Simulation Modeling of the Phase Behavior of Palm Oil–Supercritical Carbon Dioxide

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ABSTRACT: The phase behavior of crude palm oil (CPO) with supercritical CO_2 was successfully modeled in an Aspen Plus® 10.2.1 commercial simulator (Aspen Technology Inc., Cambridge, MA) using the Redlich–Kwong–Aspen (RKA) equation of state thermodynamic model. The modeling procedure involved estimating pure component vapor pressures and critical properties and computing a regression of phase equilibrium behavior. The interaction parameters for the RKA model were obtained from the regression of experimental phase equilibrium data for a binary system of palm oil components–supercritical CO_2 available in the literature. The distribution coefficients and solubilities of palm oil components obtained from this simulation showed good agreement with experimental data obtained from the literature. The model provides an efficient and cost-effective alternative for the preliminary design and optimization of a supercritical fluid extraction process involving a complex CPO–supercritical CO_2 system.

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KEY WORDS: Palm oil, phase equilibrium, supercritical carbon dioxide, thermodynamic modeling.

Over the years, supercritical fluid extraction (SFE) technology has developed rapidly and found applications in the commercial production of vegetable oils, including palm oil. Palm oil contains various components such as MG (<1%), DG (2–7%), TG (>90%), FFA (3–5%), phospholipids, pigmented compounds, and several nutritionally bioactive compounds (1). Minor components such as β-carotene and tocopherol are often degraded or lost during the bleaching and refining processes, which require high operating temperatures of up to 240°C. Selective supercritical CO_2 extraction of these high-value but thermally unstable components from crude palm oil (CPO) has enabled operation at mild temperatures of less than 100°C. In addition, the inert solvent used can be easily separated and recovered, thereby leading to a pollution-free operation. All these advantages combine to make SFE of components in palm oil a desirable alternative to conventional processing methods such as chemical and physical refining.

By correlating limited experimental data gained from literature using thermodynamic models, a general representation of the phase behavior of a system can be determined, thus making it possible to reduce experimental work. The equation of state has been shown to adequately represent the phase behavior of lipid-related components with supercritical CO_2 (2–5). It is anticipated that the equation of state also can model the phase equilibrium of a palm oil components–supercritical CO_2 system. However, a reliable phase equilibrium model is required in the analysis of the SFE process involving a palm oil–supercritical CO_2 system since the system comprises a highly dissimilar mixture of high M.W. TG and low M.W. supercritical CO_2. In addition, such a model must be applicable over a wide range of temperatures and pressures to yield some accurate quantitative values of the mutual solubilities, compositions of coexisting phases, and distribution coefficients that are of fundamental importance in the design of a countercurrent SFE process. The steps involved in modeling the phase equilibrium of palm oil components extracted with supercritical CO_2 are presented in the next section.

PHASE EQUILIBRIUM MODELING

The first step in modeling the phase equilibrium of a multicomponent palm oil–supercritical CO_2 system is to establish the composition of the multicomponent palm oil system (system characterization). This is followed by a prediction of the solubilities and distribution coefficients of the palm oil components using the Redlich–Kwong–Aspen equation of state (RKA-EOS). The RKA model can be applied to the SFE process since it is particularly suitable for modeling a mixture of polar components with light gases (such as CO_2) at medium to high pressures (6). Prior to using the RKA-EOS to predict the phase equilibria, some key physical and critical properties of the palm oil components were estimated, and the binary interaction parameters of the equation of state were calculated.

The RKA-EOS. The RKA-EOS (6) is a cubic equation of state that is an extension of the Redlich–Kwong–Soave equation of state (7). The RKA-EOS was regressed using the Data Regression System module available in the Aspen Plus® process simulator, version 10.2.1, to correlate the experimental phase equilibrium data published in the literature. Equation 1 represents the RKA-EOS used in this work for modeling the phase equilibria of the CPO–supercritical CO_2 system:

$$P = \frac{RT}{v_m - b} \frac{a}{v_m(v_m + b)} \qquad [1]$$

where P is pressure, R is the universal gas constant, T is temperature (K), v_m is molar volume, and a and b are cross-energy and co-volume parameters, respectively, for a mixture.

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Calculations of pure component parameters for the RKA-EOS. For a pure component, *i*, the parameters a_i and b_i for the RKA-EOS are functions of the critical temperature (T_{ci}) and critical pressure (P_{ci}) of the pure component (Eqs. 2 and 3),

$$a_i = \alpha_i 0.42747 \frac{R^2 T_{ci}^2}{P_{ci}} \qquad [2]$$

$$b_i = 0.08664 \frac{R T_{ci}}{P_{ci}} \qquad [3]$$

(for definition of α_i, see the following). The RKA-EOS is not accurate in predicting vapor pressures below 10 Torr (8). To improve the vapor pressure prediction for a highly nonlinear dependence of vapor pressure on temperature, Mathias (9) recommends the generalized temperature-dependent function, α_i (Eq. 4), for the subcritical component (referring to the palm oil component in this study), which considerably improves vapor pressure predictions:

$$\alpha_i(T) = \left[1 + m_i\left(1 - \sqrt{T_{ri}}\right) - \eta_i\left(1 - \sqrt{T_{ri}}\right)\left(0.7 - T_{ri}\right)\right]^2 \qquad [4]$$

where T_{ri} is reduced temperature and η_i is the polar factor of the pure component. The polar factor, η_i, which takes into account the polarity, is fitted from the pure component vapor pressure data. The constant for pure component *i* (m_i), calculated as a function of the acentric factor (ω_i), is necessary to compute Equation 4, as given in Equation 5:

$$m_i = 0.480 + 1.574\omega_i - 0.176\omega_i^2 \qquad [5]$$

Binary mixture calculation. The RKA-EOS utilizes the classical quadratic mixing rule (Eqs. 6 and 7) for a mixture. To model the molecular interactions between components *i* and *j*, the binary interaction parameters ($k_{a,ij}$, $k_{b,ij}$) are introduced through the quadratic mixing rules as follows:

$$a = \sum_i \sum_j x_i x_j \sqrt{a_i a_j}\left(1 - k_{a,ij}\right) \qquad [6]$$

$$b = \sum_i \sum_j x_i x_j \frac{\left(b_i b_j\right)}{2}\left(1 - k_{b,ij}\right) \qquad [7]$$

