



OVERALL MASS TRANSFER COEFFICIENT FOR VITAMIN E AND CAROTENOID EXTRACTION FROM PALM PRESSED FIBER USING HOT COMPRESSED WATER

(Penentuan Pekali Keseluruhan Pemindahan Jisim Vitamin E dan Karotenoid dari Gentian Kelapa Sawit Mampat Menggunakan Pengekstrakan Air Panas Termampat)

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Abstract

Palm pressed fibre (PPF) oil contains significant amount of minor components which are vitamin E (α -tocopherol and α -tocotrienol) and carotenoid (β -carotene). These compounds are highly antioxidative which contributes to health by reducing lipid oxidation, free radical damage and other aging substances. A semi-batch HCW was studied on the effect of temperature within the range of 100 to 160 °C for 30 minutes with an interval of 10 minutes at 40 bar using 1:15 sample to solid ratio. The analysis of minor components was conducted using High Performance Liquid Chromatography (HPLC) for vitamin E and UV-Spectrophotometer (UV-Vis) for β -carotene. The mass transfer coefficient was obtained at the optimum temperature which found at 110 °C. It was found that the first order model has lower Average Absolute Relative Deviation (AARD) compared to second order. The k values from the first order model for α -tocopherol and α -tocotrienol and β -carotene under optimized condition are 0.177 min⁻¹, 0.160 min⁻¹ and 0.106 min⁻¹, respectively.

Keywords: hot compressed water, palm pressed fibre, α -tocopherol, α -tocotrienol, β -carotene

Abstrak

Minyak gentian kelapa sawit termampat (PPF) mengandungi sejumlah besar komponen kecil iaitu vitamin E (α -tokoferol dan α -tokotrienol) dan karotenoid (β -karotena). Sebatian ini mempunyai antioksidanya yang tinggi, menyumbang kepada kesihatan dengan mengurangkan pengoksidaan lipid, kerosakan radikal bebas dan penuaan bahan-bahan lain. Air panas termampat kelompok separa dikaji terhadap kesan suhu dalam julat 100 hingga 160 °C selama 30 minit dengan jarak 10 minit pada 40 bar menggunakan 1:15 sampel kepada nisbah pepejal. Analisis komponen kecil dijalankan dengan menggunakan kromatografi cecair berprestasi tinggi (KCPT) untuk vitamin E dan Spektrofotometer UV (UV-Vis) untuk β -karotena. Pekali pemindahan jisim telah diperolehi pada suhu yang optimum iaitu 110 °C. Ia mendapati bahawa model tertib pertama mempunyai AARD lebih rendah berbanding dengan tertib kedua. Nilai k dari model tertib pertama untuk α -tokoferol dan α -tokotrienol dan β -karotena di bawah keadaan optimum masing – masing adalah 0.177 min⁻¹, 0.160 min⁻¹ dan 0.106 min⁻¹.

Kata kunci: air panas termampat, gentian kelapa sawit termampat, α -tokoferol, α -tokotrienol, β -karotena

Introduction

Palm pressed fibre (PPF) is a biomass residue obtained after palm oil extraction [1]. PPF is a non-hazardous biodegradable material, clean, non-carcinogenic and free from pesticides [2]. Normally, PPF is used as fuel for steam boilers at the mills [3]. In general, PPF contains 5 – 6% residual oil with significant amount of minor components such as tocopherol, tocotrienol and carotenoid which is higher compared to crude palm oil [4]. These minor components are highly valuable for pharmaceutical, food and cosmetics industries.

Vitamin E mainly consists of two main groups; tocopherol and tocotrienol with its isomers such as alpha- (α), beta- (β), gamma- (γ) and delta- (δ) isomers [5–7]. Carotenoids which is a pre-cursor to vitamin A gives colour to plant, fruit and flowers [8]. Vitamin E and carotene are good antioxidants in foods and biological systems. Antioxidant inhibits free radical reaction inside human body and oxidation of molecules [5, 6, 9] to protect cell from oxidative damage [10]. Meanwhile, consuming carotenoids also can prevent cardiovascular disease and cancer [8].

