# HIGH PRESSURE VAPOR-LIQUID EQUILIBRIA OF PALM FATTY ACIDS DISTILLATES-CARBON DIOXIDE SYSTEM[1]

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## SUMMARY

Vapor-Liquid equilibria of palm fatty acids distillates/carbon dioxide system has been investigated experimentally at temperatures of 333, 353, and 373 K and pressures of 20, 23, 26, and 29 MPa using the static method. Experimental data for the quasi-binary system palm fatty acids distillates/carbon dioxide has been correlated with Redlich-Kwong-Aspen equation of state. Modeling shows good agreement with experimental data. Selectivity obtained indicates that supercritical carbon dioxide is a reasonable solvent for separating saturated (palmitic acid) and unsaturated (oleic+linoleic acids) fatty acids from palm fatty acids distillates in a continuous multistage countercurrent column.

**Keywords:** High pressure vapor-liquid equilibrium, Experiment, Carbon dioxide, Fatty acids, Equation of state, Separation.

## RESUMO

EQUILÍBRIO LÍQUIDO-VAPOR DO SISTEMA DESTILADO ÁCIDO DO ÓLEO DE PALMA-DIÓXIDO DE CARBONO A ALTA PRESSÃO. Foi investigado experimentalmente o equilíbrio líquido-vapor para o sistema Destilado Ácido de Óleo de Palma (PFAD)/Dióxido de Carbono, nas temperaturas de 333, 353 e 373 K e pressões de 20, 23, 26 e 29 MPa, usando-se o método estático. Os dados experimentais do sistema pseudo-binário PFAD/$CO_2$ foram correlacionados com a equação de estado de Redlich-Kwong do pacote computacional ASPEN. O modelo reproduz bem os resultados experimentais. A seletividade obtida indica que o $CO_2$ supercrítico é um solvente razoável para a separação em coluna multi-estágio e contínua, do ácido graxo saturado (ácido palmítico) daqueles insaturados (ácido oleico e ácido linoleico) contidos no PFAD.

**Palavras-Chave:** Equilíbrio vapor-líquido a alta pressão, Experimento, Dióxido de carbono, Ácidos graxos, Equação de estado, Separação.

## 1 —INTRODUCTION

The increasing interest in processing biological materials and new environmental protection polces have been contributing to development of novel separation processes particularly in foodstuff and pharmaceutical industries. In conventional separation techniques such as vacuum distilation, high operating temperatures are required which result in degradation of thermally labile substances. In solvent extraction high solvent flammability and residual solvents content in the final products results in high explosion risk for process and adverse health effects for consumers. Because of these issues supercritical fluid extraction using carbon dioxide as a solvent, which is a nontoxic, colorless, odorless, tasteless, nonflammable, and cheap gas with a minimal environmental impact compared to others solvents, has been in past years intensively investigated as an alternative to replace those traditional separation process.

During the refining process of palm oil, a deodorizer condensate is obtained as by-product on the deodorization step that contains fatty acids, tocopherols and squalen. Their separation is of special interest for the pharmaceutical and foodstuff industry. Free fatty acids are the main components of palm fatty acids distillates (99 % fatty acids palmitic ® oleic + linoleic, 0,9 % squalen, and 0,1 % tocopherols), so that the multicomponent mixture can be considered as a mixture consisting of palmitic, oleic and linoleic acids. Vapor-Liquid phase equilibria for the binary system fatty acid + supercritical carbon dioxide have been investigated during the last twenty years by several authors [1-8]. Vapor-Liquid phase equilibria for the ternary system oleic + linoleic acids + supercritical carbon dioxide have been investigated by Zou et alli [9]. Recently Stoldt [10] has investigated the vapor-liquid equilibria for the multicomponent system palm fatty acids distillates + supercritical carbon dioxide. With the objective of separating palmitic acid and oleic + linoleic acids from palm fatty acids distillates in a continuous countercurrent column using supercritical carbon dioxide as solvent, vapor-liquid equilibria for the multicomponent system palm fatty acids distillates + carbon dioxide have been investigated experimentally using a static apparatus at 333, 353 and 373 K and 20, 23, 26, and 29 MPa. Phase equilibrium data for the quasi-binary system fatty acids + carbon dioxide have been correlated with the Redlich-Kwong-Aspen (EOS) with the Mathias (subcritical component) and Boston-Mathias (Supercritical component) alpha function [11].