To predict the phase equilibrium of dissimilar components such as palm oil and supercritical CO_2, binary interaction parameters are required. To improve the predictive capability of the equation of state, the interaction parameters are considered temperature-dependent (3,10–12). The RKA-EOS assumes a linear temperature dependency of the interaction parameters (6) as follows:

$$k_{a,ij} = k_{a,ij}^0 + k_{a,ij}^1 \frac{T}{1000} \qquad [8]$$

$$k_{b,ij} = k_{b,ij}^0 + k_{b,ij}^1 \frac{T}{1000} \qquad [9]$$

Palm oil system characterization. A description of complex natural systems may need a simple, although reasonable, hypothesis about the components involved. Researchers often treat the multicomponent–supercritical CO_2 mixture as a pseudo-binary system in which the main components in the oil are treated as a single component using a lumping procedure. França and Meireles (13) proposed a model that assumes the solutes extracted from pressed palm oil fibers are a mixture consisting of three key components, namely, oleic acid (as FFA), triolein (as TG), and β-carotene. Ohgaki *et al.* (14) used palmitic acid to represent the FFA, tripalmitin to represent TG, and α-tocopherol to represent vitamin E in the palm oil mixture.

Regarding the composition of CPO (15,16), the model proposed in this study considered CPO to be a mixture containing principally TG (tripalmitin and triolein) with some FFA (oleic acid) and minor components (β-carotene, α-tocopherol).

Palmitic acid and oleic acid are the major FA in palm oil TG, constituting about 90% of the total TG. The TG in palm oil exist mainly in the form of disaturated dipalmitoyl-oleoyl-glycerol (POP and PPO) and monosaturated palmitoyl-dioleoyl-glycerol (POO), as shown in Table 1. The mean M.W. and the variance (σ^2) were calculated based on the assumptions that the distribution of FA among the TG and the presence of unsaturation in FA were negligible.

Owing to the relatively wide distribution of TG in palm oil, it was insufficient to represent the complex mixture of palm oil TG as a single component. Saturated and unsaturated palm oil TG were represented by tripalmitin and triolein, respectively. The composition of the selected TG components was based on the typical FA composition in crude palm oil (17). The calculation of the composition for palm oil TG is included in Appendix 1. In this study, the palm oil TG were approximated as a mixture of 47.78 wt% tripalmitin and 52.22 wt% triolein, with an average M.W. of 846.7 g mol⁻¹.

A study on the changes in lipid class and composition in oil palm mesocarp by Sambanthamurthi *et al.* (18) suggested that FFA consist of oleic acid (45.20 wt%), palmitic acid (35.40 wt%), and linoleic acid (17.20 wt%). Oleic acid, as the most abundant component in FFA, was selected as the key component to represent the FFA in palm oil.

Development of the Aspen Plus physical property database for the palm oil component. Physical property data for the components involved in the thermodynamic modeling of the CPO–supercritical CO_2 system were not available in the Aspen Plus property database, although some physical property data for the individual components in the palm oil mix-

TABLE 1
Composition of TG in Typical Malaysian Palm Oil[a]

Carbon number	M.W. (kg kmol⁻¹)	Composition (wt%)
C44	750.9	0.07
C46	778.9	1.18
C48	806.9	8.08
C50	834.9	39.88
C52	862.9	38.77
C54	890.9	11.35
C56	918.9	0.59

[a]From Reference 17. M.W. = 848.9 kg kmol⁻¹, σ^2 = 592.78.

TABLE 2
Pure Component Parameters for the Extended Antoine Equation[a]

Component	A	B	C	D	E
Tripalmitin	108841	−4098952	19.96	−17792	−3.6 × 10^{-15}
Triolein	−514215	19737838	−91.13	83685	1.4 × 10^{-14}
Oleic acid	136.45	−19702	−0.01	−14.87	−7.2 × 10^{-19}
α-Tocopherol	−15.90	−5118	0.05	0	0
β-Carotene	−91.32	−15.90	0.239	0	0

[a]The extended Antoine equation (6) is of the form: $\ln P^{\text{sat}} = A - B/T + CT + D \ln T + ET^6$, where pressure ($P^{\text{sat}}$) is in kPa and temperature (T) is in K.

ture were available in the open literature. However, many of the physical properties of palm oil components cannot be determined experimentally due to thermal decomposition of the components at temperatures below their b.p. It was therefore necessary to estimate the critical properties of these components theoretically. These properties can actually be considered as hypothetical properties. Once the critical properties had been estimated, a set of physical properties for the components of interest could be determined.

