Simulation Modelling of the Phase Behaviour of Palm Oil with Supercritical Carbon Dioxide

Lim Chee Siang[1]   **Zainuddin Abdul Manan[2]**   **Mohd Roji Sarmidi[3]**

Faculty of Chemical and Natural Resources Engineering
Universiti Teknologi Malaysia, Skudai 81310 Johor, Malaysia.
[1] *E-mail: limcsg@hotmail.com*
[2] *E-mail: dr.zain@utm.my*

[3] *Chemical Engineering Pilot Plant (CEPP)*
Universiti Teknologi Malaysia, Skudai 81310 Johor, Malaysia.
Tel: +607-5532502, Fax: +607-5569706, E-mail: roji@cepp.utm.my

Abstract

The phase behaviour of crude palm oil (CPO) with supercritical CO_2 was successfully modelled using the Redlich-Kwong-Aspen (RKA) thermodynamic model implemented in Aspen Plus® 10.2.1 commercial simulator. The procedure for modelling involves the estimation of pure component vapour pressure and critical properties, and the regression of phase equilibrium behaviour. The interaction parameters for the RKA model were obtained from the regression of experimental phase equilibrium data for palm oil component-supercritical CO_2 binary system available in the literature. Using the temperature-dependent interaction parameters for each binary system, the RKA equation-of-state gives good correlations of the appropriate phase behaviour over wide ranges of conditions. The predicted palm oil components' distribution coefficients and solubilities showed good agreement with the experimental data reported in the literature. The simulated model provides an efficient and cost-effective alternative for the preliminary design and optimization of the SFE process for complex CPO-supercritical CO_2 system.

Keywords:

Palm oil, Phase equilibrium, Supercritical carbon dioxide, Thermodynamic modelling

Introduction

Palm oil contains various components such as monoglycerides, diglycerides, triglycerides, free fatty acids (FFA), phospholipids, pigmented compounds, as well as several nutritionally bioactive compounds [1]. Minor components such as β-carotene and tocopherol are often degraded or lost during the bleaching and refining processes that require high operating temperatures (> 240 °C).

Selective supercritical CO_2 extraction of these high-value but thermally unstable components present in CPO has enabled operation at mild temperatures of less than 100 °C.

In addition, it can be easily separated and recovered, thereby leading to a pollution-free operation. All these advantages combine to make the extraction of components in palm oil a desirable alternative to conventional processing methods such as chemical and physical refining.

A reliable phase equilibrium model is required in the analysis of SFE process involving palm oil-supercritical CO_2 system since the system comprises of a highly dissimilar mixture of high molecular weight triglycerides and low molecular weight supercritical CO_2. In addition, such model must be applicable over a wide range of temperatures and pressures in order to yield some accurate quantitative values of the mutual solubilities, compositions of coexisting phases and distribution coefficients which are of fundamental importance in the design of countercurrent SFE process. Thermodynamic models can provide a general representation of the phase behaviour of a system, thus making it possible to reduce experimental works. The equation of state has been shown to adequately represent the phase behaviour of lipid-related components with supercritical CO_2 [2-5]. It is anticipated that the equation of state can also model the phase equilibrium of palm oil components-supercritical CO_2. The steps involved in modelling the phase equilibrium of palm oil components with supercritical CO_2 are presented in the next section.

Phase Equilibrium Modelling

The first step in modelling the phase equilibrium of multicomponent palm oil-supercritical CO_2 system is to establish the composition of the multicomponent palm oil system. This is followed by the prediction of palm oil components' solubilities and distribution coefficients using the Redlich-Kwong-Aspen (RKA) equation of state. The RKA model can be applied to SFE process since it is particularly suitable for modelling a mixture of polar components with light gases (such as CO_2) at medium to high pressures [6]. Prior to using the RKA equation of state 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.

Redlich-Kwong-Aspen Equation of State

The Redlich-Kwong-Aspen [6] cubic equation of state (RKA- EOS) is an extension of the Redlich-Kwong-Soave [7] equation of state. RKA-EOS was used in this work for modelling the phase equilibria of CPO-supercritical CO_2 system by regression using the Data Regression System module available in Aspen Plus® to correlate the experimental phase equilibrium data:

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

where a and b are cross energy and co-volume parameters for a mixture.