Water is pure, safe, cheap, abundant and environmental friendly. Water has acquired attention for intensive research on the possibility of using subcritical and supercritical water on organic and inorganic synthesis [11]. The chemistry development of subcritical and supercritical water has rapidly progress in chemical science. Hot compressed water (HCW) extraction is also known as subcritical water extraction or pressurized liquid extraction is a water based extraction under subcritical region at high temperature and pressure. It operates above the normal boiling point of water at 100 °C up to its critical point, 374 °C under pressurized condition.

HCW extraction has been successfully utilized for herbal extraction for extracting gingerol compounds from ginger [12], phenolic and bioactive compounds [13] and biomass conversion [14]. The main advantageous of extracting using HCW is using water which is a non-toxic solvent used to extract polar and bioactive compound and maintains the naturalness of extracts [15]. In addition HCW extraction required shorter extraction time, higher quality of extracts, reduce the organic solvent cost [15]. Previously, researcher using organic solvent like hexane [4, 16, 17] and ethanol [18] for the extraction of these minor components. However, these organic solvents have several drawbacks like large volume used, non-environmental friendly, longer extraction time, large volume used.

The mechanism of extraction related to diffusion process can be explained based on two fundamental hypotheses which are Fick's Law and mass transfer coefficient. In this study, the mechanism is explained through mass transfer coefficient through the prediction of concentration with variation of time by neglecting the position of the desired compounds [19]. The model can be expressed based on the mass balance for the process with the assumption that the amount transferred is proportional to the concentration difference and the interfacial area as presented in equations (1) and (2). Throughout the years, there is no findings on the mass transfer coefficient of extracting vitamin E and carotene using water as solvent.

$$(\text{Amount of mass transferred}) = k \left(\frac{\text{interfacial}}{\text{area}} \right) \left(\frac{\text{Concentration}}{\text{difference}} \right) \quad (1)$$

$$V \frac{dc_1}{dt} = kA[c_1(\text{sat}) - c_1] \quad (2)$$

where V is the volume of solution, A is the particle surface area, $c_1(\text{sat})$ is the species concentration at saturation and c_1 is the species concentration in the bulk solution. Interfacial area is the area of sample that is perpendicular to the solvent.

The k value is important to determine the concentration of compound at a specific time. The aim of this study is to identify the mechanism of minor components namely α -tocopherol, α -tocotrienol and β -carotene in PPF oil through overall mass transfer coefficient by comparing with the first and second order models.

Materials and Methods

Raw Material

Dried and ground PPF is collected at Palm Oil Mill Seri Ulu Langat, Dengkil, Selangor, Malaysia. The mean particle size of PPF used in this study is between 0.89 to 3.55 mm.

Chemicals and Standards

The analytical reagents are HPLC grade of n-hexane and tetrahydrofuran (THF) from Fischer, Malaysia and 2-Propanol (99%) from R&M Chemicals, Malaysia. Distilled water was used for HCW extraction and purified nitrogen (N_2) gas was obtained from Linde, Malaysia. The standards of α -tocopherol and α -tocotrienol were purchased from Sigma Aldrich, Malaysia.

Semi-batch HCW extraction

This research using the same prototype as Sarip et. al. works [20] and the schematic diagram as shown in Figure 1.