Vapor pressure estimation. Only limited vapor pressure data could be found for tripalmitin, triolein, and α-tocopherol in the open literature (19,20), and they covered a temperature range considerably above the ones of interest in this study. For oleic acid, vapor pressure data on stearic acid (21,22), which has the same chain length but a different degree of unsaturation, was used because unsaturation has very little influence on the vapor pressure of TG (19) and methyl esters of FA (21). The experimental sublimation pressure of β-carotene reported by Cygnarowicz *et al.* (23) was used in this study.

Extrapolative and predictive methods have been used to estimate the vapor pressures for fatty oil components due to the difficulties in carrying out vapor pressure measurements at low temperatures. Equation 10 represents the extended Antoine model (6) used in this study to extrapolate the available experimental data to the temperatures of interest:

$$\ln P^{\text{sat}} = A + \frac{B}{T} + CT + D \ln T + E \ln T^6 \qquad [10]$$

where P^{sat} is vapor pressure and $A–E$ refer to regressed parameters for the extended Antoine equation.

The parameters of the extended Antoine equation were obtained by minimizing the objective function, Q (Eq. 11), using the generalized least squares regression. The least squares algorithm is available in Aspen Plus 10.2.1.

$$Q = \sum_{i=1}^{m} \left[\frac{P_i^{\text{calc}} - P_i^{\text{exp}}}{P_i^{\text{exp}}} \right]^2 \qquad [11]$$

where m is the number of experimental data points, P_i^{calc} is the calculated vapor pressure, and P_i^{exp} is the experimental vapor pressure. The parameters for the extended Antoine vapor pressure equation are summarized in Table 2.

Estimation of critical properties. The method proposed by Dohrn and Brunner (24) was used, as it required only the liquid molar volume at 20°C, V_{L20}, and vapor pressure data as the input information to obtain the critical properties of palm oil components. Table 3 summarizes the predicted critical properties of the palm oil components used in this study.

Binary interaction parameters. To calculate the binary interaction parameters for the RKA-EOS, the interaction parameters were initially assumed to be zero. The Deming algorithm (6) was applied to perform a maximum likelihood (errors-in-variables) estimation to minimize the following objective function:

$$Q = \sum_k \left(\frac{T^m - T^c}{\sigma_T} \right)^2 + \sum_k \left(\frac{P^m - P^c}{\sigma_P} \right)^2$$

$$+ \sum_k \left(\frac{x_1^m - x_1^c}{\sigma_{x_1}} \right)^2 + \sum_k \left(\frac{y_1^m - y_1^c}{\sigma_{y_1}} \right)^2 \qquad [12]$$

where T and P are the temperature and pressure of the studied phase equilibrium data, x and y are the compositions of a

TABLE 3
Predicted Physical Properties of Pure Components in Palm Oil

Component	T_B (K)[a]	T_C (K)[a]	P_C (kPa)[a]	ω[b]	V_{L20} (m^3/kmol)[c]
Tripalmitin	864.21	947.10	396.82	1.6500	0.8906
Triolein	879.92	954.10	360.15	1.8004	0.9717
Oleic acid	646.52	813.56	1250.2	0.8104	0.3172
α-Tocopherol	794.52	936.93	838.45	1.1946	0.4533
β-Carotene	908.58	1031.1	678.41	1.6255	0.5348

[a]Estimated by the method of Dohrn and Brunner (24), where t is temperature and P is pressure; see Table 2 for B and C. T_B, boiling point temperature; T_C, critical temperature; P_C, critical pressure; ω, acentric factor.
[b]Estimated using the Pitzer method (6).
[c]Liquid molar volume data (at 20°C), V_{L20}, obtained from open the literature: tripalmitin, triolein, oleic acid, (21); α-tocopherol (24); β-carotene (25).

TABLE 4
Phase Equilibrium Data from the Literature for the Binary Systems of Pure Palm Oil Components–Supercritical CO_2

Palm oil component–CO_2	Temperature (K)	Pressure (MPa)	References
Tripalmitin	333, 353	15–50	Weber and coworkers (2,26)
Triolein	333, 353	20–50	Weber and coworkers (2,26)
Oleic acid	313, 333, 353	15–30	Bharath (27)
α-Tocopherol	313, 323, 333, 343	9–26	Pereira et al. (10)
		20–30	Meier et al. (12)
β-Carotene	313, 323, 333, 353	20–28	Sovová et al. (28)
		20–32	Johannsen and Brunner (29)

component in the liquid and fluid phase, σ is the SD, c and m refer to the calculated and experimental values, and k refers to component k.

The quality of the regressed data was assessed using the average absolute deviation (AAD) between the measured and calculated data:

$$\text{AAD (\%)} = \frac{1}{N} \sum_{i=1}^{N} |d_i| \times 100\% \qquad [13]$$

where d_i is the error between the experimental and calculated values and N is the number of data points.

Phase equilibrium data available in the literature for the binary system of palm oil components–supercritical CO_2 are presented in Table 4. The solubility of β-carotene in supercritical CO_2 was calculated by assuming a liquid–fluid equilibrium using the RKA thermodynamic model. β-Carotene (solute) was treated as a "liquid" component since Aspen Plus does not generally deal with the solid–liquid–fluid equilibrium.

The solute–solute interaction parameters between palm oil components (TG, FFA, and minor components) were assumed to be zero. The reason behind this was that experimental data for the TG–FA system for palm oil were not available; hence, binary interaction parameters between these components could not be estimated. Since the two components are very dissimilar, the approximation might not be completely adequate. Nevertheless, satisfactory results have been reported in the literature from predicting the phase equilibrium of a complex oil mixture based on only supercritical solvent–solute interactions while neglecting the solute–solute interactions. Some examples include the prediction of phase equilibrium for a CO_2–soybean oil deodorizer condensates system by Araújo et al. (5), a CO_2–orange oil system by Cardozo-Filho et al. (30), and a CO_2–essential oil system by Sovová et al. (31).

