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Extraction of Oil and Minor Compounds from Oil Palm Fruit with Supercritical Carbon Dioxide

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Abstract: A significant quantity of tocochromanols and carotenoids remains in the residual from palm oil production by traditional screw pressing. Supercritical carbon dioxide extraction was used as alternative method with the purpose to recover better these valuable minor compounds. Total oil yield and co-extracted water were investigated in the course of extraction. Tocochromanols and carotenoids were evaluated, not only in the extraction oil, but also in the oil of residual fibre. Modelling of extraction process was also performed for a further up-scaling. The results showed that oil yield up to 90% could be observed within 120 min. Supercritical carbon dioxide ($SCCO_2$) could extract tocochromanols and carotenoids with concentration in the same range of normal commercial processing palm oil, while co-extracted water remained rather low at a level of 2–4%. Moreover, recovery efficiencies of these minor compounds were much higher in case of extraction processed with supercritical carbon dioxide than those with screw pressing method.

Keywords: supercritical extraction; tocopherols; tocotrienols; carotenoids; modelling

1. Introduction

Palm oil is well known all over the world because of its high quality. According to Tan 2012 [1], palm oil has a balanced fatty acid composition in which the level of saturated and unsaturated fatty acids are almost equal with 50% saturated, 40% monounsaturated and 10% polyunsaturated fatty acids. As a consequence of high polyunsaturated acid content, palm oil is a good oil with the ability to reduce blood cholesterol and the risk of coronary heart disease. Besides, palm oil contains ca. 3% of free fatty acids and 1% of other minor components. The minor constituents of palm oil include carotenoids, tocopherols, sterols, phosphatides, triterpenic and aliphatic alcohols. Among them, the most important compounds are carotenoids and tocochromanols (tocopherols and tocotrienols). Phoon et al. reported that crude palm oil contains 500–700 ppm of carotenoids and 1000–1200 ppm tocochromanols [2]. Carotenoids of palm oil are mainly in the form of alpha- and beta-carotenes, the precursor of vitamin A. The presence of these carotenes plays an important role in oxidative protection to the oil. On the other hand, the major portions of total tocochromanols in palm oil are alpha-tocopherol and gamma-tocotrienol. These compounds are also antioxidants and provide some natural oxidative protection to the oil. It is obvious that the combination effects of properties of carotenoids, tocochromanols and high portion of unsaturated acids give palm oil a higher oxidative stability compared to many other edible oils. However, these carotenoids are thermally destroyed during the deodorization stage [3]. Therefore, a lot of new and improved methods for palm oil production have been investigated and applied during the last decades.

Up to now, recovery of oil from the mesocarp of palm fruits by using crew pressing system is the most commonly used method [4]. However, a significant quantity of carotenoids (3800–7000 ppm)

and tocochromanols (1900–3000 ppm) remain in the residual oil (5–6% on dry basis) in the palm press fibres [2,5]. Recently, supercritical fluid technology has been proven to be a modern technique for extraction and reaction [6,7]. Supercritical CO_2 has been applied in extraction, purification and fractionation of crude palm oil [8–11]. Direct extraction of palm oil from palm pulp or kernel under supercritical condition has been conducted [12–15]. Besides, the waste from palm oil processes like pressed palm fibre [16–19] was also investigated. In general, extraction of palm oil from palm fruit and pressed fibre using supercritical fluid extraction has been explored. However, a full investigation about total oil yield, co-extracted water, carotenoids and tocochromanols in the extracted and the residue oil in a single run has not been fully reported. Recently palm oil has become a starting material to produce natural tocochromanols and carotenoids [5,9,20]. Therefore, the objective of the following study was to prove that using supercritical CO_2 as extraction solvent will bring more benefit in point of view to better recover these valuable minor compounds. The work included a study of extraction of palm mesocarp by supercritical CO_2 at different pressure, temperature and flow rate. Total oil yield and co-extracted water were investigated in the course of extraction. Tocochromanols and carotenoids were evaluated not only in the extraction oil but also in the oil of residual fibre. Modelling of extraction process was also performed for a further up-scaling.