## 2 —EXPERIMENTAL APPARATUS

A schematic diagram of the experimental apparatus is shown in *Figure 1*. It consists of an equilibrium autoclave with a volume of 1000 cm³, a buffer autoclave of 500 cm³ that is used to compensate the pressure drop that occurred during sampling of the gas phase and a diaphragm-type compressor (NOVA, Switzerland, type: 544-2121-1). Three heat jackets (2500 W) at the equilibrium cell and a heat bandage (1400 W) at the buffer autoclave, both controlled by a computer were used to maintain the operating temperature constant. The equilibrium cell and buffer autoclave were isolated to avoid heat loss. The temperatures inside the equilibrium cell and buffer autoclave were measured with NiCr-Ni thermocouples (SAB GmbH & Co, type: MTE-303, Viersen, Germany) with a precision of 0.1 K . The pressures inside the equilibrium cell and buffer autoclave were measured by means of electrical pressure transducers (STW, Kaufbeuren, Germany, type: A05-H) with a precision of 0.05 MPa. All the temperatures and pressures inside the equilibrium cell and buffer autoclave are displayed on a computer. A stirrer with a magnetic coupling (MRK41, Buddeberg, Mannheim) is used to achieve equilibrium between the phases.

A schematic diagram of the sample unit is shown in *Figure 2*. The sample unit consisting of two capillaries (0.25 mm for the gas phase, and 0.5 mm for the liquid phase) connected with 1/8" valves (SW-2081, Autoclave Engineers), a vacuum pump (RZ5, Vakuumbrand, Wertheim), cold traps, and a system consisting of graduated glass columns, allows to collect the condensates and to determine the amount of carbon dioxide. In addition a temperature controller was used to maintain the temperature of the high pressure valves and capillaries constant and equal to that in the equilibrium cell.
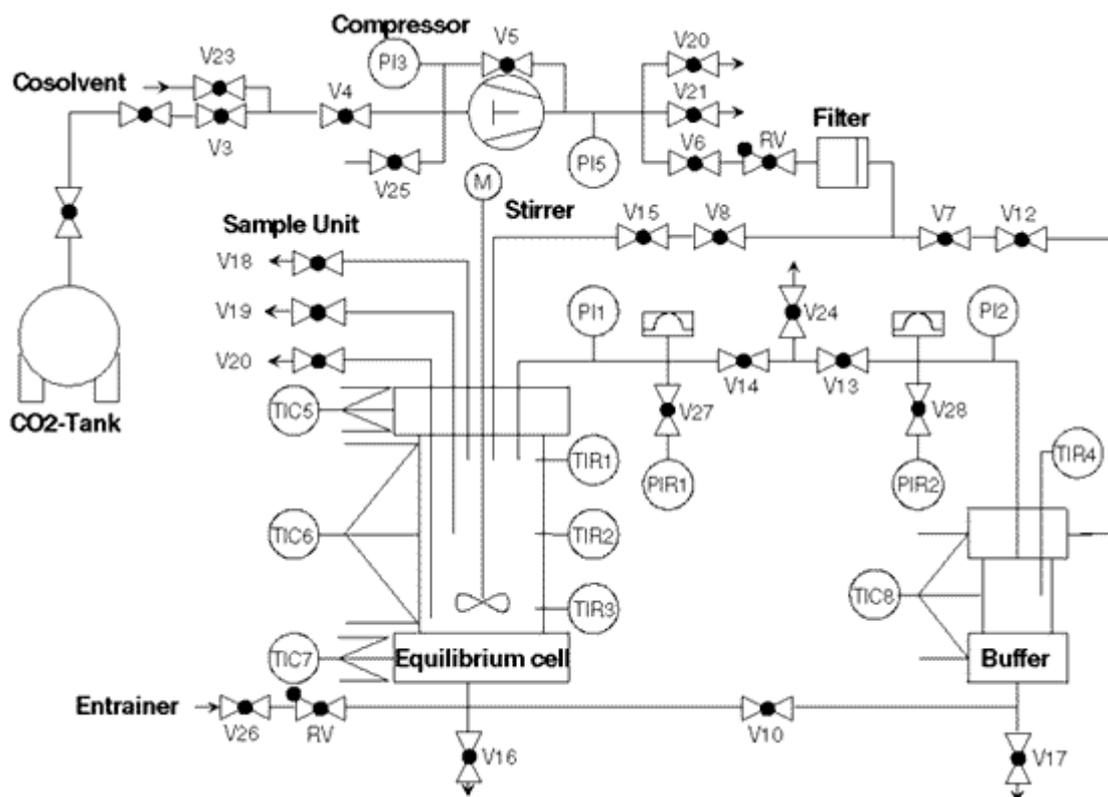
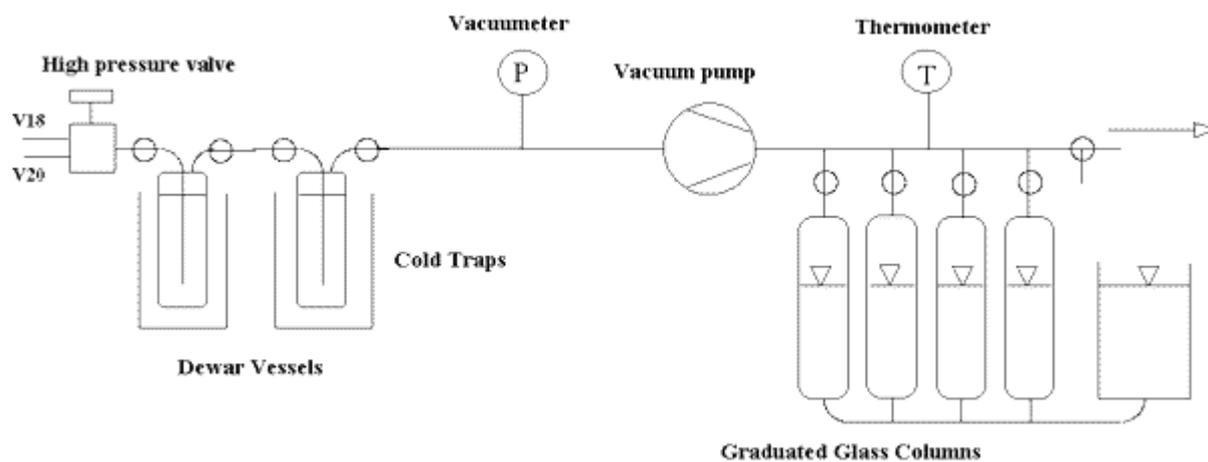**FIGURE 1.** Schematic diagram of the experimental apparatus for VLE measurements.