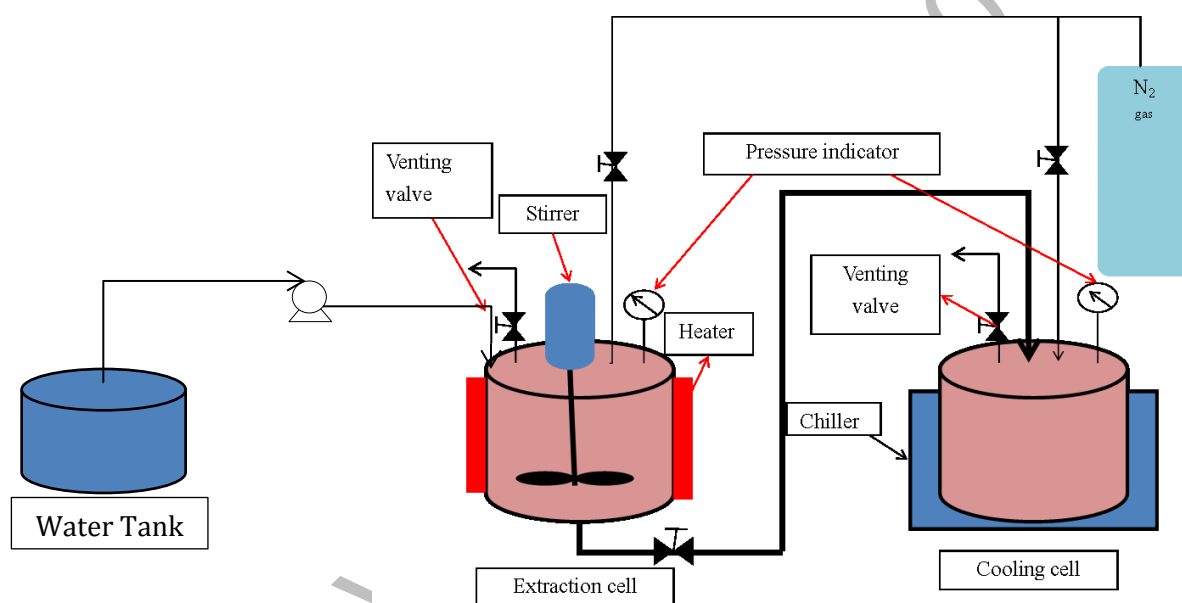


Figure 1. Schematic diagram of HCW extractor

About 40g of PPF sample was inserted into a stainless-steel mesh cylindrical container (14cm x 8cm) with mesh size of 26 μ m and loaded into the extraction vessel. 600 mL of distilled water was poured into the extraction vessel. Both vessels were covered tightly with the respective lids to avoid pressure leaking during the extraction process. Purified N_2 was supplied through one of the ports on the lid of the extraction vessel. N_2 was used to purge out dissolved oxygen and air in water as well as to maintain the required pressure during extraction process. The HCW extraction was done duplicate.

The effect of temperature was studied in the range of 100 $^{\circ}$ C to 160 $^{\circ}$ C with 10 $^{\circ}$ C increment with fixed pressure of 40 bar, constant stirring at 500 rpm and 30 minutes extraction at 10 minutes intervals. When the set temperature was reached, the extraction was timed for 10 minutes. After every 10 minutes extraction interval, the extract was removed and fresh water was replaced for the next 10 minutes batch of extraction. After completing the 10 minutes extraction, the heater was switch off and the media transfer valve was slowly opened. The extract was transferred to the cooling vessel by releasing the pressure at venting valve. The transfer was considered completed once both pressure vessels reached equilibrium. The extraction process using HCW was repeated for each interval times using the same PPF sample. Minor component analysis was done for each 10-minute interval extract.

The HCW extract was filtered using vacuum filter (DOA-P504-BN, Gast Manufacturing, Mich, USA) to remove sediments. The filtered extract was then subjected to centrifuge (Centrifuge 5804, Eppendorf, Hamburg, Germany) at 7000 rpm for 10 minutes to further separate the PPF oil and fine particles. Since the PPF extracted oil was very low, the extract was subjected to liquid-liquid extraction using hexane. In this procedure, 1 mL of the filtered extract and 0.6 mL hexane was shaken for 15 minutes. The shaken mixture was then covered with aluminum foil and left to stand in a fume hood for 24 hours [21] after which the mixture was poured into a separating funnel to separate out the PPF oil and hexane. The separated PPF oil was weighted and dissolved with 10 mL hexane. The mixture was poured into an amber bottle to be used for further analysis and all analysis was done triplicate.