2. Materials and Methods

2.1. Materials

Hexane and butyl methyl ether (HPLC grade), acetone (>99.8%), Hydranal-Composite 5 were purchased from Lab-Scan (Dublin, Ireland), Sigma (Saint-Quentin Fallavier, France), Prolabo (Fontenay-sous-Bois, France) and Riedel-de Häen (Seelze, Germany), respectively. Standards were supplied by Merck (Darmstadt, Germany).

Palm fruit (*Elaeis guineensis*) was from Malaysia. The fruits were separated into skin, mesocarp and kernel. The yellow part of the mesocarp is investigated. The average particle size of the pulp for supercritical extraction was about 1 × 2 × 6 (mm × mm × mm).

2.2. Equipment and Experiment Procedure

A standardized supercritical extraction system, developed at the Institute for Thermal and Separation Processes–at the Hamburg University of Technology (TUHH), was used. The simplified flow sheet is shown as Figure 1. Liquefied CO_2 (purity of 99.95%) from the reservoir tank were pumped by a Maximator pump (max. 600 bar) to the 100 mL steel extractor cell, which was loaded with 14.5 g of palm mesocarp (fixed bed) for each run. The system was monitored at the investigated pressure (200–400 bar) and temperature (45–65 °C) with the specific flow rate from 14 to 56 kg h^{-1} of gas per kg of sample. The extracts were collected continuously in 10 mL glass vials, used as sample collectors at atmospheric pressure.

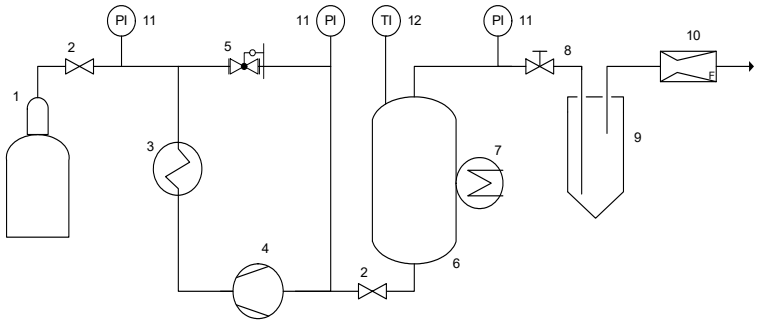

Figure 1. Flow-sheet of the extraction unit.

2.3. Analytical Method

(a) High Performance Liquid Chromatography (HPLC)

A HPLC system from Gynkotek with RF 1002 Fluorescent detector was used for analysis. Tocopherols and tocotrienols in the oil samples were separated on a LiChrosorb Diol, 5 µm, 250 × 4.6 mm column (Chrompack N° 612834). The mobile phase was hexane (96%) and butyl-methyl-ether (4%) at a flow rate of 1300 µL/min. Injection volume was 20 µL. External standard curves were used to determine tocochromanols content in the oil samples.

(b) UV-Vis Spectroscopy

UV-Vis Spectroscopy (spectrometer UV-120-02 from Shimadzu, Kyoto, Japan) was used to determine the content of carotenoids in the analysed samples. For a measurement, an amount of 10 to 20 mg of oil sample is diluted with 2 mL mixture of acetone and hexane (30:70 by Vol.%). The absorbance was recorded at the wavelength of 450 nm and compared with the standard curve determined with a series of samples with a known amount of β-carotene.

(c) Soxhlet extraction

A Soxhlet extraction was used to extract the total oil of the original palm mesocarps and the residual fibres. Hexane was used as the extraction solvent. The extraction time was 8 h.

(d) Karl—Fischer water titration

Dead-Stop Titrator TR 52 (Schott, Hofheim, Germany) was used to determine the water concentration from the supercritical extracts. Hydranal-Composite 5 were used as titrating agents. To obtain the water content, first the titre number was determined regularly by titrating known amounts of distilled water.

$$Titer = \frac{m_{H_2O}}{V_T} \quad (1)$$

where m_{H2O}: amount of water in mg; V_T: volume the titrant in mL.