RESULTS AND DISCUSSION

Interaction parameters for the palm oil components–supercritical CO_2 binary system. Owing to the extremely low vapor pressures of TG and the considerable difficulty in predicting the vapor pressure of TG from experiments (19) carried out only at high temperature (>240°C), the polar factor (η_i) for palm oil TG was computed simultaneously with binary interaction parameters ($k_{a,12}$ and $k_{b,12}$) from palm oil TG–supercritical CO_2 phase equilibrium data. The polar factor of oleic acid calculated from the vapor pressure data (21) yielded a value of –1.1197, compared with –1.0873 (at 333 K) and –1.1316 (at 353 K), which were calculated from oleic acid–supercritical CO_2 binary phase equilibrium data (27).

Table 4 shows the source of the experimental phase equilibrium data for the palm oil component–supercritical CO_2 binary system. By using the calculated polar factor for the palm oil component and the binary interaction parameters for the palm oil component–supercritical CO_2 binary system, the calculated liquid phase and supercritical fluid phase composition for the palm oil components–supercritical CO_2 system were compared to literature data as shown in Table 5. The maximum AAD of the RKA-model predictions from these data were calculated to be 2.78% for the liquid phase and 0.76% for the fluid phase. The very small deviations indicated that the regressed data are very reliable.

(i) Ternary system. The ternary phase equilibrium for a CO_2–TG–FA system at 333 K and 20–30 MPa was predicted using the pure component parameters and the binary interaction parameters for the RKA model. Figure 1 provides a comparison between the ternary data for a CO_2–triolein–oleic acid system reported by Bharath (27) and the results obtained in this work using the RKA model. The comparison shows that the RKA-predicted ternary phase diagrams are in good agreement with experimental data (27). The results also suggest that the assumption of negligible TG–FA solute–solute interaction is acceptable.

(ii) Temperature-dependent polar factor and interaction parameters. The temperature-dependent polar factor (η_i) and binary interaction parameters (k_a, k_b) were obtained by using a linear function to correlate the polar factor and binary interaction parameters obtained (Table 5) for use at the temperature range of interest. The polar factor and interaction parameters were regressed using the linear regression function in the Microsoft® Excel. The resulting temperature-dependent polar factor and binary interaction parameters (with $R^2 > 0.9$) are shown in Table 6.

Phase equilibrium calculation for the palm oil–supercritical CO_2 system. The phase equilibrium calculations were carried out using a P–T isothermal flash algorithm implemented in Aspen Plus. Phase equilibrium (flash) calculations were

TABLE 5
Optimal Parameters[a] for the Redlich–Kwong–Aspen (RKA) Model of a Binary System: Palm Oil Component (1)–Supercritical CO$_2$ (2)

	T (K)	η_1	$k_{a,12}$	$k_{b,12}$	AAD$_x$ (%)	AAD$_y$ (%)
Tripalmitin	333	–2.4016	0.0397	–0.0186	1.4708	0.0631
	353	–1.9559	0.0526	–0.0316	0.9729	0.0832
Triolein	333	–3.6063	0.0289	–0.0153	1.5666	0.3559
	353	–3.2353	0.0392	–0.0065	2.9560	0.1931
Oleic acid	313	–1.1772	0.0705	–0.0073	0.4898	0.1187
	333	–1.0873	0.0819	0.0036	0.9411	0.4304
	353	–1.1316	0.0879	0.0136	0.2997	0.0811
α-Tocopherol	313	–0.9467	0.0519	–0.0301	0.5316	0.0536
	323	–0.5891	0.0620	–0.0191	1.0383	0.2537
	333	–0.4412	0.0668	–0.0237	1.5168	0.0821
	343	–0.3010	0.0741	–0.0154	0.5362	0.1403
	353	0.0289	0.0905	0.0155	0.8488	0.0539
β-Carotene	313	–1.4439	0.0696	–0.0634	—	9.2076
	323	–1.2325	0.0691	–0.0772	—	5.3675
	333	–1.0210	0.0713	–0.0908	—	19.6337
	353	–0.545	0.0665	–0.1275	—	31.0576

[a]T, temperature; η, polar factor; $k_{a,12}$ and $k_{b,12}$, binary interaction parameters of components 1 and 2; AAD, average absolute deviation.

performed throughout a multicomponent process simulation run for a supercritical fluid–liquid split to obtain the phase compositions of palm oil components. Simulations were performed on a stand-alone PC with a Microsoft Windows operating system running with a Pentium III/1.0 GHz processor.

Table 7 provides a comparison between the phase equilibria of palm oil–supercritical CO$_2$ systems reported in the literature (32–34) and that predicted by the RKA model in this work. Results were obtained within 50 iterations corresponding to computation times of less than 0.5 CPU seconds. The phase equilibrium of palm oil–supercritical CO$_2$ predicted using the RKA-EOS agrees well with the experimental data

of Stoldt and Brunner (33) and Brunner (34). This was evident from the overall AAD of the RKA-model predictions, which were calculated to be 5.06% for the liquid phase and 0.275% for the fluid phase.

