Phase Equilibrium Feasibility Studies of Free Fatty Acids Extraction from Palm Oil Using Supercritical Carbon Dioxide

Mario Kabbour[1*] M. Syarhabil Ahmad[1]
1. School of Bioprocess Engineering, University Malaysia Perlis 02600 Arau, Perlis, Malaysia.
* E-mail of the corresponding author: mariokabbour007@hotmail.com

Abstract
This work investigates the modeling of saturated fatty acids from palm oil using co-solvent modified supercritical carbon dioxide (SC-CO_2). The objective of this work is the assessment of the feasibility studies of phase equilibrium mutual solubility process utilizing supercritical carbon dioxide. The knowledge of the phase equilibrium is one of the most important factors to study the design of extraction processes controlled by the equilibrium. The applied pressure was ranging from 60 to 180 bars and the extraction temperatures were 313.15 and 353.15 K. A thermodynamic model based on the Universal Functional Activity Coefficient (UNIFAC) used to predict the activity coefficients' expression for the system carbon dioxide / fatty acid. The parameters such as adsorption, diffusion, mass transfer coefficient, solubility, and desorption were determined using mass transfer modeling.

Keywords: *Supercritical Carbon Dioxide; Free Fatty Acids; UNIFAC; Activity Coefficient; Mass Transfer Modeling.*

1. Introduction

As Malaysia is the second largest palm oil producer around the world [1], the Malaysian palm-based industry has been advancing rapidly and is producing an increasing number of products like fatty acid methyl esters, fatty alcohols and glycerin [2]. Palm oil contains of two categories of minor components. The first one is made up of derivatives of fatty acid, mono-glycerides, di-glycerides, tri-glycerides, phosphatides, esters, and sterols. The second is non-fatty acid compounds, particularly hydrocarbons, and these include aliphatic alcohols, tocopherols, free sterols and pigments. Palm oil is high in saturated fatty acids. It contains 45% palmitic acid and 5% stearic acid [3]. Three techniques are being used in Malaysia for the extraction process: screw press, solvent extraction, and pre-pressing followed by solvent extraction. Supercritical fluid extraction has become an important extraction technique in many fields, with the supercritical extraction technique; it is possible to extract sensitive compounds such as fatty acids and avoiding the residual toxic solvent as hexane [4]. The most commonly solvent used in supercritical fluid is carbon dioxide; carbon dioxide has the additional advantage of being cost-effective, non-toxic, non-flammable, easily removed from the extract following decompression and due to its low critical temperature (31.1^{o}C), it may be ideal technique to study the thermally labile compounds [14,15]. Supercritical carbon dioxide is a good solvent for non-polar compounds extraction such as hydrocarbons [16]. Usually, addition of a small amount of a liquid co-solvent (modifier) can enhance significantly the extraction efficiency and, consequently, reduce the extraction time [17].

Phase equilibria mutual solubility for carbon dioxide solvent with fatty acids systems at high pressure and temperature are very important in many chemical processes. Liquid phase solubility is available technique but had limited use due to concern over a residual solvent present in the process system. The uses of the equation of state are not accurate enough and therefore, would be for the prediction of solubility related to vapor phase only. Thus, the estimation of some of the parameters required for the prediction would be difficult if the solute was a complex substance about which little was known apart from its structural formula. An alternative procedure for the prediction mutual solubility data is to apply activity coefficient expression of the regular solution theory based on the type to each phase. The UNIFAC model based on thermodynamic is a good agreement for the prediction phase equilibria solubility, though interaction parameters involved between the groups for calculation phase activity coefficient (γ) as well as other values for Gibbs's function (Q), its gradient (dQ) and (d^2Q) at required pressure and temperature.

2. Materials and Methods

2.1Plant materials

The palm fruits were supplied by the region of Kuala Ketil, Malaysia (Norstar Palm Oil Mill Sdn Bhd). After drying in oven at low temperature, the palm fruits samples were crushed in a mechanical blender and sieved to obtain a 500µm particle size. Then, the samples were stored in an air tight sealed container at ambient conditions.