The titrating solutions had a water equivalent of approximately 5 mg H_2O/mL. Water content (%) in the samples was finally determined as:

$$H_2O(\%) = \frac{V_T \times Titer \times 100}{m_P} \quad (2)$$

where m_P: amount of sample in mg.

(e) Extraction modelling

In this study, the Supercritical carbon dioxide ($SCCO_2$) extraction of palm fruit process is described by applying the VTII-Model for the extraction from solids using supercritical solvents [21].

3. Results and Discussion

3.1. Effect of Process Parameters on Batch Extraction

Solubility of a compound in a dense fluid varies with pressure and temperature which can change fluid density and solvent power. Figure 2 shows that total palm oil yields are significantly affected by the pressure and temperature applied. At 65 °C and specific flow rate of 35 kg h^{-1} kg^{-1}, increasing pressure from 300 to 400 bar increased the total oil yield from 80 to 92% after 120 min of extraction. In general, it is observed that the extraction yield increases with higher pressure at any temperature. On the other hand, at a high pressure (300 or 400 bar), extraction yield increases with higher temperature. This phenomenon has been reported in $SCCO_2$ extraction of other oil [22]. It can be explained by the fact that effect on palm oil vapor pressure is more pronounced than effect of decreasing solubility when changing extraction temperature.

The flow rate is another factor, which affects total oil recovery and the mass transfer inside the palm pulp. It is observed that an increase in flow rate will increase the amount of the collected oil, therefore shorten the extraction time. However, a balance between additional oil recovery and extra cost should be considered in the economical point of view. Brunner [21] pointed out that a high

solvent ratio causes enhanced operating costs and higher capital costs, because the equipment is more expensive due to its larger size.

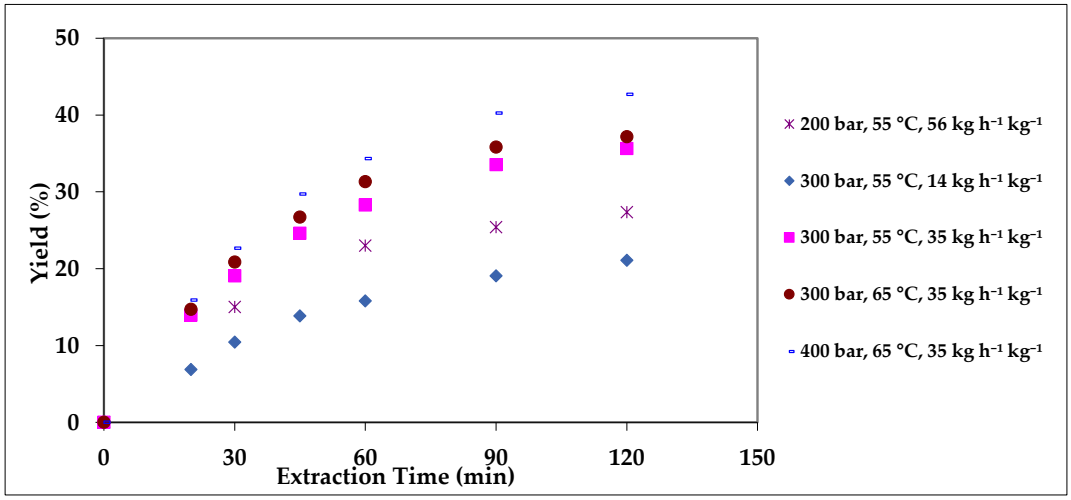

Figure 2. Extraction of palm oil from mesocarp with $SCCO_2$.

It can be concluded that the extraction was not sufficient for oil recovery at 200 bar, even with a very high flow rate. At a high pressure, $SCCO_2$ at 400 or 300 bar with a specific flow rate of 35 kg h^{-1} kg^{-1}, palm oil could be recovered up to 60–70% after 60 min of extraction or 80–90% after 120 min. In other work, Lau et al. obtained 77.3% oil yield at 300 bar and 80 °C [12].