Solubility of CPO in supercritical CO$_2$. Solubility is used to define the maximum yield obtainable in an extraction process occurring in a hypothetically infinite contact time. Therefore, the oil concentration in the supercritical phase is lower than the equilibrium value because thermodynamic equilibrium cannot be reached in an industrial extractor owing to the finite contact time between the solvent and the solute (35). Ooi *et al.* (36) observed that the solubility of palm
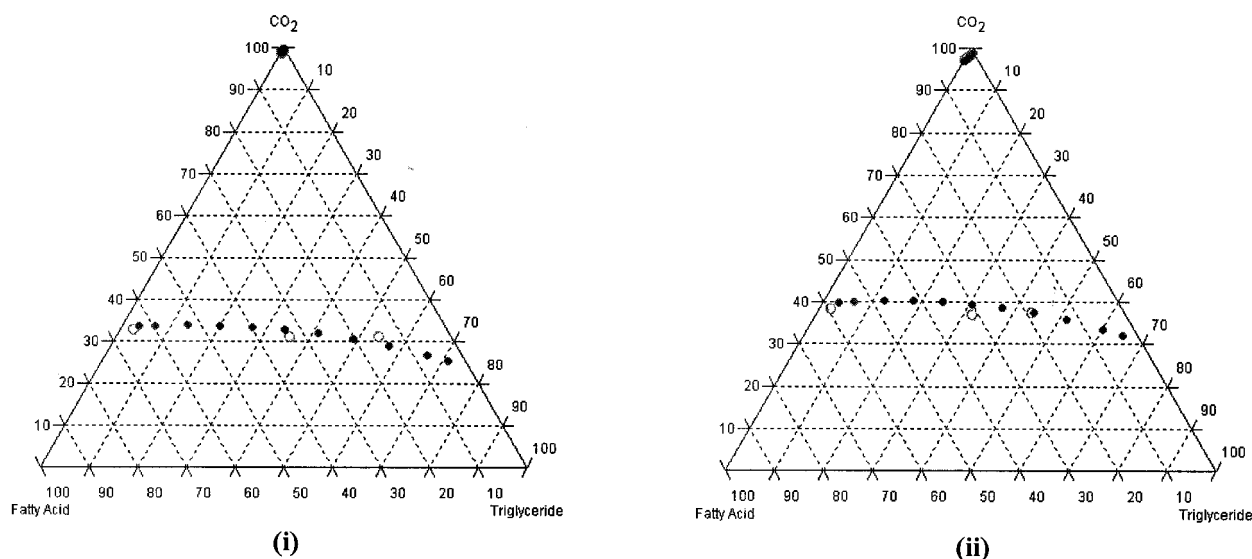
FIG. 1. Phase equilibrium for a pseudo-ternary supercritical CO$_2$–FA–TG system at 333 K and (i) 20 MPa and (ii) 30 MPa. (○) Experimental data (27) for the ternary system CO$_2$–triolein–oleic acid. (●) Predicted data for the ternary system CO$_2$–TG–FA.

TABLE 6
Temperature (*T*) Dependence of the RKA Model[a] Polar Factor (η) and Binary Interaction Parameters (*k_a*, *k_b*) for Palm Oil Components–Supercritical CO_2 Systems

	Polar factor (η_i)	Binary interaction parameters
Tripalmitin	$0.0225T - 9.8778$	$k_a = 0.0007T - 0.1942$
		$k_b = -0.0006T + 0.1952$
Triolein	$0.0185T - 9.7834$	$k_a = 0.0005T - 0.1428$
		$k_b = 0.0004T - 0.1635$
Oleic acid	$0.00004T - 1.1515$	$k_a = 0.0004T - 0.0391$
		$k_b = 0.0005T - 0.1655$
α-Tocopherol	$0.0224T - 7.9068$	$k_a = 0.0009T - 0.2286$
		$k_b = 0.0009T - 0.3305$
β-Carotene	$0.0225T - 8.4999$	$k_a = 0.0001T + 0.0920$
		$k_b = -0.0016T + 0.4417$

[a]For abbreviation see Table 5.

oil in the equilibrium state is higher than that under continuous processing conditions. Therefore, the empirical extraction stage efficiency (η_E) must be used to correct the departures of oil solubility under continuous operating conditions from those of equilibrium solubility:

$$\eta_E = \frac{\text{solubility (continuous processing)}}{\text{solubility (equilibrium condition)}} \times 100\% \qquad [14]$$

In this study, an extraction efficiency of 55% was assumed. Reverchon and Osseo (35) and Stahl *et al.* (37) suggest an extraction efficiency of 60% with respect to equilibrium value in their work involving a soybean oil–supercritical CO_2 system.

It has been reported that oil solubility depends highly on composition, especially on the composition of FFA, which are more soluble than TG in supercritical CO_2 (38–41). The FFA content used to compute the solubility of palm oil was assumed to be 2.35 wt%. This is the same as the FFA content reported by Ooi *et al.* (36). Figure 2 compares the solubility of crude palm oil in CO_2 predicted in this work with that determined experimentally by Ooi *et al.* (36) at 60°C. An example calculating the palm oil solubility in supercritical CO_2 is given in Appendix 2.