2.2Supercritical fluid extraction

One hundred grams of the sample were loaded into the basket and were placed into the laboratory-scale supercritical fluid extraction system using carbon dioxide (99.95%) as a solvent. The temperature was controlled by a thermostat (± 1°C) and pressure was controlled by a back-pressure regulator. At the desired pressure, the compressed carbon dioxide was continuously supplied through to the sample in the extraction vessel to extract at desired volumetric flow rate and temperature. The co-solvent was introduced to the supercritical carbon dioxide before the extraction vessel. Before the commencement of any of these experiment procedures, the vials were weighted and tagged for identification, and it is placed in a collection chamber to collect the extracted fatty acids sample. The collected sample vial is then weighted again to determine the total amount of the extract. This allows for calculation of mole fraction of the extract. The extracts were taken and kept in vials and stored in -10°C for analysis.

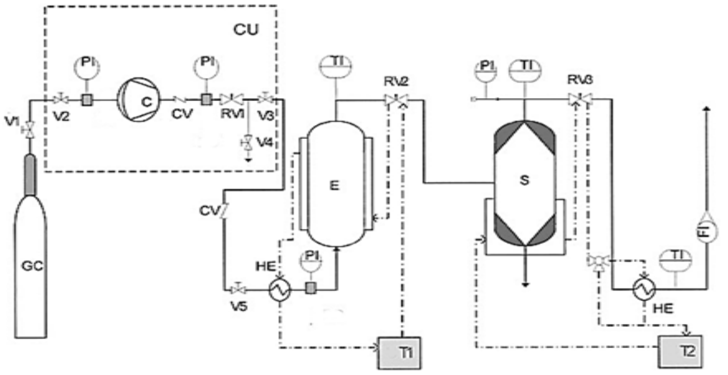

Fig.1. Supercritical carbon dioxide apparatus schematic diagram, carbon dioxide gas cylinder (GC) , compressor (C), pressure (PI), regulation valve (RV), compressor unit (CU), extractor (E), heat exchanger (HF), separator (S), thermostat (T), on-off valve (V), cut-off valve (CV), pressure indicator (PI), temperature indicator (TI), flow indicator (FI).

2.3Free Fatty Acid Analysis

The Free fatty acid (FFA) content was determined by Shimadzu Gas Chromatography AOC-20i. The free fatty acids were separated on (30m x 0.25) mm capillary column. The initial temperature was 160°C, programmed to 250°C at 5 min, which was maintained at 200°C up to 10 min. Spilt injection were carried out with the split ratio of 10:1. Helium was used as a carrier gas, flow rate of 1.0 ml/min, and the injector temperature set at 250°C.

3. Thermodynamic Model

3.1 The UNIFAC model

The UNIFAC and similar expression for activity coefficients, the activity coefficients may be regarded from the basic thermodynamic principles [5] as follows

$$G = H - T\,S \tag{1}$$

$$RT\ln yi = \left[\frac{d(nG^{Excess}_{mixing}}{dni}\right]_{T,P,n_j\neq 1}$$

$$= \left[\frac{d(nH^{Excess}_{mixing}}{dni}\right]_{T,P,n_j\neq 1}$$

$$= T\left[\frac{d(nS^{Excess}_{mixing}}{dni}\right]_{T,P,n_j\neq 1} \tag{2}$$

Where
n: The total number of moles in system.
n_i: The number of moles of component (i).
$n_j \neq 1$: The restraint that the number of moles of all components except (i) remain constant during the differentiation process.
G_m^E : The molar excess Gibbs function of mixing. i.e., the excess of the actual Gibbs function of mixing over that form ideal solution.
(H_m^E) and (S_m^E): is the molar excess enthalpy of mixing and molar excess entropy of mixing respectively.
Then:

$$\ln \gamma i = (\ln \gamma)^{Extract} + (\ln \gamma)^{Solute} \tag{3}$$

Using UNIFAC method [6] for predicating activity coefficient for the system as follows:

$$\ln \gamma_i^c = 1 - Ji + \ln Ji - 5.qi.\left(1 - \frac{Ji}{Li} + \ln\frac{Ji}{Li}\right) \tag{4}$$

$$\ln \gamma_i^R = qi.(1 - \ln Li) - \sum_k (\theta k.\frac{s_{ki}}{\eta_k} - Gki.\ln\frac{s_{ki}}{\eta_k}) \tag{5}$$