3.2. Co-Extracted Water during $SCCO_2$ Extraction

Water is always found in natural plant products. The studied palm mesocarp contained ca. 20% of water. Among the investigated fluids, $SCCO_2$ has ability to dissolve a small amount of water [23,24]. Therefore, knowledge about co-extracted water with palm oil in $SCCO_2$ is required. Figures 3 and 4 show the amount of water and oil co-extracted by $SCCO_2$ at 300 and 400 bar and at different temperatures. In extraction pressure and temperature ranges of the experiments, the extracted oil had only ca. 2–4% water content. That value is rather small. Crude palm oil, extracted from palm fruit by pressing, contains more than 10% water with impurities consisting of vegetable matter [25]. As a consequence, the process for removing water from palm oil can be reduced.

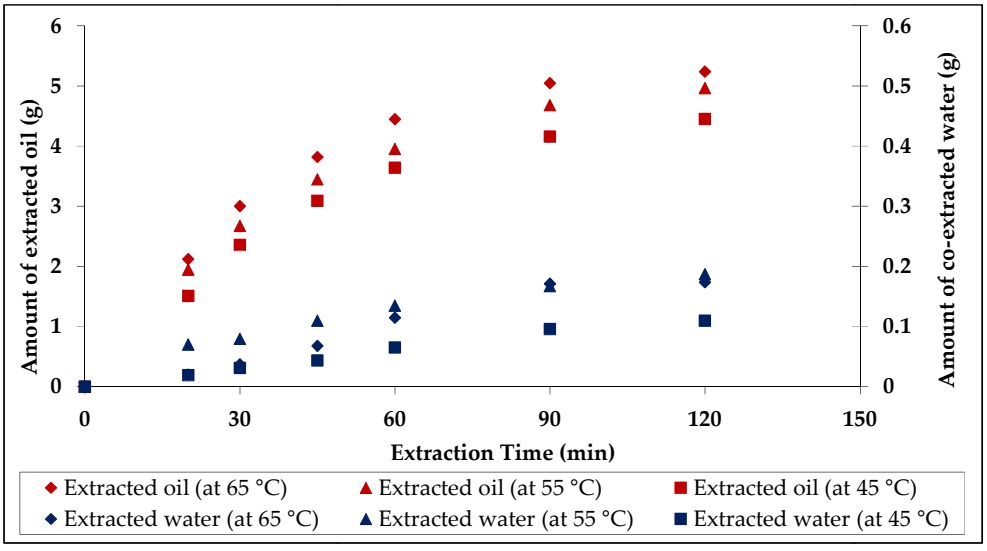

Figure 3. $SCCO_2$ extraction of oil and water at 300 bar, 35 kg h^{-1} kg^{-1} with 14.5 g of palm mesocarp.

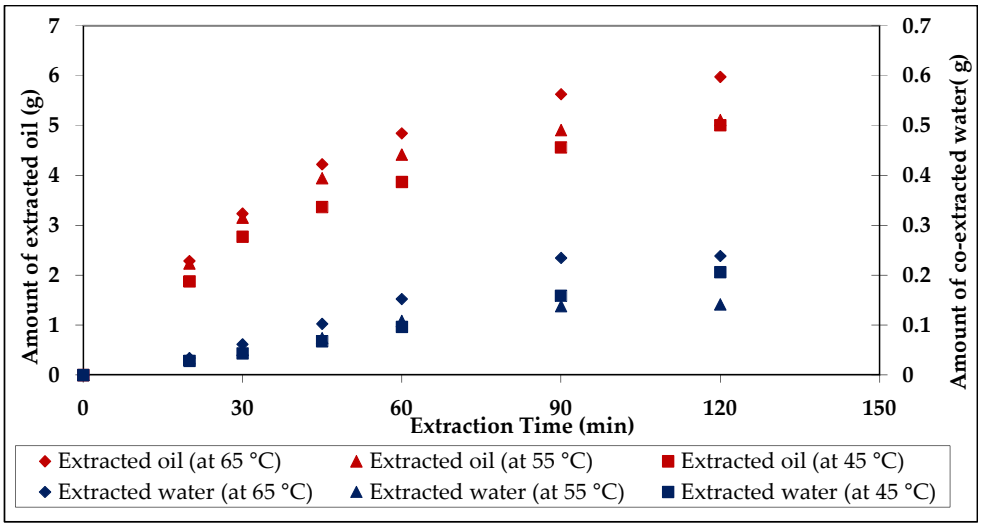

Figure 4. $SCCO_2$ extraction of oil and water at 400 bar, 35 kg h^{-1} kg^{-1} with 14.5 g of palm mesocarp.