Distribution coefficients of palm oil components. The composition of palm oil components in the liquid and supercriti-
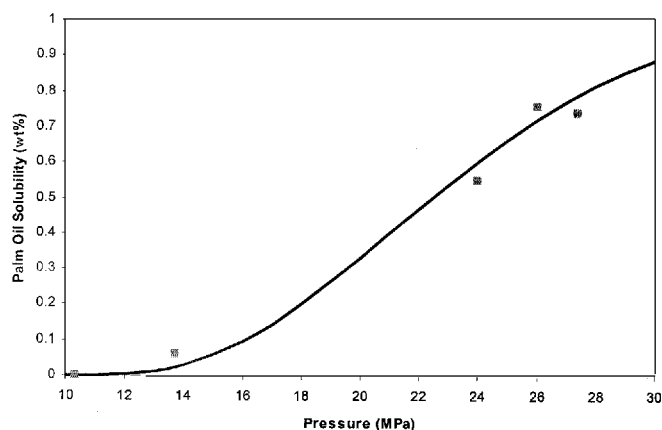
FIG. 2. Effect of pressure on the solubility of palm oil in supercritical CO_2 at 50°C (solvent-to-feed ratio of 40 ± 5). Experimental palm oil solubility (36) (■ under continuous processing); calculated palm oil equilibrium solubility (—— this work).

cal fluid phase can be described by using the distribution coefficient K_i:

$$K_i = y_i / x_i \qquad [15]$$

K_i was calculated on a solvent-free basis since CO_2 is completely removed after the extraction process. An example calculating the distribution coefficients of palm oil components is given in Appendix 3.

Figures 3 and 4 provide the distribution coefficients of palm oil components predicted using the RKA model and those reported in the work of Gast *et al.* (42) at 343 K, respectively. Note that FFA and α-tocopherol are enriched in the fluid phase, whereas TG and β-carotene are enriched in the liquid phase. With respect to the distribution coefficient of α-tocopherol, a discrepancy existed between the experimental value and the value predicted based on the RKA-EOS. Contrary to our predicted value, Gast *et al.* (42) reported that the FA in a palm oil mixture are more soluble than tocopherol in supercritical CO_2. However, Škerget *et al.* (43) and Stoldt and Brunner (33) observed that α-tocopherol has a smaller distribution coefficient than FFA in either milk thistle seed oil–

TABLE 7
Comparison of Predicted Phase Equilibrium for a Palm Oil–Supercritical CO_2 System with Literature Data[a]

Temperature (°C)	Pressure (bar)	CO_2 in liquid (wt%)			CO_2 in vapor (wt%)		
		This work	Experimental data	Deviation* (%)	This work	Experimental data	Deviation** (%)
50	208.1	31.04	38.6[a]	21.71	99.19	98.61[a]	0.66
60	208.2	25.93	36.3[a]	26.70	99.54	99.24[a]	0.32
80	208.0	19.86	33.1[a]	36.40	99.80	99.75[a]	0.06
70	200.0	21.79	23.66[b]	2.87	99.77	99.72[b]	0.05
70	300.0	28.95	27.64[b]	7.20	98.99	98.91[b]	0.14
70	350.0	30.33	29.73[b]	4.57	98.84	98.16[b]	0.73
75	202.0	20.52	25.3[c]	13.95	99.80	99.79[c]	0.02
75	308.0	28.03	31.7[c]	8.52	99.03	98.83[c]	0.24

[a]Experimental data by [a]Kalra *et al.* (32); [b]Stoldt and Brunner (33); and [c]Brunner (34). *Deviation = $|(y^{exp} - y^{calc})|/y^{exp} \times 100\%$ (for vapor phase). **Deviation = $|(x^{exp} - x^{calc})|/x^{exp} \times 100\%$ (for liquid phase).
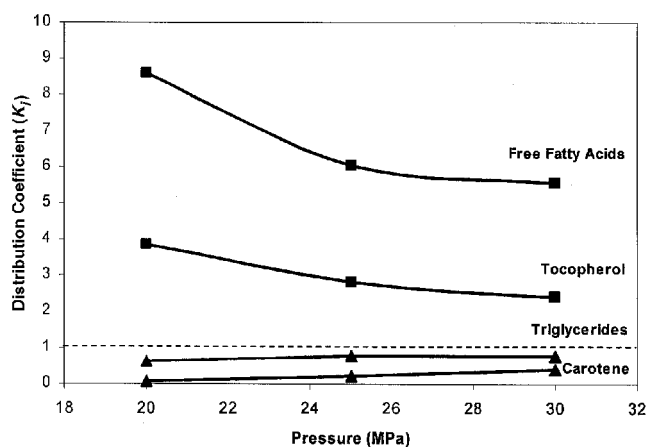
FIG. 3. Predicted distribution coefficients for palm oil components (CO$_2$-free basis) at 343 K.

supercritical CO$_2$ system or a palm deodorizer condensates–supercritical CO$_2$ system, respectively. These results are consistent with our findings.

The distribution coefficients for the FFA and TG provide information on the removal of FFA from the palm oil mixture. Figure 5 shows that as pressure increases, the K-value of FFA decreases. The opposite trend was observed with regard to the K-value of palm oil TG (Fig. 6). Note that a K-value of FFA that is greater than 1.0 means that FFA are enriched in the extract phase (supercritical CO$_2$-rich phase). A distribution coefficient for TG of less than 1.0 indicates that TG are enriched in the raffinate phase. A higher K-value for FFA compared to that for TG indicates that FFA have a higher solubility in supercritical CO$_2$.