Method for minor component analysis

The analysis of α -tocopherol and α -tocotrienol was carried out using HPLC (Agilent Technologies, Santa Clara, USA) equipped with fluorescence detector and standard autosampler. A Zorbax SIL auto sampler normal phase silica column (5 μ m, 150mm x 4.6mm i.d.) (Zorbax, USA) with mobile phase of n-hexane/THF/2-propanol (1000:60:4 by vol.) at constant flow rate of 1.0 mL min⁻¹. An amount 1.0 mL of the prepared solution was filtered using syringe filter (PTFE, 0.45 μ m, Whatman, USA) before injected into the HPLC.

The analysis of β -carotene was measured using a UV-Vis (DR 2800 Hach, Colorado, USA). An amount 1 mL of solution was diluted in 10 mL of hexane and transferred into a 1-cm quartz cuvette. The absorbance was read at 446 nm based on the previous studies [22, 23]. The concentration of β -carotene was calculated using equation (3) and the quantification is expressed as ppm.

$$\text{Concentration of } \beta\text{-carotene} = V \times \frac{383}{100W} \times (a_s - a_b) \quad (3)$$

where a_s is the absorbance of sample at 450 nm and a_b is the cuvette error, 383 is the extinction coefficient for carotenoids. W is weight of PPF oil in grams and V is volume of hexane (10 mL).

Mass transfer model

The experimental data on minor components was used to describe the extraction mechanism through mass transfer coefficient model. First and second order mass transfer models were implemented in this study. The first order mass transfer model, k_1 is a mass balance of compound by assuming the total amount of mass transferred in the process is equivalent to the concentration difference of compound [20]. The first order mass transfer model is expressed in equation (4). The integration was made through conditions of $t = 0$ to t and $C_t = 0$ to C_t as shown in equation (5).

$$\frac{dC_t}{dt} = k_1 (C_{eq} - C_t) \quad (4)$$

$$k_1 t = \ln \left(\frac{C_{eq}}{C_{eq} - C_t} \right) \quad (5)$$

where k_1 is first order is the mass transfer mass transfer coefficient. C_{eq} is assumed to be the maximum concentration of minor components obtained in the PPF oil. C_t is the species concentration in the liquid extract at a specific time. The k_1 value was identified from the slope of $\ln \frac{C_{eq}}{C_{eq} - C_t}$ against t . C_{eq} is determined through the integration of the experimental data.

The second order mass transfer model was demonstrated to give an accurate mechanism of the solid-liquid extraction process using water [20], [24], [25] which is similar to HCW extraction. The second order mass transfer model is expressed as in equation (6).

$$\frac{dC}{dt} = k_2 (C_{eq} - C_t)^2 \quad (6)$$

where k_2 is the mass transfer coefficient (g of dried PPF/g of minor components. min). C_{eq} is a maximum concentration achieved at a specific condition and varies for each experimental condition. The integration was made through conditions of $t = 0$ to t and $C_t = 0$ to C_t is expressed as equation (7) and linearized as equation (8):

$$C_t = \frac{C_{eq}^2 k_2 t}{1 + C_{eq} k_2 t} \quad (7)$$

$$\frac{t}{C_t} = \frac{1}{k_2 C_{eq}^2} + \frac{t}{C_e} \quad (8)$$

The initial extraction rate defined as h (g- species/g-dried PPF. min) when t and C_t approach 0 is expressed as equation 9 below:

$$h = k_2 C_{eq}^2 \quad (9)$$

Rearranging equations (8) and (9), resulted in equation (10) as below:

$$\frac{t}{C_t} = \frac{1}{h} + \frac{t}{C_{eq}} \quad (10)$$

The value of h , C_{eq} and k_2 were determined from y intercept and slope of $\frac{t}{C_t}$ against t . The first and second order models were solved using Matlab R2015b (Math Works, Inc, USA). The predictive capability between experimental and predicted concentration were evaluated based on the, AARD (%) using equation (11):