Calculations of Pure Component Parameters for RKA-EOS

For a pure component i, the parameters a_i and b_i for RKA-EOS are functions of the pure component's critical temperature (T_{ci}) and critical pressure (P_{ci})

$$a_i = \alpha_i 0.42747 \frac{R^2 T_{ci}^2}{P_{ci}} \quad (2)$$

$$b_i = 0.08664 \frac{RT_{ci}}{P_{ci}} \quad (3)$$

To improve the vapour pressure prediction for highly non-linear dependence of vapour pressure on temperature, Mathias [8] recommends the generalized temperature-dependent function, α_i, for the subcritical component (referring to palm oil component in this study) that considerably improve vapour pressure predictions:

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

where

T_{ri} = reduced temperature

η_i = pure component polar factor

The polar factor, η_i which takes into account the polarity, is normally fitted from the pure component vapour pressure data. The constant for pure component i (m_i), calculated as a function of acentric factor (ω_i), as follow:

$$m_i = 0.480 + 1.574\omega_i - 0.176\omega_i^2 \quad (5)$$

The RKA-EOS utilizes the classical quadratic mixing rule 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:

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

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

For the prediction of phase equilibrium of palm oil-supercritical CO_2, binary interaction parameters are required. The interaction parameters are considered as temperature-dependent in order to improve the predictive capability of the equation of state, [3, 9-11]. The RKA-EOS assumes linear temperature dependency of the interaction parameters as follows:

$$k_{a,ij} = k_{a,ij}^0 + k_{a,ij}^1 \frac{T}{1000} \quad (8)$$

$$k_{b,ij} = k_{b,ij}^0 + k_{b,ij}^1 \frac{T}{1000} \quad (9)$$

Palm Oil System Characterization

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 [12] propose a model which assumes the solutes extracted from pressed palm oil fibres as a mixture consisting of three key components namely oleic acid (as free fatty acids), triolein (as triglycerides) and β-carotene. Ohgaki et al. [13] use palmitic acid to represent the free fatty acids, tripalmitin to represent triglycerides and α-tocopherol to represent vitamin E in palm oil mixture.

In this study, crude palm oil was considered as a mixture containing principally triglycerides (tripalmitin and triolein) with some free fatty acids (oleic acid) and minor components (β-carotene, α-tocopherol) according to the composition of crude palm oil [14,15].

The triglycerides in palm oil exist mainly in the form of di-saturated dipalmitoyl-oleoyl-glycerol (POP and PPO) and mono-saturated palmitoyl-dioleoyl-glycerol (POO) as shown in Table 1. The mean molecular weight (MW) and the variance (σ^2) were calculated based on the assumption that the distribution of fatty acids among the triglycerides and the presence of unsaturation in fatty acids were negligible.

Table 1 – Composition of triglycerides in typical Malaysian palm oil [16]

Carbon No.	Mol. Wt.	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
MW = 848.9 kg kmol^{-1}; σ^2 = 592.78		

Due to a relatively wide distribution of the triglycerides in palm oil, it is therefore insufficient to represent the complex mixture of palm oil triglycerides as a single component. Saturated and unsaturated palm oil triglycerides were represented by simple triglycerides, namely tripalmitin and

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triolein. The composition of the assumed triglyceride components was based on the typical fatty acid composition in crude palm oil [16]. The calculation of the composition of palm oil triglycerides is included in Appendix. In this study, the palm oil triglycerides were approximated as a mixture of 47.78 wt % tripalmitin and 52.22 wt % triolein.

Study on the changes in lipid class and composition in oil palm mesocarp by Oo et al. [17] suggest that free fatty acids consisted of oleic acid (45.2 wt %), palmitic acid (35.4 wt %) and linoleic acid (17.2 wt %). Oleic acid was selected as the key component to represent the free fatty acids in palm oil.