Since
Subscript (i) identifies species, and (j) is a dummy index running over all species. Supercritical carbon dioxide interaction parameters for UNIFAC model were calculated using the Chen's empirical correlation [13].
An alternative approach which was used in the UNIFAC model was to establish an analytical expression for a function (Q) and its derivative with respect to mole fraction given us:

$$Q_i = -[X_i * \ln(X_i * \gamma_i) + X_j \ln(X_j * \gamma_j)] = -\frac{G_m^{mixing}}{R*T} \tag{6}$$

$$\left(\frac{dQ_i}{dX_i}\right)^{Extract} = \left(\frac{dQ_i}{dX_i}\right)^{Solute} = \frac{Q^{Extract} - Q^{Solute}}{X_i^{Extract} - X_i^{solute}} \tag{7}$$

$$\frac{dQ_i}{dX_i} = -\ln\left(\frac{\gamma_i * X_i}{\gamma_j * X_j}\right) \tag{8}$$

$$\frac{d^2Q_i}{dX_i^2} = -\frac{d\ln\left[\frac{\gamma_i * X_i}{\gamma_j * X_j}\right]}{dX_i} \tag{9}$$

G_m^{mixing} = The molar Gibbs function of mixing and from standard thermodynamic relations, it follow that (d^2Q_i/dX_i^2) should be negative at all points in a completely miscible system. If the system is partially miscible then will be a region over which (d^2Q_i/dX_i^2) is positive.

3.2 *Mass transfer model*

The mass transfer parameters are the axial dispersion coefficients in the fluid phase (D_L), the mass transfer coefficient to the bulk phase (k_f) and the effective pore diffusivity in the particles (D_e) were estimated with using empirical correlations [7,8]

$$Sh = 2 + 1.1Sc^{1/3}\,Re^{0.6} \tag{10}$$

$$Pe = 0.187\,Re^{0.265}\,Sc^{-0.919} \tag{11}$$

The solubility of fatty acids in supercritical carbon dioxide given by [9]

$$\ln(C_{sat}) = k\ln\rho - {}^{\Delta H}/_{RT} + A \qquad 12)$$

Where;

k is the number of gas molecules associating with one molecule of solute to from a solvato complex. For palmitic acid, $k = 7.3 \mp 0.5$ and for stearic acid, $k = 3.7 \mp 0.5$ in supercritical carbon dioxide [10], A is a function of molecular weight of the solute and the gas equal -34.28 [8] and $\Delta H = 7.2 x 10^4$ J mol^{-1} [9]. Carbon dioxide density was estimated by Rackett equation and Hankinson-Brobst-Thomson (HBT) method [11] and the viscosity determined using empirical expression with ± 3% accuracy by Lucas [12].

4. Result and Discussion

In this study, the effects of pressure and temperature on the extract mole fraction were investigated, and the experimental and model results were found. Using experimental data at pressures at 60, 90, 120, 150, and 180 bars and temperatures at 313.15, and 353.15 K, these data together, with the thermodynamic designed model used for to calculate activity coefficients described above as shown in tables 1 and 2. Parameter (d^2Q/dx_i^2) (molar Gibbs function second derivative) shows that it should be negative at all points in a completely miscible system. If the system is partially miscible these will be a region over which the parameter is positive. Figs. 3, 5 show parameter (d^2Q/dx_i^2) for carbon dioxide against the pressure at constant various temperatures for the system carbon dioxide – palmitic acid and stearic acid, those curves confirm that the both systems always are miscible in the considered conditions. The miscibility decreased by increasing of the pressure and increasing by increasing of the temperature.

