected and trace metals analysis was conducted using Inductively Couple Plasma-Mass Spectrometry (ICP-MS). The result showed that the highest yield was obtained at 40 minutes of sterilization with 19.9 ± 0.21 % (w/w). There was no significant different ($p < 0.5$) in total trace metals content between the degrees of the heat treatment. Na^+ was found as the highest trace metals content in the extract with mean concentration ranging from 1.05 ± 0.03 ppm to 2.36 ± 0.01 ppm. 40 minutes of heating time was predicted to have good oil quality due to higher content in trace metals that inhibit the lipase enzyme activity.

Keywords: Trace metals; Heat treatment; Palm oil whole extract; ICP-MS.

1. Introduction

Palm oil is derived from the fleshy mesocarp of the oil palm fruits, *Elaeis guineensis.* About 80% of palm oil production is destined for human consumption with the balance going to animal feed and to various industries. Harvesting, handling and processing methods used are known to influence the quality of the extracted palm oil. Fruit sterilization is one of the basic operations to obtain palm oil besides of fruit loosening, fruit digestion, oil extraction and oil clarification. Sterilization is a heat rendering operation involves steaming of fruits and reported as an important process because it determines the efficiency and effectiveness of the downstream and the refining processes in producing high grade palm oil. Increased in sterilization time has been found to increase yield of palm oil [1-3].

Palm oil is the world's second most important vegetable oil after soybean oil [4]. The fact that palm oil has both oil and fat fractions is a big advantage over other oils. This composition results in an edible oil that is suitable for use in a variety of food applications. Many fats and oils contain substances that are not triglycerides. These may be natural constituents, adulterants or contaminants. One of the most common contaminants in crude palm oil is iron. Iron is as a result of wear and tear of machinery in the mills and transportation tank [5]. It is known that zinc, copper and iron are prooxidant metals which can catalyze the oxidation process and contributing to the oxidative deterioration. It was reported that copper accelerates the hydroperoxides destruction rate thereby increasing the production of secondary oxidation products while iron increase the rate of peroxide formation. Concentration of trace metals gives a great affect of oil qualities with regards to freshness, storage stability and their influence on human nutrition and health. The determination of trace levels of some metals is important because it could catalyze oxidation of fatty acid chains exerting deleterious effect on shelf life and nutritional value [6].

In the present paper, the total concentration of trace metals in heat treated palm oil whole extract was determined and the initial prediction on the quality of the extract was made. A comparison of heated and unheated palm fruits on the palm oil yield was also investigated.

2. Materials and method

2.1 Materials

Fresh fruit bunches (FFB) was obtained from Universiti Teknologi Malaysia's plantation, Skudai, Johor. The oil palm fruits were freshly harvested, reddish in color and of full maturity. The fruitlets have an average dimension of 4 cm in length and 2.5 cm in diameter. All chemicals used were of analytical high performance liquid chromatography (HPLC) grade.

2.2 Sample preparation

2.2.1 Stripping of fresh fruit bunches

The method was adapted from [7] with some modification. Palm fruitltes were removed from the bunch manually. The fruit-laden spikelets were cut from the bunch with a machete. Then, the fruits were separated manually from the spikelets before washing. Washing was necessary in order to remove dirt and foreign matter present in the fruitlets.

2.2.2 Heating of Palm Fruitlets

The method was adapted from [7] with some modification. Three batches of cleaned fruitlets were divided equally into two fractions. For each batch, a set of oil palm fruitlets was heated while another set was not heated. Heat treatment was operated at constant temperature and pressure with 121˚ C and 4 MPa, respectively for 20, 40 and 60 minutes using a sterilizer (HV-110, Pyrometro Services (M), Hirayama, Japan).

2.3 Extraction of palm oil mesocarp

The extraction of oil palm mesocarp was carried out using two different methods; laboratory scale expeller and Soxhlet extraction. Soxhlet extraction was carried out to determine the theoretical extractable oil content from the mesocarp. The yield represents a benchmark for the oil yield from laboratory scale expeller. Soxhlet extraction was taken as the maximum extractable oil from the samples.The extraction efficiency, percentage yield and relative recovery were then determined [8].