3.3. Tocochromanols and Carotenoids Extraction

Tocochromanols and carotenoids are interesting valuable minor components in supercritical fluid extraction [9,20]. It was shown that the amount of carotene extracted from the residue from mechanical processing of palm oil is not high enough to allow an economic industrial size $SCCO_2$ extraction [26]. Therefore, efficient recovery of these compounds during oil extraction by $SCCO_2$ alternatively is expected. Concentrations of tocochromanols and carotenoids in the extracted oil depend on their solubilities and those of the other compounds at the same time. Figure 5 shows how a concentration of carotenoids changes with extraction time using $SCCO_2$. Different fractions at different extraction time (20–30 min, 45–60 min, 60–90 min and 90–120 min) were analysed. It is observed that at a low pressure (200 bar), carotenoids content increased with extraction time. This agrees with results reported in the extraction of crude palm oil at a similar condition [8]. Therefore, it is also suggested that palm oil can be separated into different carotenoids fractions at the pressure of 200 bar, although carotenoids is not well soluble in $SCCO_2$. In contrast, at a higher pressure (300 or 400 bar), the carotenoids concentration remains constant. The fractionated oil can reach the same carotenoids value as in commercial crude palm oil. This agrees with the conclusion from Lau et al. for $SCCO_2$ extraction of dried palm fruits [12]. However, the residual oil contains fewer minor compounds than in a screw pressing process.

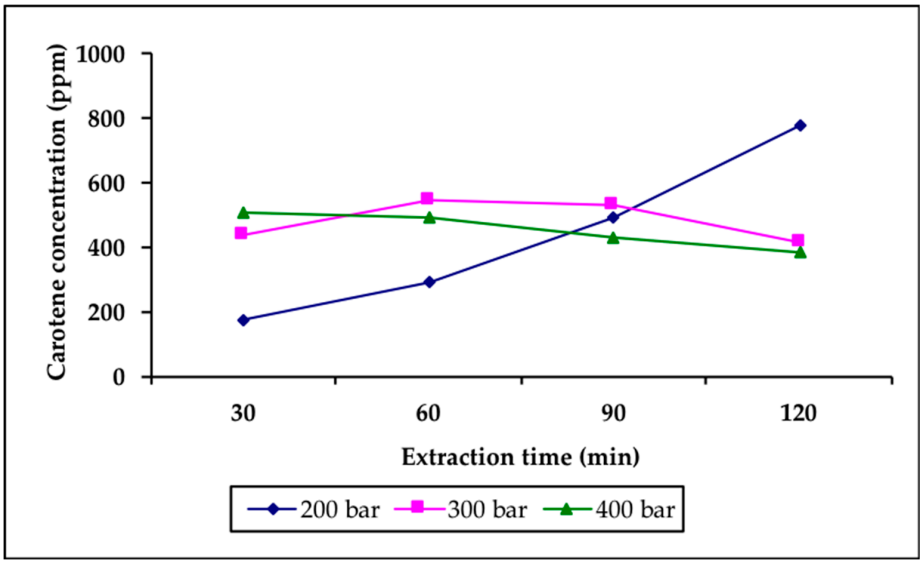

Figure 5. Carotenoids as extracted with $SCCO_2$ at 45 °C and 14 kg h^{-1} kg^{-1}.