Separation factor between palm oil components. The separation factor, α_{ij}, is defined as the ratio of distribution coefficients between two components (i, j):

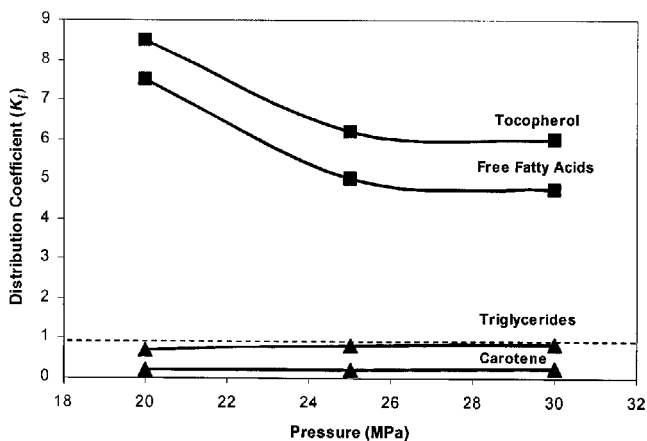$$\alpha_{ij} = \frac{y_i x_j}{x_i y_j} = \frac{K_i}{K_j} \qquad [16]$$

FIG. 4. Experimental distribution coefficients (42) or palm oil components (CO$_2$-free basis) at 343 K.
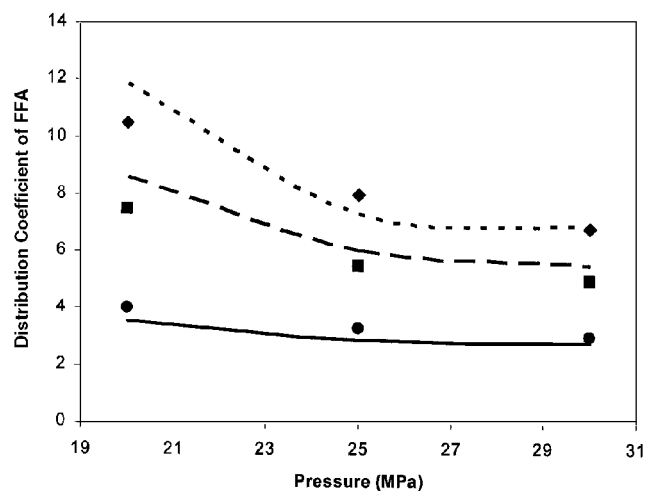

FIG. 5. Distribution coefficients of FFA (CO$_2$-free basis). Experimental data by Gast *et al.* (42): (◆) 370 K; (■) 340 K; (●) 310 K. Predicted results (this work): (- - -) 370 K; (– – –) 340 K; (—) 310 K.

An example calculating the separation factor according to Equation 16 is provided in Appendix 3.

The separation factor between FFA and TG indicates the thermodynamic feasibility of the separation of FFA from palm oil. The separation factors between FFA and palm oil TG in crude palm oil were available in the literature. Figure 7 compares the separation factor obtained from the experimental data (42) and those calculated at various temperatures using Equation 16. The results show that the separation factors predicted by the RKA model are in good agreement with the experimental data. The average deviation was 15.81% over a wide range of temperatures (313–373 K) and pressures (20–30 MPa). This confirms that the model is a reliable alternative for predicting the distribution of palm oil components in supercritical CO$_2$ at various extraction conditions.

In conclusion, the phase equilibrium behavior of CPO with supercritical CO$_2$ was successfully modeled in an Aspen Plus
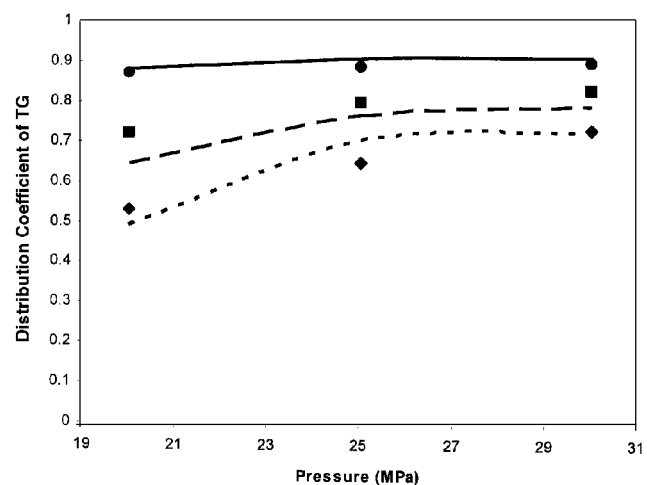

FIG. 6. Distribution coefficients of TG (CO$_2$-free basis). Experimental data by Gast *et al.* (42): (◆) 370 K; (■) 340 K; (●) 310 K. Predicted results (this work): (- - -) 370 K; (– – –) 340 K; (—) 310 K.
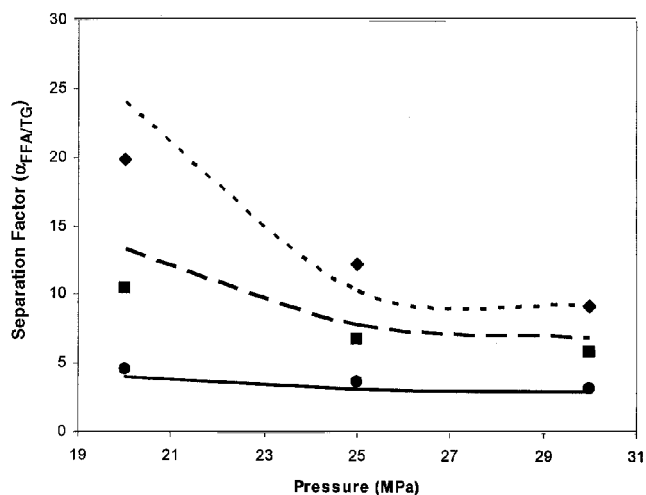
FIG. 7. Separation factor between FFA and palm oil TG in a crude palm oil–supercritical CO_2 system. Experimental data by Gast *et al.* (42): (◆) 370 K; (■) 340 K; (●) 310 K. Predicted results (this work): (⋯) 370 K; (– – –) 340 K; (—) 310 K.