2.3.1 Soxhlet method

The Soxhlet method was carried out according to PORIM Test Method, 1995 [9]. Soxhlet extraction was carried out using Soxhlet apparatus (Model EAM 9204, MTOPS) to determine the total extractable oil content in mesocarp extract. A 20g of mesocarp was weighed and transferred into a filter paper extraction thimble and then inserted into a 500 ml reflux flask. 300 ml of hexane was used as solvent at its boiling point. Extraction was terminated after six hours. The extract was then concentrated by removing the hexane using rotary evaporator and left in the oven at 60 ˚C. The extraction was done in triplicates using the same amount of the sample and within the same duration. The oil yield obtained was expressed in terms of mass percentage of the samples and calculated as:

$$Total\ yield\ (\%\ (w/w)) = \frac{Mass\ of\ oil\ extract\ (g)}{Mass\ of\ fruit\ pulps\ (g)}\ x\,100 \quad (1)$$

The relative recovery was then determined as Equation 2:

$$Relative\ recovery\ (\%) = \frac{Expellable\ yield\ from\ expeller\ (\%\ (w/w))}{Total\ yield\ from\ Soxhlet\ extraction\ (\%\ (w/w))}\ x\,100 \quad (2)$$

2.3.2 Laboratory scale expeller

The method was adapted from Owolarafe and Faborode [10] with some modification. The heated and unheated mesocarp of palm fruitlets were pressed using stainless steel laboratory scale expeller, The Baker (Premium Quality, Malaysia). Pressing was done by loading the inlet hopper with weighed mesocarp and the mesocarp starts to be pressed. The puree containing oil was then released through a filter and collected. Pressing process was done for several times until no oil secreted. The resulting puree was then centrifuged using KUBOTA KR- 20000T centrifuge (Kubota Medical Appliance Supply, Japan) to separate the oil and the impurities. The process was operated at 4000 rpm for 30 min. The oil yield was calculated as:

$$Expellable\ yield\ (\%\ (w/w)) = \frac{Mass\ of\ oil\ obtained\ (g)}{Mass\ of\ puree\ (g)}\ x\ 100 \qquad (3)$$

2.4 Determination of trace metal content

The trace metals in the palm oil whole extract were analyzed using inductively coupled mass spectrometry (ICP/MS) was based on the standard method of Sabri [11]. 5 mL acid hydrochloric was mixed with 0.1g sample of crude palm oil before adding with 4.0mL demineralized water. Then, the solution was heated on the hot plate until it boiled. Demineralized water was added to make a 20 mL solution. 0.2 µm nylon filter was used to filter the sample solution. The samples were then injected for the analysis using PerkinElmer SCIEX ELAN ICP/MS, PerkinElmer (Massachusetts, USA).

3. Results and discussion

3.1 Yield of heat treated palm oil whole extract

Figure 1 showed the result obtained in the form of relative extraction recoveries. It was found that the highest recovery was noted at 40 minutes of sterilization. Statistical evaluation shows that the yield was significantly difference between unheated and heated mesocarp, $p < 0.05$. The percentage of yield obtained increased slightly with increasing sterilization time. Higher oil yield for heated compared to unheated mesocarp is expected since sterilization is a heat rendering and moisture adsorption process which achieves the objectives of lowering the viscosity of oil as well as coagulation of protein [1, 2, 10]. Little amount of yield obtained in the unheated mesocarp were due to fibrous and loose pounded mass fruit which are not able to squeeze out all the oil from the voids in the fibre since there was no heat applied to soften the tissues of oil-bearing material. Of all, 40 minutes of sterilization gives maximum oil yield compared to others at constant temperature of 121˚C and constant pressure of 4MPa.