As shown in Figure 6, there is different behaviour in tocochromanols and carotenoids extraction with $SCCO_2$. Besides, the composition of palm mesocarp varies with the size and the age of palm fruits. Thus, to objectively evaluate the efficiency of recovery of tocochromanols and carotenoids by using different supercritical extraction conditions (after 120-min extraction time), a relative comparison of the concentration of these compounds in extracted oil and residue oil was used with enrichment factor *K* (Table 1). Enrichment factor *K* of component *X* is defined as following equation:

$$K(X) = \frac{concentration\_of\_component\_X\_in\_the\_extracted\_oil}{concentration\_of\_component\_X\_in\_the\_residue\_oil} \quad (3)$$

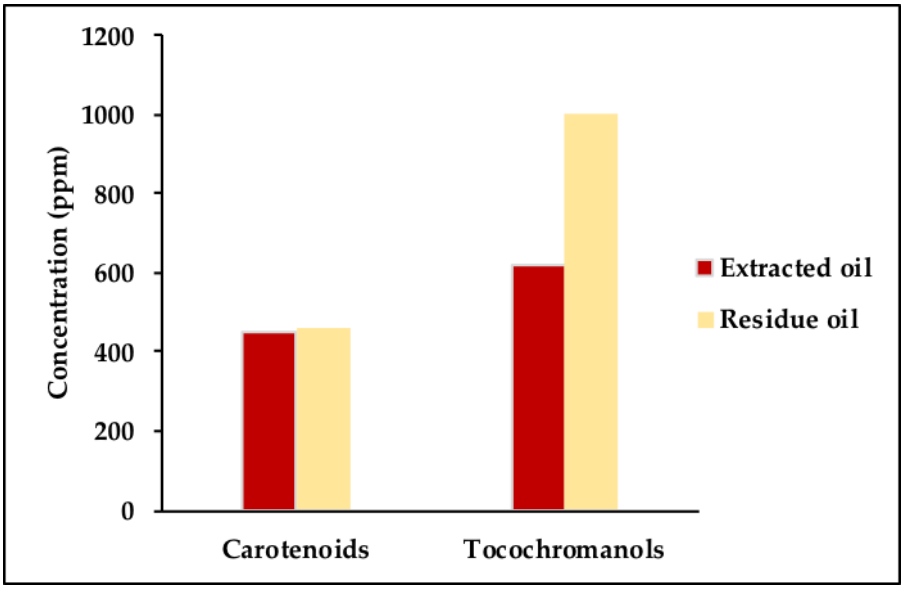

Figure 6. Concentration of carotenoids and tocochromanols in extracted and residue oils by $SCCO_2$ extraction at 400 bar, 55 °C, 35 kg h^{-1} kg^{-1}.

Table 1. Enrichment factors of tocochromanols and carotenoids with different extraction techniques.

Technique	Temp. (°C)	*K* (Carotenoids)	*K* (Tocochromanols)
$SCCO_2$ 300 bar	45 °C	0.79	0.67
	55 °C	1.21	0.41
	65 °C	0.79	0.41
$SCCO_2$ 400 bar	45 °C	1.19	0.54
	55 °C	0.98	0.62
	65 °C	0.90	0.86
Screw pressing *calculated after* Phoon et al. [2]		ca. 0.11	ca. 0.45

As a result, the extraction technique with a higher value of *K(X)* gives a better potential to recover component *X*.

The results show that much more tocochromanols and carotenoids can be recovered by using $SCCO_2$ than by traditional screw pressing. It has been reported that extractions of carotenoids and tocochromanols from fibre residues were not high enough for a possible industrial application. Supercritical CO_2 extraction of palm oil, simultaneously recovering its high valuable minor components from the palm fruits could open a new way for an alternative extraction method.

3.4. Mathematical Extraction Modelling

The so-called VT II model [21] integrates a complete mass transfer to a fluid phase side. Additionally, solid particles are considered as simple spheres with a mean diameter. A linear driving force due to the differences of concentration from the solid to the fluid phase is assumed. This model was previously used for the simulation of $SCCO_2$ extraction of oil from rice bran [27]. Equations (4) to (9) present the key equations of the model [21].