Development of Aspen Plus® Physical Property Database for Palm Oil Component

Physical property data for the components involved in the thermodynamic modelling of CPO-supercritical CO_2 system were not available in the Aspen Plus® property database even though some physical property data for the individual component in palm oil mixture are available in open literature. However, many of the physical properties for palm oil components cannot be determined experimentally due to thermal decomposition of the components at temperatures below the components' boiling points. It is therefore necessary to theoretically estimate the critical properties of these components. 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.

Critical Properties Estimation

The method proposed by Dohrn and Brunner [22] was used as it required only the liquid molar volume at 20 °C, V_{L20}, and vapour pressure data as the input information to obtain the critical properties of palm oil components. Table 2 summarizes the predicted critical properties of the palm oil components used in this study.

Table 2 – Predicted physical properties of pure components in palm oil

Comp.	T_B (K)	T_c (K)	P_c (kPa)	ω	V_{L20} (m³/kmol)
Tripalmitin	864.2[a]	947.1[a]	397[a]	1.650[b]	0.8906[c]
Triolein	879.9[a]	954.1[a]	360[a]	1.800[b]	0.9717[c]
Oleic acid	646.5[a]	813.6[a]	1250[a]	0.810[b]	0.3172[c]
Tocopherol	794.5[a]	936.9[a]	838[a]	1.195[b]	0.4533[c]
β-carotene	908.6[a]	1031[a]	678[a]	1.625[b]	0.5348[c]

[a] Estimated by the method of Dohrn and Brunner [20]

[b] Estimated using the Pitzer's method [6]

[c] Liquid molar volume data (at 20 °C): (tripalmitin, triolein, oleic acid) [18]; α-tocopherol [20]; β-carotene [21]

Binary Interaction Parameters

For the calculation of binary interaction parameters for RKA-EOS, the Deming algorithm was applied to perform maximum likelihood (errors-in-variables) estimation to minimize the following objective function:

$$Q = \sum_k \left(\frac{P^m - P^c}{\sigma_P} \right)^2 + \sum_k \left(\frac{x_i^m - x_i^c}{\sigma_{x_i}} \right)^2 + \sum_k \left(\frac{y_i^m - y_i^c}{\sigma_{y_i}} \right)^2 \quad (10)$$

where

P	= pressure of the studied phase equilibrium data
x, y	= composition in liquid and fluid phase
σ	= standard deviation
c, m	= calculated and experimental values
k	= component k

The average absolute deviation (AAD) between the measured and calculated data was used to assess the quality of the regressed data:

$$AAD\,(\%) = \frac{1}{N} \sum_{i=1}^{N} |d_i| \times 100\% \quad (11)$$

where

d_i	= error between experimental and calculated data
N	= 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 3.

Table 3 – Literature phase equilibrium data for binary systems of pure component-supercritical CO_2

Palm Oil Component + CO_2	Temp (K)	Pressure (MPa)	References
Tripalmitin	333, 353	15 – 50	Weber et al. [2,22]
Triolein	333, 353	20 – 50	Weber et al. [2,22]
Oleic acid	313, 333, 353	15 – 30	Bharath [23]
Tocopherol	313-333 343	9 – 26 20 – 30	Pereira et al. [9] Meier et al. [11]
β-carotene	313-333 353	20 – 28 20 – 32	Sovová et al. [24] Johannsen and Brunner [25]

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 were assumed to be zero due to fact that the experimental data for the triglyceride-fatty acid for palm oil was not available, and 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 on the prediction of the phase equilibrium of complex oil mixture based only on supercritical solvent-solute interactions while neglecting the solute-solute interactions. Some examples include the phase equilibrium prediction of CO_2 - soybean oil deodorizer condensates system by Araújo *et al.* [5], CO_2 - orange oil system by Meireles *et al.* [26], and CO_2 - essential oil system by Sovová *et al.* [27].

Results and Discussions

Interaction Parameters for Palm Oil Component-Supercritical CO_2 Binary System

The predicted liquid phase and supercritical fluid phase composition for palm oil components-supercritical CO_2 system were compared to the literature data as shown in Table 4. 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.