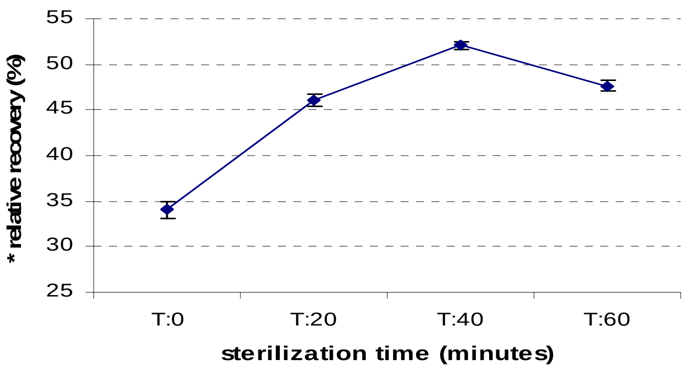

Figure 1. Effect of sterilization time on small scale expeller efficiency (error bars represent SEM of results, n = 3); *(weight of palm oil whole extract using small scale expeller/ weight of palm oil whole extract using Soxhlet) x 100

3.2 Trace metals content in heat treated palm oil whole extract

Table 1 shows a total of twelve trace metals elements found in the palm oil whole extract of all treatments. The results of statistical analysis showed that there was no significant different in total trace metals content between the degrees of the heat treatment. The analysis indicated that, the Na^+ was found as the highest trace metals content in the extract with mean concentration ranging from 1.05 ± 0.03 ppm to 2.36 ± 0.01 ppm. It was then followed by K^+ (ranging from 0.85 ± 0.03 ppm to1.19 ± 0.01 ppm) and Fe^{2+} (ranging from 0.73 ± 0.04 ppm to1.15 ± 0.05 ppm).

Table 1. Metals contents (ppm) in the palm oil whole extract for different heating time.

Trace metals[a] (ppm)	Heating time (minute)			
	0 (Treatment 1)	20 (Treatment 2)	40 (Treatment 3)	60 (Treatment 4)
K	1.19 ± 0.01	1.12 ± 0.02	0.85 ± 0.03	1.03 ± 0.03
Ca	0.39 ± 0.01	0.33 ± 0.01	0.46 ± 0.04	0.65 ± 0.01
Mg	0.08 ± 0.01	0.08 ± 0.01	0.12 ± 0.02	0.09 ± 0.01
Cr	0.25 ± 0.02	0.15 ±0.01	0.25 ± 0.01	0.11 ± 0.03
Al	0.26 ±0.01	0.07 ±0.02	0.16 ± 0.01	0.22 ± 0.03
Cu	0.02 ± 0.00	0.03 ± 0.02	0.05 ± 0.00	0.02 ± 0.00
Na	1.73 ± 0.02	1.05 ± 0.03	2.36 ± 0.01	2.28 ± 0.02
Fe	1.03 ± 0.01	0.73 ± 0.04	1.05 ± 0.01	1.15 ± 0.05
Mn	0.03 ±0.01	0.04 ± 0.00	0.07 ± 0.00	0.04 ± 0.00
Pb	0.92 ±0.01	0.32 ± 0.02	1.12 ± 0.04	1.05 ± 0.01
Cd	0.02 ± 0.00	0.01 ± 0.01	0.02 ± 0.00	0.02 ± 0.00
Zn	0.24 ±0.00	0.36 ± 0.02	0.12 ±0.01	0.15 ±0.03

[a] Mean ± SEM (Standard Error Method) of triplicate determination.

The results of the ICP/MS analysis tabulated in Table 2 shows that the palm oil whole extract in this study contain appreciable amount of K^+, Ca^{2+}, Mg^{2+}, Cr^{3+} and Al^{3+}. These metal ions were categorized as stimulators to the lipase enzyme activity [12-14]. The abundance of these trace metals was in agreement with previous findings where K^+, Ca^{2+} and Mg^{2+} represent the most abundant metal constituents of many plants [13, 15]. A clearer picture on the mean concentration for these metals content in the palm oil whole extract is shown in Figure 2.

Table 2. The content of trace metals which act as stimulators and inhibitors to lipase activity found in this study

	Heating time (minute)			
	Stimulators to lipase activity[a] (ppm)			
	0	**20**	**40**	**60**
K	1.19 ± 0.01	1.12 ± 0.02	0.85 ± 0.03	1.03 ± 0.03
Ca	0.39 ± 0.01	0.33 ± 0.01	0.46 ± 0.04	0.65 ± 0.01
Mg	0.08 ± 0.01	0.08 ± 0.012	0.12 ± 0.02	0.09 ± 0.012
Cr	0.25 ± 0.02	0.15 ± 0.01	0.25 ± 0.01	0.11 ± 0.03
Al	0.26 ± 0.01	0.07 ± 0.02	0.16 ± 0.01	0.22 ± 0.03
Total	**2.17± 0.02**	**1.75 ± 0.02**	**1.66 ± 0.02**	**2.10 ± 0.02**
	Inhibitors to lipase activity[a] (ppm)			
Cu	0.02 ± 0.002	0.03 ± 0.017	0.05 ± 0.002	0.02 ± 0.002
Na	1.73 ± 0.02	1.05 ± 0.03	2.36 ± 0.01	2.28 ± 0.02
Total	**1.74 ± 0.02**	**1.09 ± 0.02**	**2.42 ± 0.012**	**2.31 ± 0.01**