4.1 Effect of pressure

The influence of the pressure has been studied at the temperature of 313.15, and 353.15 K. the corresponding saturated fatty acids mole fraction extracted data are reported in Figs. 2, 4.

The axial dispersion coefficient decreased but the effective diffusivity, solubility of saturated fatty acids acid, mass transfer coefficient and carbon dioxide density increase by increasing the pressure at the constant temperatures. At the same time, internal and external mass transfer resistances had increased by decreasing of the diffusivity and mass transfer coefficient.

4.2 Effect of temperature

By increasing the temperature from 313.15 to 353.15 K at a constant pressure, the solubility of saturated fatty acids increases then the extraction mole fraction of saturated fatty acids increases.

Also the by increasing the temperature axial dispersion coefficient and effective diffusivity increased as shown in tables 2, 4. While the mass transfer coefficient decreased by the increasing of the temperature.

TABLE 1
The experimental data of carbon dioxide – palmitic acid system extracted at various pressures and temperatures together with the thermodynamic equation based on UNIFAC model used to obtain the activity coefficients and Gibbs function, gradient Gibbs function and second gradient Gibbs function.

***P* (bar)**	***T* (K)**	***$X_{C16:0}$* (Mole fraction)**	***γ_1* (CO$_2$ activity coefficient)**	***Q***	***dQ***	***d^2Q***
60	*313.15*	*0.0246*	*0.8386*	*0.8329*	*25.6893*	*-42.4203*
	353.15	*0.0255*	*0.6444*	*1.3114*	*33.1811*	*-40.9843*
90	*313.15*	*0.0283*	*0.8075*	*0.925*	*24.1142*	*-37.1142*
	353.15	*0.0286*	*0.6073*	*1.4106*	*30.8693*	*-36.7408*
120	*313.15*	*0.0309*	*0.786*	*0.9864*	*23.1148*	*-34.1471*
	353.15	*0.0347*	*0.543*	*1.587*	*27.1213*	*-30.6085*
150	*313.15*	*0.0355*	*0.7493*	*1.089*	*21.5279*	*-29.9645*
	353.15	*0.0431*	*0.4704*	*1.7975*	*23.1831*	*-25.012*
180	*313.15*	*0.0417*	*0.7026*	*1.2166*	*19.6884*	*-25.7911*
	353.15	*0.0553*	*0.3893*	*2.0536*	*19.047*	*-19.9231*

TABLE 2
Physical properties of supercritical carbon dioxide and palmitic acid at the experimental conditions.

P (bar)	**T (K)**	**ρ (kg m^{-3})**	**$\mu * 10^{-5}$ (kg m^{-1} s^{-1})**	**De * 10^{-10} (m^2s^{-1})**	**$k_f * 10^{-5}$ (m^2s^{-1})**	**$D_L * 10^{-6}$ (m^2s^{-1})**	**$C_{sat} * 10^{-15}$ (kg m^{-3})**
60	313.15	381.62	2.257	4.334	4.474	2.606	0.003
	353.15	362.15	2.383	4.412	4.292	2.908	0.045
90	313.15	572.44	2.957	6.398	6.214	1.552	0.061
	353.15	542.97	3.122	6.417	5.902	1.757	0.940
120	313.15	763.25	3.583	9.136	8.276	0.999	0.527
	353.15	723.89	3.782	9.032	7.785	1.146	8.128
150	313.15	954.07	4.157	12.75	10.74	0.673	2.811
	353.15	904.01	4.389	12.45	10.01	0.782	43.02
180	313.15	1144.88	4.694	17.56	13.72	0.467	11.03
	353.15	1085.99	4.956	16.92	12.68	0.548	170.2

TABLE 3
The experimental data of carbon dioxide – stearic acid system extracted at various pressures and temperatures together with the thermodynamic equation based on UNIFAC model used to obtain the activity coefficients and Gibbs function, gradient Gibbs function and second gradient Gibbs function.