10.2.1 commercial simulator by using the RKA-EOS thermodynamic model. The key steps in modeling involved the characterization of palm oil mixture, the estimation of pure component vapor pressures and critical properties, and the regression of experimental phase equilibrium data for the palm oil component–supercritical CO_2 binary system available in the literature to yield the binary interaction parameters for the RKA-EOS. The ultimate aim of modeling was to generate solubility data and distribution coefficients for palm oil components in supercritical CO_2, which are crucial for process design and optimization of a separation system utilizing the SFE technique. The suitability of the RKA model to represent the phase equilibrium data for a palm oil–supercritical CO_2 system was demonstrated well through a good agreement between the experimental and simulated data. Specifically, the RKA-EOS was able to adequately predict the mutual solubility of the palm oil–supercritical CO_2 system in the temperature range of 313–373 K and at high pressures of between 20 and 30 MPa, which are within suitable operating conditions for the SFE process. The use of thermodynamic models and regression algorithms implemented in a commercial software package such as Aspen Plus that is readily available in the market would expedite design calculations for process development. Thus, the simulation model provides an efficient and cost-effective alternative for the preliminary design and optimization of the SFE process involving a complex CPO–supercritical CO_2 system.

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APPENDIXES

Appendix 1

The composition of palm oil reported by Tan and Oh (17) is given in Table A1. The major FA of palm oil TG are palmitic acid and oleic acid, with compositions of 43.5 and 39.8 wt%, respectively. Normalized, the compositions of both FA are as follows:

$$\text{Composition of tripalmitin} = \frac{x_{16:0}}{\sum x_{16:0} + x_{18:1}} \quad \text{[A1]}$$
$$= 43.5/(43.5 + 39.8)$$
$$= 52.22 \text{ wt\%}$$

$$\text{Composition of triolein} = \frac{x_{18:1}}{\sum (x_{16:0} + x_{18:1})} \quad \text{[A2]}$$
$$= 39.8/(43.5 + 39.8)$$
$$= 47.78 \text{ wt\%}$$

TABLE A1
Composition of Palm Oil[a]

FA	Composition (wt%)	Range observed	SD
12:0 (lauric acid)	0.3	0–1.0	0.12
14:0 (myristic acid)	1.1	0.9–1.5	0.08
16:0 (palmitic acid)	43.5	39.2–45.8	0.95
16:1 (palmitoleic acid)	0.2	0–0.4	0.05
18:0 (stearic acid)	4.3	3.7–5.1	0.18
18:1 (oleic acid)	39.8	37.4–44.1	0.94
18:2 (linoleic acid)	10.2	8.7–12.5	0.56
18:3 (linolenic acid)	0.3	0–0.6	0.07
20:0 (arachidic acid)	0.2	0–0.4	0.16

[a]From Reference 17.

Appendix 2

Extraction stage efficiency = 55%

Solvent-to-feed (S/F) ratio used in the study of Ooi *et al.* (36) = 40

Crude palm oil feed rate = 60 g/s

Supercritical CO₂ required
(under continuous operation) $= 0.5 \times 40 \times 0.6$

$= 1.2 \text{ g/s}$

Flash calculation results conducted at the above conditions (24 MPa, 50°C) are given in Figure 1A.

Palm oil solubilized in supercritical CO_2

$$= \left[(1.312415) - (1.297979)\right] \text{ kg/s} \qquad [A3]$$

$$= 14.4363 \text{ g/s}$$

Palm oil solubility (under continuous operation)

$$= \frac{14.4363 \text{ g oil/s}}{(40 \times 60) \text{ g } CO_2/\text{s}} \qquad [A4]$$

$$= 0.6015\%$$

Appendix 3

The simulated liquid phase and supercritical fluid phase compositions were used as the basis for calculating the distribution coefficient and separation factor. Figure A2 shows the data generated from a flash calculation (at 30 MPa and 343 K) using the Aspen Plus 10.2.1 process simulator. Transformation of the multicomponent data to a CO_2-free basis is given in Table A2.

Distribution coefficients of palm oil components were calculated by Equation 15 (see text):

$$K_{FFA} = 0.2436/0.0438$$
$$= 5.5646$$
$$K_{TG} = (0.4934 + 0.2605)/(0.4651 + 0.4896)$$
$$= 0.7897 \qquad [A5]$$
$$K_{tocopherol} = 0.0024/0.0010$$
$$= 2.3960$$
$$K_{carotene} = 0.0001/0.0005$$
$$= 0.2227$$

Separation factors between palm oil components were calculated according to Equation 16 (see text):

$$\alpha_{FFA/TG} = K_{FFA}/K_{TG}$$
$$= 5.5646/0.7897 \qquad [A6]$$
$$= 7.04$$

FIG. A1. Flash calculation results at 24 MPa and 50°C.

FIG. A2. Flash calculation of the simulated liquid phase and supercritical fluid phase compositions at 30 MPa and 343 K using the Aspen Plus 10.2.1 process simulation.

TABLE A2
Multicomponent Data Transformed to a CO_2-Free Basis

	Fluid phase		Liquid phase	
	(kg/s)	(wt%)	(kg/s)	(wt%)
Tripalmitin	0.1816	0.4934	27.7357	0.4651
Triolein	0.0959	0.2605	29.1944	0.4896
Tocopherol	0.0009	0.0024	0.0591	0.0010
Carotene	4.45×10^{-5}	0.0001	0.0324	0.0005
FFA	0.0897	0.2436	2.6103	0.0438
Total (CO_2-free)	0.3681	1.0000	59.6319	1.0000