[a] Mean ± SEM (Standard Error Method) of triplicate determination.

In Table 2, non heated fruitlets contain the highest stimulators with 2.17 ± 0.02 ppm compared to others. Meanwhile, 40 minutes of heating was recorded as the lowest stimulators with only 1.66 ± 0.02 ppm. Higher content in these metal ions lead to the easier FFA formation since the lipase enzyme will be easily activated. It is important to note that the high rate of hydrolysis is due to the activity of the fruit lipase which is activated [14].

From the result obtained it can be predicted that the non heated fruitlets has higher FFA content which leads to lower oil quality since the hydrolysis reaction occurred faster than other treatments. Lower content of stimulators in 40 minutes of heating provides a good initial hypothesis; it will be able to produce good oil quality. The results also show that 40 minutes of heating contain the highest amount of Cu^{2+} and Na^+ with 2.42 ± 0.012 ppm. These metal ions were grouped as metal that inactivate the lipase enzyme. Figure 3 shows the distribution of these metals at different heating time. The statistical analysis showed that the variation in the results was significantly different $p < 0.05$ in total stimulators (K, Ca, Mg, Cr and Al) as well as in total inhibitors (Cu and Na) for all treatments.

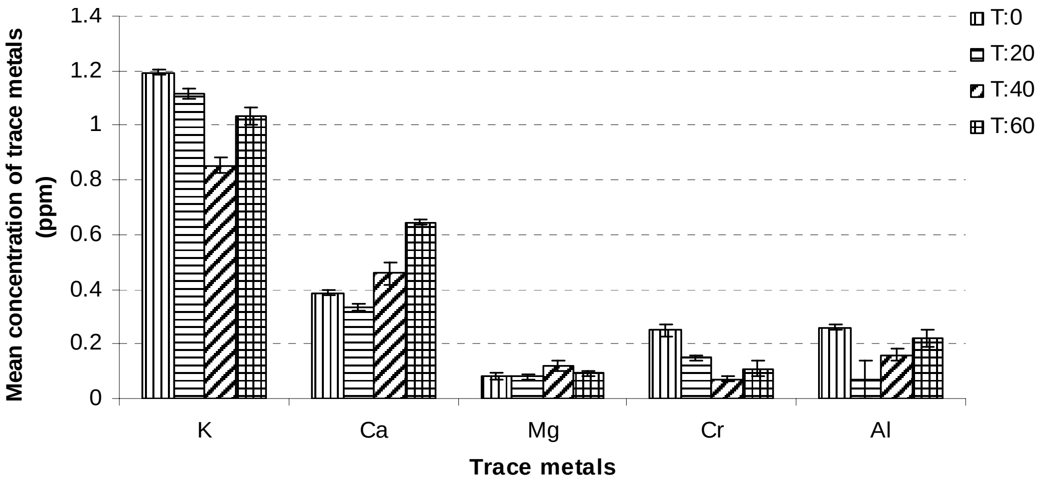

Figure 2. The mean concentration of K, Ca, Mg, Cr and Al (as proactivated lipase enzymes) found in palm oil whole extract for different heating time. T was denoted as heating time in minutes. Values are mean ± SEM for triplicate determination