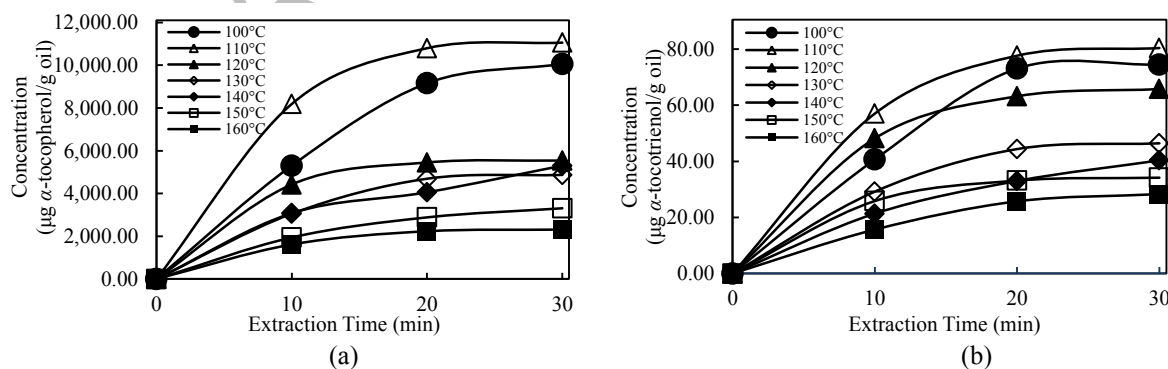
$$\text{AARD (\%)} = \sum \frac{1}{N} \left| \frac{x_{exp} - x_{predicted}}{x_i} \right| \times 100 \quad (11)$$

where N is the number of runs for one experimental condition, x_{exp} and $x_{predicted}$ are the experimental and predicted data respectively. The lower value of AARD (%) shows better predictive capability of the model.

Results and Discussion

HCW extraction mechanism

The cumulative extraction trend of minor components in semi-batch mode for 30 minutes extraction time with 10 minutes interval can be clearly seen through the graph of concentration versus time. Teo et al. [26] stated that, a semi batch process enhances the extraction mechanism compared to batch process. Figure 2 shows the cumulative curve for extraction mechanism of α -tocopherol, α -tocotrienol and β -carotene against time at the experimental temperature range from 100 °C to 160 °C.



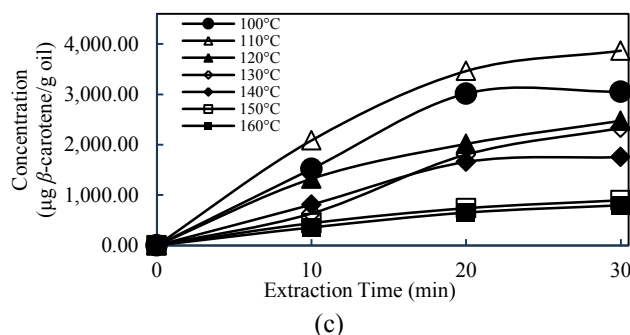


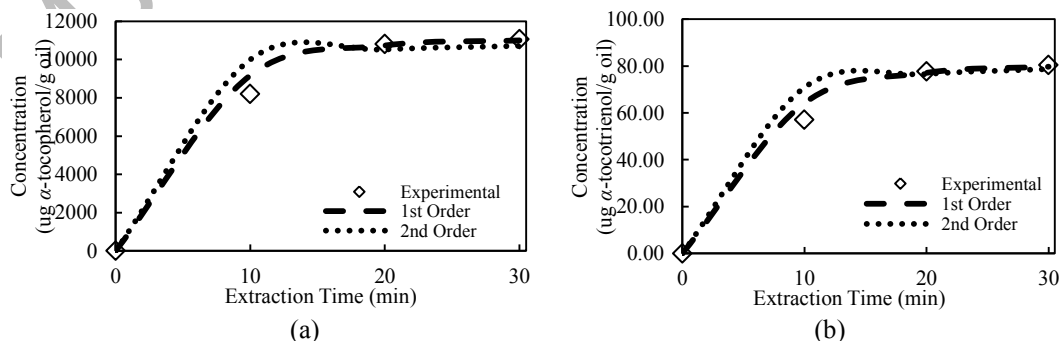
Figure 2. The cumulative extraction curve of (a) α -tocopherol (b) α -tocotrienol and (c) β -carotene with time at various temperatures