P (bar)	**T (K)**	**$X_{C18:0}$ (Mole fraction)**	**γ_1 (CO_2 activity coefficient)**	**Q**	**dQ**	**d^2Q**
60	313.15	0.0014	0.999	0.062	42.554	-716.03
	353.15	0.0017	0.9944	0.1332	74.0055	-589.977
90	313.15	0.0029	0.9958	0.1241	40.3525	-346.575
	353.15	0.0030	0.9841	0.226	68.9725	-335.078
120	313.15	0.0035	0.9941	0.1481	39.6071	-287.463
	353.15	0.0049	0.9628	0.3511	62.9053	-205.831
150	313.15	0.0039	0.9927	0.1638	39.1368	-258.16
	353.15	0.0076	0.9251	0.5112	56.015	-133.334
180	313.15	0.0071	0.9785	0.2837	35.887	-142.602
	353.15	0.0093	0.899	0.6034	52.4256	-109.286

TABLE 4
Physical properties of supercritical carbon dioxide and stearic acid at the experimental conditions.

P (bar)	**T (K)**	**ρ (kg m^{-3})**	**$\mu * 10^{-5}$ (kg m^{-1} s^{-1})**	**De * 10^{-10} (m^2s^{-1})**	**$k_f * 10^{-5}$ (m^2s^{-1})**	**$D_L * 10^{-6}$ (m^2s^{-1})**	**$C_{sat} * 10^{-15}$ (kg m^{-3})**
60	313.15	381.62	2.257	4.116	4.321	2.733	0.047
	353.15	362.15	2.383	4.412	4.292	2.908	0.899
90	313.15	572.44	2.957	6.398	6.214	1.552	0.256
	353.15	542.97	3.122	6.417	5.902	1.757	4.731
120	313.15	763.25	3.583	9.132	8.273	0.999	0.834
	353.15	723.89	3.782	9.032	7.785	1.146	15.38
150	313.15	954.07	4.157	12.76	10.74	0.673	2.081
	353.15	904.01	4.389	12.45	10.01	0.782	38.26
180	313.15	1144.88	4.694	17.56	13.72	0.467	4.395
	353.15	1085.99	4.956	16.92	12.68	0.548	81.16

5. Conclusion

The saturated fatty acids from palm fruits were extracted by using modified supercritical carbon dioxide as a solvent. The activity coefficient for solvent was defined using the UNIFAC model as well as the Gibbs function and its derivatives are calculated using the same model. The mass transfer coefficient, the effective diffusivity in the particle, the axial dispersion and the solubility of fatty acid in supercritical carbon dioxide were determined using the mass transfer model.

Nomenclature

Q_k	Area parameter, contribution of molecular group
R_k	Volume parameter, contribution of molecular group
Q	Gibbs function
γ	Activity coefficients
ξ_k	Group surface area fraction
C_{sat}	Solubility of Oleic acid in supercritical carbon dioxide
D_e	Effective diffusivity
D_L	Axial dispersion coefficient
k_f	Film mass transfer coefficient
Re	Reynolds number
Sc	Schmidt number
Sh	Sherwood number

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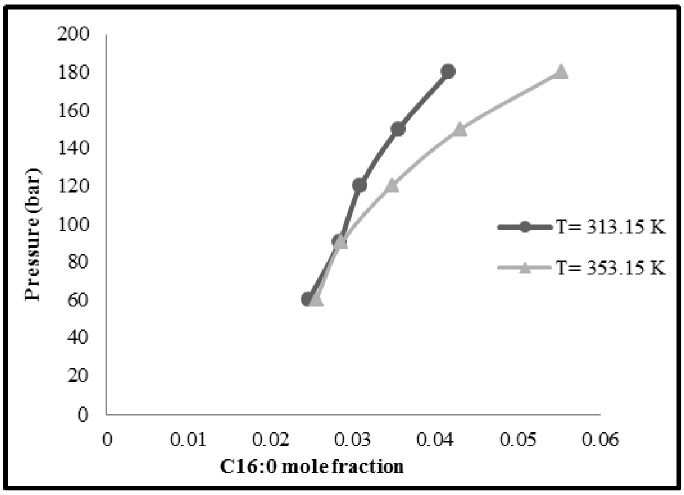

Fig.2. The palmitic acid mole fraction extract against the pressure in bar at various temperatures.

