Hot compressed water extraction curve for palm oil and beta carotene concentration

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Abstract. Hot compressed water extraction (HCWE) is a promising green alternative for palm oil milling. The kinetic characteristic of HCWE for palm oil and its beta-carotene concentration was experimentally investigated in this study at different temperature and pressure. Semi-batch HCW extractor from 120 to 180 °C and 30 to 50 bar was used to evaluate the process for 60 mins of extraction in 10 mins interval. The results obtained using the HCWE process was compared with other extraction methods. The oil extraction achieved the maximum extraction rate within 20 mins of extraction in most of the conditions and started to decrease until 60 mins of extraction time. The extraction rate for beta-carotene was achieved the maximum rate in 10 mins and started to decrease until 30 mins. None of beta-carotene concentration had been extracted out from the palm oil mesocarp after 30 mins of extraction in all conditions. The oil recovery of using HCWE was relatively low compared with the mechanical screw press, subcritical R134b, supercritical carbon dioxide and hexane extraction due to the oil loses in the oil-water emulsion. However, the beta-carotene concentration in extracted oil using HCWE was improved compared with commercial crude palm oil (CPO) and subcritical R134a extraction.

1. Introduction
Palm oil industry has contributed significantly to the Malaysia economy since 1950s. In 2014, Malaysia has produced about 20 million tons of crude palm oil (CPO) with the trade value of RM 50 billion. Oil palm can produce two main products that are CPO which being extracted from the palm oil mesocarp, and crude palm kernel oil (CPKO) which extracted from the palm oil kernel. Currently, CPO is extracted using screw press technology with the single or double system preceded by the
sterilization process in the palm oil mill. The process contribute to the overall oil loses of 8% dry basis (w/w) which about 2% (w/w) and 6% (w/w) in the sterilizer and screw press respectively [1]. The oil loses in screw press system is due to the press pressure limitation where the process are expose to the nut breakage at about 0.0625 % broken nut/bar as demonstrated in Mongana Report (1955) [2]. As a result, the pressed palm oil fiber extraction shows that about 5-6% dry basis (w/w) oil remains in the fiber after pressing process [3].

Thus, hot compressed water extraction (HCWE) process is proposed in this study for CPO extraction. This process used water in subcritical region between the normal boiling point and the critical point; from the temperature of 100 to 374°C and pressure up to 22.08 MPa. Since 1990s, this green process is proven to improve the extractions of food [4], plant material [5], and microalgae [6]. Not limited to that, this process also proven to reduce the extraction time to 20 min from 180 mins using hydro distillation [4]. This improvement would decrease the energy consumption of the process and reduce the operating cost. Although HCWE is never being uses for palm oil, this system seems to be an alternative that provides green and effective processes for CPO extraction.

In this study, the HCWE curve was experimentally examined in semi batch process for about 60 mins of extraction in 10 mins interval at different temperature and pressure. Two process responses were evaluated including overall oil yield (g-oil/ g-dried mesocarp) and β-carotene concentration (ppm). The efficiency of the process are also being compare with the mechanical screw press, subcritical R134a, supercritical carbon dioxide and hexane extraction.

2. Material and method
2.1. Raw material and chemical
Fresh oil palm fruits bunch were collected at Felda Mempaga Satu, Bentong, Pahang, Malaysia. The bunch was treated within 120 mins after the harvesting time using autoclave at 130°C and 40 mins. After that, the mesocarps were shredded out from loose fuitlet as shown in figure 1 prior to the extraction process. The high performance liquid chromatography (HPLC) grade of Hexane (Friendemann Schmidt, Australia) was used for β-carotene analysis and soxhlet extraction. Distilled water generated from water distiller (Favorit, Thailand) was used in the HCWE process.

2.2. Hot compressed water extraction
HCWE was done semi-batch wisely using the fabricated equipment in this laboratory as shown in Fig. 2. This equipment is consist of two vessels with one litre volume each; the extraction and cooling vessel which connected by 3/8 inch stainless steel pipeline.