Mass balance for the fluid phase is:

$$\frac{\partial c_F}{\partial t} = D_{ax} \cdot \frac{\partial^2 c_F(z)}{\partial z^2} - \frac{u_z}{\varepsilon} \cdot \frac{\partial c_F(z)}{\partial z} - \frac{1-\varepsilon}{\varepsilon} \cdot \frac{\partial \bar{c}(z)}{\partial t} \tag{4}$$

And mass balance for the solid phase is:

$$\frac{\partial \bar{c}(z)}{\partial t} = a \cdot k_{oG} \cdot \left(c_F(z) - \bar{c}_s(z) \cdot \frac{K(\bar{c}_s)}{\rho_S} \right) \tag{5}$$

Equilibrium of substrate between fluid phase and solid phase could be written:

$$K(\bar{c}_s) = \frac{c_F^*}{\bar{c}_s} \tag{6}$$

$$K(\bar{c}_s) = k_1 . \bar{c}_s exp^{-k_2} \tag{7}$$

And the overall mass transfer coefficient could be expressed as:

$$\frac{\beta_F}{k_{oG}} = 1 + \frac{Bi \cdot K(\bar{c}_s)}{6} \tag{8}$$

$$Bi = \frac{\beta_F R K}{D_{es}} \tag{9}$$

where:

$\bar{c}_s$ = mean concentration of extract components in the solid phase
c_F = concentration of extract in the fluid
D_{ax} = axial dispersion coefficient
u_z = void volume linear velocity of supercritical solvent
c_f^* = equilibrium concentration of extract in the fluid phase
K = equilibrium distribution coefficient between liquid and solid phase
D_{es} = effective diffusion coefficient in the solid phase
k_{oG} = overall mass transfer coefficient for the gas phase
z = coordinate in axial direction
ε= porosity of the fixed bed
t = time of extraction
a = specific surface of solid phase
ρ_s = density of the solid material
k_1, k_2 = coefficients of the sorption isotherm (Freundlich's isotherm)
β_F = mass transfer coefficient for the fluid phase
R = solid particle's diameter

By least-square fitting of the experimental data, the process parameters for diffusion, desorption and dispersion could be estimated. The fitted parameters, together with characteristic dimensionless numbers are presented in Table 2. It is observed that the mass transfer coefficient for the fluid phase β_F increases with increasing temperature. While, a higher axial dispersion coefficient D_{ax} tends to be achieved at a lower temperature. It is also shown that Reynolds number increases with temperature

but decreases with pressure. A higher temperature increases kinetic energy of the fluid affecting the fluid moving and direction. In contract, an increase in pressure directly relates to the increasing in solvent density and viscosity, resulting in a lower Reynolds number.

Table 2. Parameters fitted for SFE of palm mesocarp with the VTII model.

Parameter	Unit	400 bar, 65 °C	400 bar, 55 °C	400 bar, 45 °C	300 bar, 65 °C	300 bar, 55 °C	300 bar, 45 °C
ε	-	0.65	0.65	0.65	0.65	0.65	0.65
k_1	-	3.10×10^{-2}	3.90×10^{-2}	4.20×10^{-2}	3.50×10^{-2}	3.10×10^{-2}	2.60×10^{-2}
k_2	-	3.50×10^{-1}	2.90×10^{-1}	2.80×10^{-2}	2.90×10^{-1}	3.10×10^{-1}	3.30×10^{-1}
K	-	8.43×10^{-3}	1.39×10^{-2}	3.79×10^{-2}	1.22×10^{-2}	1.24×10^{-2}	8.22×10^{-3}
D_{ax}	m^2/s	5.56×10^{-2}	5.74×10^{-2}	9.61×10^{-2}	1.60×10^{-1}	1.64×10^{-1}	1.67×10^{-2}
β	m^2/s	3.73×10^{-6}	3.47×10^{-6}	1.32×10^{-6}	2.84×10^{-6}	2.61×10^{-6}	2.41×10^{-6}
Re	-	6.65	6.07	5.52	7.89	7.08	7.08
Sc	-	1782	1988	2863	2674	3023	4961
Sh	-	6.09	6.09	6.09	6.09	6.08	6.09
Bi	-	0.18	0.30	0.42	0.33	0.27	0.23

A comparison of experimental data with the calculated curves is presented in Figure 7. The results show that this model can be used to describe the palm oil extraction by $SCCO_2$. The VTII model is fitting well the extracting curves and can also define the extracting process. This model has been successfully applied for the calculation of the extraction of theobromine with a scale up factor of 40 in a pilot plant [21]. Therefore, results can be used for an up-scaling purpose.