**FIGURE 2.** Schematic diagram of the sample unit.

# 3 —PROCEDURE

In order to start the experiments, the equilibrium cell and the buffer autoclave are evacuated by means of the vacuum pump, then both autoclaves are loaded with known amounts (» 300 g) of palm fatty acids distillates. The pressure in the equilibrium cell was increased to 7 MPa by means of carbon dioxide addition. After the desired temperature is achieved, the system is agitated by means of the stirrer. The intensive mass transfer between the gas and liquid phases causes a decreasing of the pressure, because the carbon dioxide dissolves in the liquid phase, so that more carbon dioxide must be added until the desired pressure is achieved. The stirrer is operated additionally 4 hours in order to assure equilibrium. In addition it is necessary to wait at least 3 hours for the complete separation of both liquid and gas phases. After equilibrium was achieved, samples were collected by using the following procedure: 1) the cold traps is evacuated (0.2-0.4 mbar); 2) after opening the high pressure valve (SW-2081, Autoclave Engineers), the supercritical carbon dioxide containing the solubilized fatty acids was expanded into the evacuated system and the fatty acids that precipitated because of the pressure reduction were separated from carbon dioxide in a cold trap immersed in water at 50°C (palm fatty acids distillates is solid at 38 °C) . The amount of carbon dioxide was determined by measuring the water level deflection in the system consisting of graduated glass columns (50 cm$^3$, 400 cm$^3$, 1000 cm$^3$, and 1000 cm$^3$). The pressure in the evacuated sample unit system was measured before and after sampling with a vacuummeter (Kammerer, Bergisch-Gladbach) with 0.01 mbar accuracy and the temperature with a NiCr-Ni thermocouple (SAB GmbH & Co, type: MTE-303, Viersen, Germany). Three samples of both liquid and gas phases were collected in order to ensure reproducibility. A pressure drop of 0.3 bar in the equilibrium cell was always observed after the third sampling of the liquid phase, on the other hand a pressure drop between 2-8 bars *(DR depends on the amount of sample taken to obtain measurable quantities of condensates in the cold trap)* was observed for each sampling of the gas phase, so that after the first sampling, the valve connected to the buffer autoclave (V10) have to be carefully opened (only the liquid phase flows into the equilibrium cell) to compensate the pressure drop. Because both pressures in the equilibrium cell and buffer autoclave are lower than the desired operating pressure after the second sampling, carbon dioxide has to be added to the buffer autoclave in order to carry out the third sampling. The mutual solubilities were calculated using the method developed by Stoldt [10].