![Figure 1. Treated palm oil mesocarp](image1.png)

![Figure 2. Schematic diagram for hot compressed water extractor](image2.png)
The treated palm oil mesocarp was weighed and loaded into a covered stainless steel mesh cylinder before being placed into the extraction cell. The distilled water was added into the cell. The cell was then securely covered with a stainless steel lid. N\textsubscript{2} gas was then passed through the cell for 2 mins to purge out air and dissolved oxygen. Excess pressure was relieved through the release valve. The temperature was set according to the required experiment. The electrically jacketed extraction cell took 10–15 mins to achieve the desired temperature. The 60 mins extraction time with 10 mins interval started once the set temperature was achieved as indicated by the temperature indicator in the extraction cell. Every 10 mins interval, the water extract was simultaneously transferred into cooling vessel and the new distilled water was adding up into the extraction vessel. The water extract was subjected to the post treatment process prior to further analysis.

2.3. Analysis of oil
In order to recover the palm oil from the water extract, the extract was going through the post treatment process for the oil and water separation by clarifying and centrifuging process. The water extract was clarified using separating funnel for 60 mins at temperature of 60°C to form three distinguish layer of oil, oil-water emulsion and water. After that, the layer of oil and oil-water emulsion was centrifuged at 7000 rpm and 10 mins. The accumulated palm oil was measured and collected prior to the analysis. The overall oil yield was calculated based on the measured palm oil volume using (1).

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\text{Overall oil yield, } \frac{g_{\text{oil}}}{W_{\text{dried mesocarp}}} = \frac{V_{\text{oil}} \times \rho_{\text{oil}}}{W_c}
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Where \(V_{\text{oil}}\) is volume of palm oil recovered from extraction (ml), \(\rho_{\text{oil}}\) is density of the palm oil (g/ml), \(W_c\) is dry mesocarp weight, g. The concentration of \(\beta\)-carotene was measured based on MPOB test method using a spectrophotometer (UV–Vis, Shimadzu, Japan) [7].

3. Result and discussion
3.1. The extraction curve for overall oil yield at different temperature and pressure.

The cumulative overall oil yield extracted by unit time or extraction curve at different temperature and pressure is tabulated in figure 3a, 3b, 3c. At 30 bar and 120°C, the HCW was extracted 35.8 % (w/w) of the oil in 20 mins and it rate was slowly decrease with increasing of only 9 % (w/w) of yield at 50 mins of extraction. After that, the cumulative of extracted oil are constant in 50 to 60 mins of extraction which showing none of the oil being extracted in the last 10 mins of extraction. Similar trend can be observed for temperature of 140 and 180°C at constant pressure of 40 and 50 bar at different magnitude of oil yield. However, the different observation can be seen for temperature of 160°C and constant pressure of 30, 40 and 50 bar. The oil was effectively being extracted at 43 % (w/w) in 10 mins of extraction time. Then, the rate was decreased with extracting only 10 %(w/w) of oil after 40 mins of extraction. The extraction rate is constant in 40 to 60 mins of extraction. At 160°C and 40 bar, 43 % (w/w) oil yield was extracted in 20 mins of extraction.