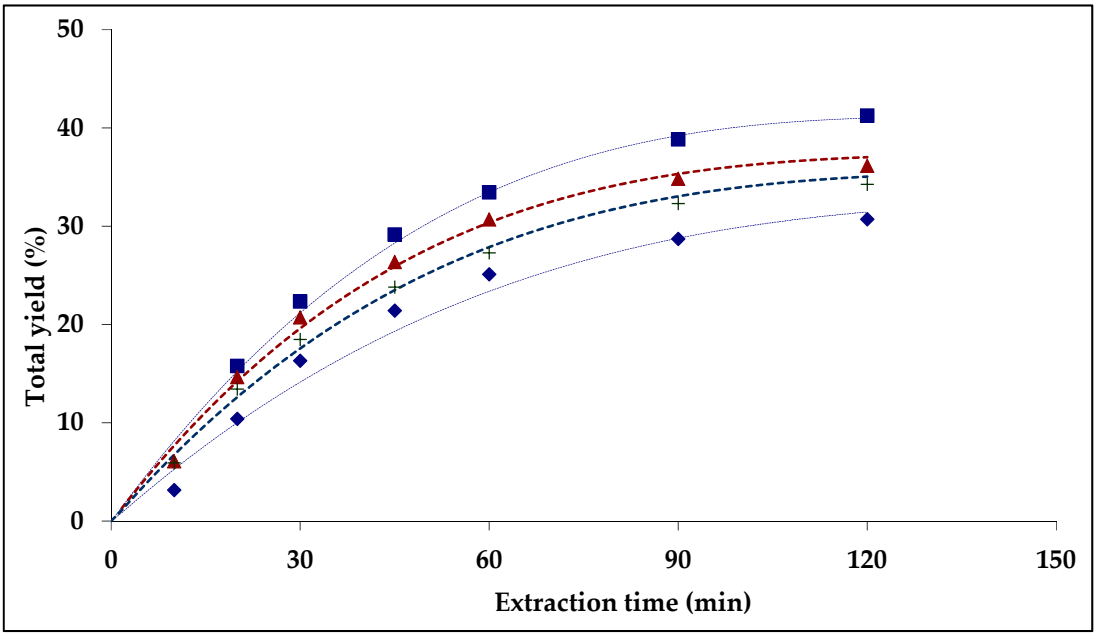

Figure 7. Comparison of experimental data with calculated curves at 35 kg h^{-1} kg^{-1}. (♦) 300 bar, 45 °C; (+) 300 bar, 55 °C (▲) 300 bar, 65 °C; (■) 400 bar, 65 °C; (.....) VTII model.

4. Conclusions

$SCCO_2$ can be used to extract palm oil with a very small amount of water and co-extract valuable minor compounds with concentrations in the same range as a normal screw-pressing oil. Extraction of palm fruit with $SCCO_2$ can be more advantaged, when the target is recovery of oil and valuable minor compounds like tocochromanols and carotenoids, compared to traditional mechanical pressing. The study showed that with a specific flow rate of 35 kg h^{-1} kg^{-1}, oil could be recovered up to 60–70% after 60 min of extraction or 80–90% after 120 min. Using supercritical CO_2 can recover much more

tocochromanols and carotenoids than using traditional screw pressing. VT II model was successfully applied for the calculation of overall extraction curves. The calculated model parameters can be applied for further up-scaling.

Author Contributions: Conceptualization, G.B. and H.P.T.; methodology, G.B. and H.P.T.; formal analysis, H.P.T.; investigation, H.P.T.; resources, G.B.; writing—original draft preparation, H.P.T.; writing—review and editing, G.B. and H.P.T.; visualization, H.P.T.; supervision, G.B.; project administration, G.B.; funding acquisition, G.B.

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