In general, extraction temperature affects the rate of extraction which is the change in concentration with respect to time. The optimum temperature was 110 °C for all the compounds studied α -tocopherol, α -tocotrienol and β -carotene. The highest cumulative concentration for 30 min extraction achieved at this condition were 11059.02 ± 0.02 $\mu\text{g/g}$ oil, 80.37 ± 0.02 $\mu\text{g/g}$ oil and 3866.53 ± 0.03 $\mu\text{g/g}$ oil for α -tocopherol, α -tocotrienol and β -carotene respectively. Mazaheri et al. stated that, at higher temperatures, the tendency of degradation to the extract increase and some of molecule starts to undergo hydrolysis, oxidation, methylation, isomerization and other chemical reactions depending on the structure of molecule and operating condition. This phenomenon is observed in this study where at higher temperature, the concentration of minor components decreases. Apart from the possible degradation of extracted oil, it was also due to re-absorption of the oil into the disintegrated fibre structure at higher temperature as explained earlier [27].

The extraction rates for the minor components α -tocopherol, α -tocotrienol and β -carotene from 100 until 160 °C have similar trend which could be divided into two different regions. The first region indicated in the early 20 minutes of extraction, shows the higher extraction rate for all the compounds studied α -tocopherol, α -tocotrienol and β -carotene indicating a rapid and gradual mild extraction rate. Meanwhile, the second region shows a constant concentration is approached due to lacking extracted compounds under those conditions.

Overall mass transfer coefficient of minor components in HCW extraction

To describe the mechanism of HCW extraction, mass transfer coefficient, k was calculated using first and second order mass transfer models to explain the extraction curve for vitamin E (α -tocopherol and α -tocotrienol) and β -carotene using HCW extraction. The predictive mass transfer coefficient for both models was determined at 110 °C which is the optimum temperature for the three compounds studied. The cumulative curves of the minor components concentration predicted using first and second order mass transfer models are compared with the experimental data as shown in Figure 3.



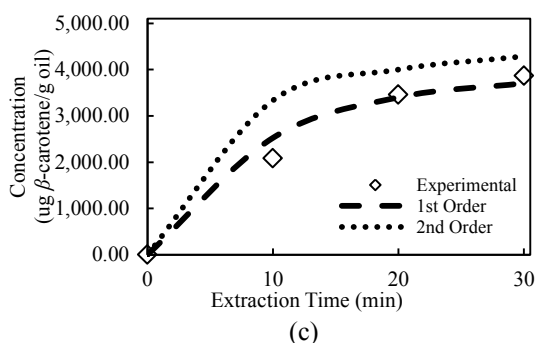


Figure 3. Experimental and predicted data for extraction mechanism of (a) α -tocopherol, (b) α -tocotrienol and (c) β -carotene at 110 °C

From Figure 3, the mechanism of HCW extraction of minor components can be divided into 2 phases. The first phase is in the first 20 mins where the entrainment of the PPF oil into the bulk of HCW. Oil is practically insoluble in water; therefore, the dissolution process does not occur. During the HCW extraction, with the support of agitation, a slight dissolution process slightly occurred to form heterogeneous mixture of HCW and PPF oil. At this phase, the hydrolyses reaction of hemicellulose into glucose also occurred simultaneously. According to Phaiboonsilpa et al., hemicellulose start to hydrolyzed at 20 °C [28]. The second phase is the last 10 minutes where the process is stagnant indication the limit concentration of minor components.