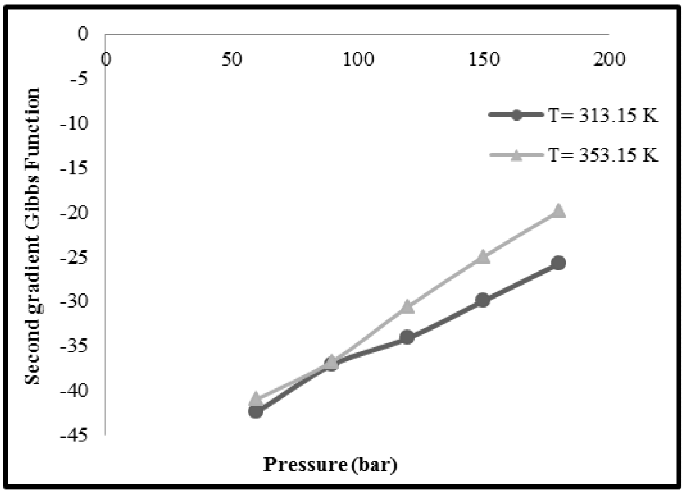

Fig.3. The second gradient Gibbs function predicted by UNIFAC model for the system carbon dioxide – palmitic acid against the pressure in bar at various temperatures.

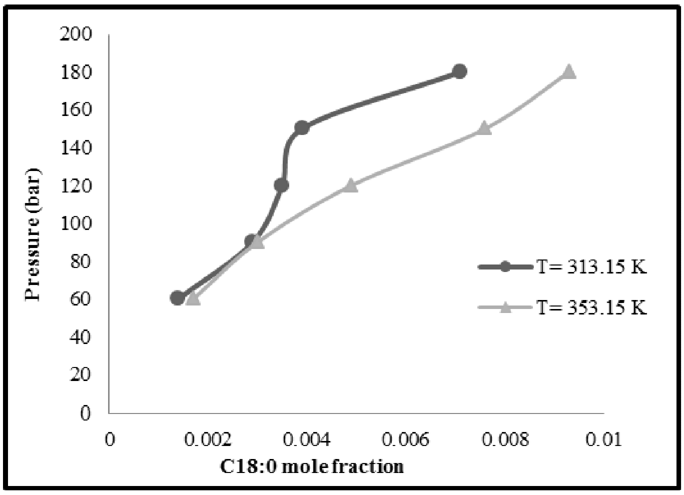

Fig.4. The stearic acid mole fraction extract against the pressure in bar at various temperatures.

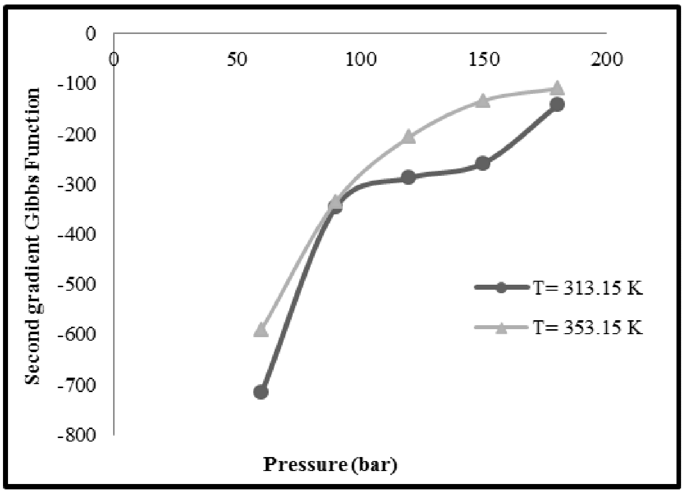

Fig.5. The second gradient Gibbs function predicted by UNIFAC model for the system carbon dioxide – stearic acid against the pressure in bar at various temperatures.

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