Table 4 – Optimum parameters for RKA model for binary system of palm oil component (1) - supercritical CO_2 (2)

|	T (K)	η_I	$k_{a,12}$	$k_{b,12}$	AAD_x (%)	AAD_y (%)
TP	333	-2.401	0.039	-0.018	1.470	0.063
	353	-1.955	0.052	-0.031	0.972	0.083
TO	333	-3.606	0.028	-0.015	1.566	0.355
	353	-3.235	0.039	-0.006	2.956	0.193
OA	313	-1.177	0.070	-0.007	0.489	0.118
	333	-1.087	0.081	0.003	0.941	0.430
	353	-1.131	0.087	0.013	0.299	0.081
TCP	313	-0.946	0.051	-0.030	0.531	0.053
	323	-0.589	0.062	-0.019	1.038	0.253
	333	-0.441	0.066	-0.023	1.516	0.082
	343	-0.301	0.074	-0.015	0.536	0.140
	353	0.028	0.090	0.015	0.848	0.053
CRT	313	-1.443	0.069	-0.063	-	9.207
	323	-1.232	0.069	-0.077	-	5.367
	333	-1.021	0.071	-0.090	-	19.63
	353	-0.545	0.066	-0.127	-	31.05

Ternary System

The ternary phase equilibrium for CO_2-triglyceride-fatty acid system at 333 K and 20–30 MPa were predicted using the pure component parameters and the binary interaction parameters for RKA model. **Figure 1** provides a comparison between the ternary data for CO_2-triolein-oleic acid system reported by Bharath [23] 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. The results also suggested that the assumption of negligible triglyceride-fatty acid solute-solute interaction as acceptable.

Figure 1 – Phase equilibrium for the pseudo-ternary supercritical CO_2 - fatty acid - triglyceride system at 333 K
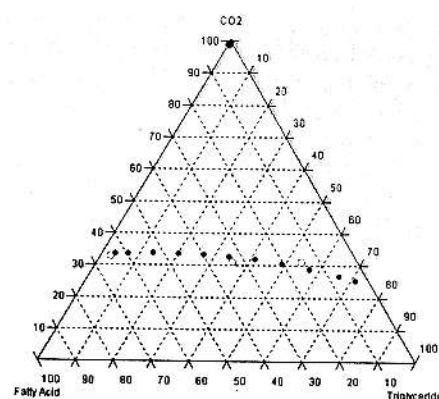
(i) At 20 MPa
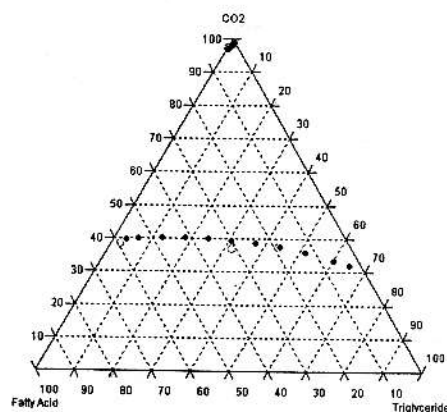
(ii) At 30 MPa

o Experimental data [23]; • Predicted data

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 employing linear function to correlate the polar factor and binary interaction parameters obtained in Table 4 for use at the temperature range of interest. The resulting temperature-dependent polar factor and binary interaction parameters are shown in Table 5.

Table 5 – Temperature dependence of polar factor and binary interaction parameters for palm oil component-supercritical CO_2 system

	Polar factor, η	Binary Interaction Parameters
TP	$0.0225T - 9.8778$	$k_a = 0.0007T - 0.1942$ $k_b = -0.0006T + 0.1952$
TO	$0.0185T - 9.7834$	$k_a = 0.0005T - 0.1428$ $k_b = 0.0004T - 0.1635$
OA	$0.00004T - 1.1515$	$k_a = 0.0004T - 0.0391$ $k_b = 0.0005T - 0.1655$
TCP	$0.0224T - 7.9068$	$k_a = 0.0009T - 0.2286$ $k_b = 0.0009T - 0.3305$
CRT	$0.0225T - 8.4999$	$k_a = 0.0001T + 0.0920$ $k_b = -0.0016T + 0.4417$

Phase Equilibrium Calculation for Palm Oil-Supercritical CO_2 System

The phase equilibrium calculations were carried out using *P-T* isothermal flash algorithm implemented in Aspen Plus®. **Table 6** provides a comparison between phase equilibrium of palm oil-supercritical CO_2 system reported in the literature [29-31] to that predicted by the RKA model in this work. The phase equilibrium of palm oil-supercritical CO_2 predicted using RKA-EOS agrees well with the experimental data of Stoldt and Brunner [29], and Brunner [31]. 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.