The maximum cumulative yield of 51 % (w/w) was achieved at 60 mins of extraction. Meanwhile, at 160°C and 50 bar, 50 % (w/w) of oil was extracted in 30 mins of extraction and keep steady until the end of the extraction process. In HCWE process, the extraction starts with the breaking of the cell wall by the hydrolysis of fiber to sugar [8]. This mechanism promotes the entrainment of the oil from its original structure to the HCW and increased the oil extraction as observed by higher extraction in the first 20 mins of the extraction. Not limited to that, the increasing of temperature is also promoting the higher cell wall breaking thus increase the overall oil yield at higher temperature. However, the decreasing of extraction rate at 180°C may be due degradation of the oil at the higher temperature.
The cumulative $\beta$-carotene extracted by unit time at different temperature and pressure is tabulated in figure 3(d), 3(e) and 3(f). Similar trend can be observed in $\beta$-carotene concentration comparable with oil extraction where the optimum temperature of 160 $^\circ$C was obtained. However, the effect of pressure on $\beta$-carotene extraction was more significant compared with temperature. At 30 bar and 160$^\circ$C, the concentration of $\beta$-carotene extracted is 258.4 ± 0.6 ppm which is very low compared with pressure of 40 bar at 834.5 ± 0.1 ppm. Then, it is slightly increases to 857.7 ± 0.4 ppm at 50 bar. As the time increase, the rate of $\beta$-carotene extraction was decrease where approximately 85 % of the compound was extracted out after 20 mins extraction and everything will be extracted out in 30 mins. Thus, the optimum condition 160 $^\circ$C, 50 bar and 30 mins was identified as the optimum condition of $\beta$-carotene concentration.

**Figure 3.** The extraction curve for overall oil yield and $\beta$-carotene at different temperature and constant pressure; (a.) Overall oil yield at 30 bar (b.) Overall oil yield at 40 bar (c.) Overall oil yield at 50 bar (d.) $\beta$-carotene concentration at 30 bar (e.) $\beta$-carotene concentration at 40 bar (f.) $\beta$-carotene concentration at 50 bar
As the temperature increased, the solubility of \( \beta \)-carotene in HCW was also increased by the decreasing of dielectric constant, \( \varepsilon \) of water. The \( \varepsilon \) of water decreases from 75 at 20°C to 60 at 120°C and decreased to 40 at 160°C [9] which make it behaves like the organic solvent. This situation is providing the suitable condition for the compound to soluble in HCW thus increased the extraction efficiency. After that, the rapid increased of extraction rate which observed at temperature of 160°C was possibly caused by the significant reduce of the hydrogen bonding between water molecule at this temperature and above as discussed by Shinoda (1977) [10]. The reducing of the hydrogen bonding promotes the interaction between \( \beta \)-carotene and water. After that, \( \beta \)-carotene extraction was decreased at 180°C is possibly caused by the thermal hydrolysis and polymerization. Furthermore, the increased of pressure from 30 to 50 bar has decreased the oil extraction rate and shift the effective extraction time from 10 mins at 30 bar to 30 mins at 50 bar. As the conclusion, the develop extraction curve for both components later will be used to characterise the kinetic behaviour of the process [11].

3.2. Comparison with other extraction method

The comparison between HCWE and others extraction is shown in figure 4. As shown in figure 4, the optimum HCWE condition give the lowers overall oil yield of 0.54 g-oil/g-dried mesocarp compare with supercritical CO\(_2\) at 0.77 g-oil/g-dried ginger [12], hexane extraction at 0.76 g-oil/g-dried mesocarp and subcritical R134a at 0.66 g-oil/g-dried mesocarp [13] and lab scale screw press with microwave pretreatment process at 0.62 g-oil/g-dried mesocarp [14]. This probably caused by the oil loses in the oil-water emulsion after extraction process. Thus, effective oil-water emulsions separation need to be establish to improve the oil recovery. The yield for the commercial CPO is not available from the literature.

![Figure 4. Comparison between HCWE and other extraction method](image)

However, it is important to note that HCWE was able to produce the palm oil with high concentration of \( \beta \)-carotene compare with hexane extraction, subcritical R134a and commercial CPO. This would create an added value for the palm oil product with the higher \( \beta \)-carotene concentration.
4. Conclusion
As a conclusion, the HCWE curve for overall oil yield and $\beta$-carotene was successfully developed at various temperatures of 120 to 180°C and pressure of 30 to 50 bar. These curves can be utilized to characterise the kinetic behaviour of the process with mass transfer mechanism and solubility correlation. Besides that, further research on oil-water emulsion needs to be explore to improve the overall oil yield.

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