To verify the overall mass transfer coefficient, a predicted concentration of α -tocopherol, α -tocotrienol and β -carotene has been calculated. The percentage error between experimental and predicted data concentration of minor components was identified using AARD. The AARD of first and second mass transfer models is shown in Table 1.

Table 1. Comparison of first and second mass transfer models on minor components

Mass Transfer	Validation	1 st Order		2 nd Order			
	R ²	k ₁ (min ⁻¹)	AARD (%)	k ₂ (g/g)	Ceq (μg/g)	h	AARD (%)
α -tocopherol	0.9696	0.177	6.24	0.0000810	11111	10000	12.62
α -tocotrienol	0.9715	0.160	6.69	0.0068	83.33	46.95	13.16
β -carotene	0.9618	0.106	12.65	4.44E-05	5000	1111.11	35.38

The values of AARD are used to evaluate the goodness of model for a given experimental and predicted data set. The first order mass transfer model shows good prediction with AARD values of 6.24 for α -tocopherol, 6.69 for α -tocotrienol and 12.65 for β -carotene respectively. However the values of AARD is a greater than 5% but lower than acceptable deviation values which is 20% [29]. Meanwhile, the second order mass transfer model shows poor performance of AARD values which 12.62 for α -tocopherol, 13.16 for α -tocotrienol and 35.38 for β -carotene, respectively. The second order mass transfer model give high AARD and not suitable to be used to explain the HCW extraction mechanism. Therefore, minor components extraction using HCW extraction followed the first order mass transfer model.

Residual oil is located at the fibrous material which is different compared to CPO extraction [20], where the palm mesocarp contain abundance of oil. In palm oil mill, palm mesocarp undergoes sterilization, digestion and screw pressed to obtain the CPO and by-product, PPF. There is residual oil in the PPF and no longer in the cell wall of palm fibrous. The extraction of oil from PPF is a direct process due to the location of oil which is attach to PPF. Therefore, the extraction mechanism can be explained using first order model. Meanwhile, the extraction of oil from

mesocarp with abundance of oil inside the mesocarp is complex and required advance model such as second order mass transfer model to explained the extraction process.

k value represents the efficiency of extraction process. The higher k value shows higher rate of solute movement from the solid matrix into a solvent. Comparison were made between k value of β -carotene using SFE-CO₂ is 0.003 per min [30] which is lower compared to extraction of β -carotene using HCW extraction. the k value is basically depending on the initial concentration of compound. The initial concentration can be low or high is basically depends on the origin of the sample and also the sample preparation [12]. Different origin of fresh palm oil fruit, the oil content also different hence give different concentration of minor components. Therefore, the k value obtain from HCW extraction and SFE-CO₂ is not comparable except if the determination of k value using the same sample.

The overall mass transfer coefficient model is efficient at optimum condition. In this study, the optimum temperature for extraction of α -tocopherol, α -tocotrienol and β -carotene is at 110 °C. Furthermore, the model effectively represents each compound and each compound has a unique k value. The mechanism of α -tocopherol, α -tocotrienol and β -carotene is successfully modelled by the mass transfer coefficient with the linear correlation based on r^2 value is 0.9696, 0.9715 and 0.9618, respectively. Therefore, the overall mass transfer coefficient for α -tocopherol, α -tocotrienol and β -carotene at 110°C by using HCW extraction are 0.177 min⁻¹, 0.160 min⁻¹ and 0.106 min⁻¹.

Conclusion

The extraction mechanism of minor components using HCW extraction can be explained through first order mass transfer model. At optimum condition which is at temperature of 110°C, the overall mass transfer coefficient, k of extraction α -tocopherol, α -tocotrienol and β -carotene were 0.177 min⁻¹, 0.160 min⁻¹ and 0.106 min⁻¹. However, the exploration of advance mass transfer model like power law equation and two-site kinetic equation can improve the AARD values.

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