Temp (°C)	Press (MPa)	CO₂ in Liquid (wt %)		CO₂ in Vapor (wt %)	
		This work	Exp. Data	This work	Exp. Data
50	208.1	31.04	38.6 [a]	99.19	98.61 [a]
60	208.2	25.93	36.3 [a]	99.54	99.24 [a]
80	208.0	19.86	33.1 [a]	99.80	99.75 [a]
70	200.0	21.79	23.66 [b]	99.77	99.72 [b]
70	300.0	28.95	27.64 [b]	98.99	98.91 [b]
70	350.0	30.33	29.73 [b]	98.84	98.16 [b]
75	202.0	20.52	25.3 [c]	99.80	99.79 [c]
75	308.0	28.03	31.7 [c]	99.03	98.83 [c]

Experimental data by: [a] Kalra *et al.* [30]; [b] Stoldt and Brunner [29]; [c] Brunner [31].

Palm Oil Components' Distribution Coefficient

The composition of palm oil components in the liquid and supercritical fluid phase can be described using the distribution coefficient, K_i:

$$K_i = y_i / x_i \qquad (12)$$

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

Figure 2 and 3 provide the distribution coefficients for palm oil components predicted using the RKA model and those reported in the work of Gast *et al.* [32] at 343 K, respectively. Note that, the free fatty acids and α-tocopherol are enriched in the fluid phase whereas triglycerides and β-carotene are enriched in the liquid phase.

Figure 2 – Predicted distribution coefficients for palm oil component (on CO_2 free basis) at 343 K
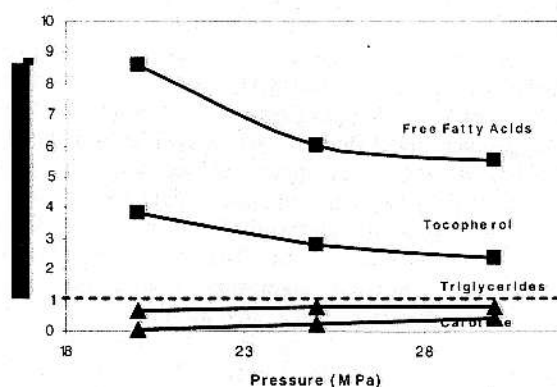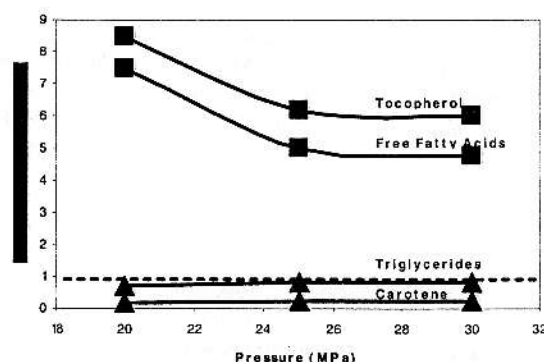

Figure 3 – Experimental distribution coefficients [32] for palm oil components (on CO_2 free basis) at 343 K

With respect to the distribution coefficient of α-tocopherol, discrepancy exists between the experimental value and the value predicted based on RKA-EOS. Contrary to our predicted value, Gast *et al.* [32] reported that the fatty acids in palm oil mixture are more soluble than tocopherol in supercritical CO_2. Škerget *et al.* [33] and Stoldt and Brunner [29] however observe that α-tocopherol has smaller distribution coefficient than FFA in Milk Thistle seed oil-supercritical CO_2 system and in palm deodorizer condensates-supercritical CO_2 system respectively. These results are consistent with our findings.