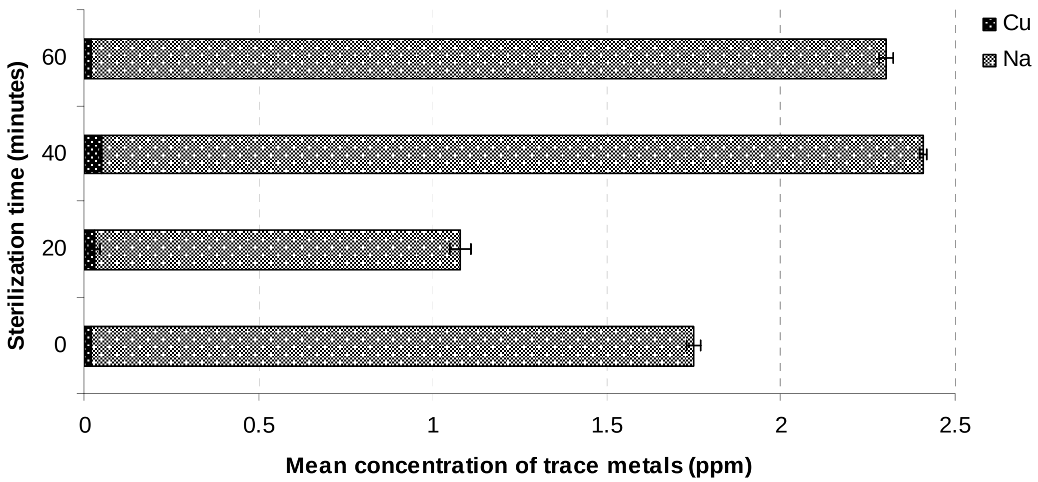

Figure 3. Total mean concentrations of Cu and Na ions which inhibit the lipase enzyme activity found in palm oil whole extract for different heating time. Values are mean ± SEM for triplicate determination

4. Conclusion

As a conclusion, initial prediction of enzymatic hydrolysis can be done after reviewed the content of trace metals in the palm oil whole extract. Higher content in trace metals that inhibit the lipase enzyme activity and lower content in trace metals that stimulate the lipase activity in fruitlets with 40 minutes of heating time was predicted to have good oil quality. The existence of trace metals in the extract was most probably due to the natural metal sources and also environmental pollution.

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Noor Akhmazillah bt Mohd Fauzi obtained her M.Eng on Bioprocess from UniversitiTeknologi Malaysia in 2010 and her B.Eng on Biotechnology Engineering from International Islamic University Malaysia in 2005. Her major interest is in Bioprocess and Biotechnology (food). Now, she pursuing her PhD in Chemical and Process Technology at University of Auckland, New Zealand. She has published more than 10 publications in the journals and conferences on the research of Tongkat Ali and Palm Oil. She also has obtained a few awards nationally and internationally such as (i) GOLD MEDAL and (ii) SPECIAL AWARD, Kulliyyah of Engineering Research and Innovation Exhibition (KERIE) award, 20-21 Dec. 2005, International Islamic University Malaysia, (iii) GOLD MEDAL. 23-15 Feb 2006. Malaysia Technology Expo. 2006. Kuala Lumpur. Ministry of Science, Technology and Innovation, Malaysia (iv) SILVER MEDAL, 7 APRIL 2006. 34th.International Exhibition of Inventions, New Techniques and Products, Geneva, Switzerland. Ms Noor is a Member of Board of Engineers Malaysia (BEM).
E-mail address: akhma@uthm.edu.my, Tel: +607 453 7764

Mohd Roji Sarmidi obtained his PhD on Chemical Engineering from Aston University in 1993. His M.Sc. (Eng.) Biochemical Engineering was from Birmingham University, U.K in 1986 and his B.Sc. Chemical Engineering University of Surrey, U.K in 1984. He is now professor at Faculty of Chemical Engineering, University Teknologi Malaysia and Deputy Director of Chemical Engineering Pilot Plant (CEPP), UTM. His area of expertise are Wellness Biotechnology, Bioprocessing and Metabolomics. Prof Mohamad Roji has published more than 60 publications in the journals and articles internationally, has coordinated more than 40 postgraduates students. He is very active in research, leading 10 main projects (as a project leader) and contributes as a team member in other 10 research projects. He also been as invited speakers for more than 20 conferences national and internationally. Prof Mohamad Roji is Deputy Secretary, Council Member Institution of Chemical Engineers Malaysia (IJKM), Member of Malaysian Microbiology Society and member of Board of Engineer Malaysia.
E-mail address: mroji@cepp.utm.my, Tel: +607 553 3202