Conclusion

The phase equilibrium behaviour of crude palm oil with supercritical CO_2 was successfully modelled in Aspen Plus® 10.2.1 commercial simulator using the Redlich-Kwong-Aspen equation of state (RKA-EOS) thermodynamic model. The key steps in modelling involve the characterization of palm oil mixture, the estimation of pure component vapour pressures and critical properties and the regression of experimental phase equilibrium data for 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 modelling is to generate solubility data and distribution coefficients for palm oil components in supercritical CO_2 which are crucial for process design and optimization of separation system utilizing supercritical fluid extraction (SFE) technique. The suitability of the RKA model to represent the phase equilibrium data for palm oil-supercritical CO_2 system is well-demonstrated through the good agreement between the experimental and simulated data. 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 complex CPO-supercritical CO_2 system.

Acknowledgments

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Appendix

Calculation of palm oil triglycerides' composition:

Palm oil composition reported by Tan and Oh [16] is given as follows:

Fatty acid	Composition (wt %)
C12:0 (Lauric acid)	0.3
C14:0 (Myristic acid)	1.1
C16:0 (Palmitic acid)	43.5
C16:1 (Palmitoleic acid)	0.2
C18:0 (Stearic acid)	4.3
C18:1 (Oleic acid)	39.8
C18:2 (Linoleic acid)	10.2
C18:3 (Linolenic acid)	0.3
C20:0 (Arachidic acid)	0.2

The major fatty acids of palm oil triglycerides are palmitic acid and oleic acid with composition of 43.5 wt % and 39.8 wt % respectively.

Normalized the composition of both fatty acids:

$$\text{Composition of tripalmitin} = \frac{x_{C16:0}}{\Sigma\left(x_{C16:0} + x_{C18:1}\right)}$$

$$= 43.5 \ / \ (43.5 + 39.8)$$

$$= 52.22 \ \text{wt\%}$$

$$\text{Composition of triolein} = \frac{x_{C18:1}}{\Sigma\left(x_{C16:0} + x_{C18:1}\right)}$$

$$= 39.8 \ / \ (43.5 + 39.8)$$

$$= 47.78 \ \text{wt\%}$$

Calculation of palm oil components' distribution coefficient:

The simulated liquid phase and supercritical fluid phase compositions are the basis for the calculation of distribution coefficient and separation factor. The following table shows the data generated from a flash calculation (at 30 MPa and 343 K) using Aspen Plus® 10.2.1 process simulator:

Display: | Format: | Stream Table

Mass Flow kg/sec			TOP	BOTTOM
TRIPALM	27.91731	0.0	.1816115	27.73569
TRIOLEIN	29.29029	0.0	.0959064	29.19438
TOCOPHRL	.0600000	0.0	8.74502E-4	.0591254
CAROTENE	.0324000	0.0	4.44736E-5	.0323555
OLEIC-A	2.700000	0.0	.0896632	2.610336
CO2	0.0	60.00000	35.30042	24.69958
Total Flow kmol/sec	.0774187	1.363333	.8027563	.6379951
Total Flow kg/sec	60.00000	60.00000	35.66852	84.33148

Transformation of multicomponent data to a CO_2-free basis:

	Fluid phase		Liquid phase	
	(kg/sec)	(Wt %)	(kg/sec)	(Wt %)
TP	0.1816	0.4934	27.7357	0.4651
TO	0.0959	0.2605	29.1944	0.4896
TCP	0.0009	0.0024	0.0591	0.0010
CRT	4.5×10^{-5}	0.0001	0.0324	0.0005
OA	0.0897	0.2436	2.6103	0.0438
Total (CO_2 free)	0.3681	1.0000	59.6319	1.0000

Distribution coefficients of palm oil components are calculated by equation (12):

$K_{free\ fatty\ acids}$ = 0.2436 / 0.0438
= 5.5646

$K_{triglycerides}$ = (0.4934+0.2605) / (0.4651+0.4896)
= 0.7897

$K_{tocopherol}$ = 0.0024 / 0.0010
= 2.3960

$K_{carotene}$ = 0.0001 / 0.0005
= 0.2227