# 4 —ANALYSIS OF FATTY ACIDS

The condensates were analyzed twice by gas chromatography using the following procedure: 1 ml of a standard solution (1:1 vol.) of n-Hexane (Type: Analysis, Merck-Darmstadt) and acetone (Type: Analysis, Merck-Darmstadt), containing » 0.9 mg of squalen (> 99 %, Riedel- de Haen, internal standard) was added to approximately 20-30 mg of condensates; then, 1 ml of the solution was injected into an HP 5890A gas chromatographer equipped with a capillary column and a FID detector. The column was a 30 m x 0.245 mm ID fused silica open tubular column coated with 0.25 mm (5 %-Phenyl) Methylpolysiloxane (DB-05 from J&W Scientific). Helium was the carrier gas, and the following temperature program was used : Initial temperature 70 °C; 70-250 °C (25 °C/min); 250-350 °C (4 °C/min); and 15 minutes at 350 °C. The chromatographic response factors for the different fatty acids were determined by analyzing standard solutions prepared gravimetrically. Palmitic acid (> 99 %, Merck-Darmstadt), oleic acid (> 99 %, Merck-Darmstadt), and linoleic acid (> 98 %, Merck-Darmstadt) of analytical grade were used to prepare the standard solutions. The fatty acids mass fraction (w) in palm fatty acids distillates in solvent-free basis was determined using the relation

$$w_i = \frac{A_i . m_{IStd} . RF_i}{A_{IStd} . m_{sample}} \quad (1)$$

where $A_i$ and $A_{Istd}$ are the chromatograms areas of component i and internal standard, $m_{sample}$ and $m_{Istd}$ are the mass of the sample and internal standard in mg, and $RF_i$ the response factor of component i. The mass fraction in solvent basis is determined using the relation

$$w_{i,solvent} = w_{i,solvent-free}\left(1 - w_{solvent}\right) \quad (2)$$

because the sum of the mass fractions of the components being always smaller than one ($\sum_i w_i \approx 0{,}94$), equation (1) was normalized using the relation

$$w^*_{i,normalized} = \frac{w_i}{\sum_i w_i} \quad (3)$$

## 5 — MATERIALS

Carbon dioxide with 99.99 % purity was obtained from KWD (Bad Hönningen, Germany) and the palm fatty acids distillates from Nobel Gmbh (Hamburg-Harburg, Germany).

Table 1 shows the gas chromatographic analysis of palm fatty acids distillates used for the experiments. Tocopherols could not be detected by GC, because they are present as traces.

TABLE 1
Composition of palm fatty acids distillates in wt. %.

| Components | Palmitic (C16) | Oleic (C18.1) | Linoleic (C18.2) | Squalen | Tocopherol |
|---|---|---|---|---|---|
| Composition | 50.32 | 40.30 | 8.93 | 0.4 | traces |

**TABLE 1.** Composition of palm fatty acids distillates in wt. %.

## 6 — EXPERIMENTAL RESULTSAND DISCUSSION

Vapor-liquid equilibria provide information about the mutual solubilities, the solvent capacity, the composition of the coexisting phases, the distribution coefficients, and the selectivity. High pressure vapor-liquid equilibria for the system palm fatty acids distillates + carbon dioxide was measured and the results are presented in Tables 2 and 3. Table 2 also include the experimental data of Stoldt [10].

| TABLE 2 Vapor-liquid equilibrium data of the system palm fatty acids distillates-CO$_2$. | | | | | | |
|---|---|---|---|---|---|---|
| P [Mpa] | | T [K] | | | Weight fraction of CO$_2$ | |
| | | | Vapor | Liquid | Data of Stoldt | |
| | | | | | Difference in (%) | |
| 20.04 | | 333 | 0.98984 | 0.2929 | | |
| 23.05 | | 333 | 0.98043 | 0.3234 | | |
| 26.00 | | 333 | 0.97411 | 0.3463 | | |
| 29.03 | | 333 | 0.96231 | 0.3751 | | |
| 20.12 | | 353 | 0.99575 | 0.2722 | | |
| 23.03 | | 353 | 0.98818 | 0.2999 | 0.77 | 2.88 |
| 26.07 | | 353 | 0.98299 | 0.3231 | | |
| 29.20 | | 353 | 0.97009 | 0.3653 | | |
| 20.07 | | 373 | 0.99747 | 0.2465 | | |
| 23.05 | | 373 | 0.99333 | 0.2725 | | |
| 26.00 | | 373 | 0.98567 | 0.3084 | | |
| 29.03 | | 373 | 0.97739 | 0.3531 | 1.37 | 13.13 |
| Difference (%) = (X, Y This work-X, Y Literature) * 100 /(X, Y Literature) | | | | | | |

**TABLE 2.** Vapor-liquid equilibrium data of the system palm fatty acids distillates-C0$_2$.

Measurements were carried out with a similar feed material and at the same equilibrium cell as used by Stoldt [10]. Calculations were also performed using the same method. Experimental data reported by Stoldt [10] agree well with the values obtained in this work for both gas and liquid phases, taking into account the uncertainty of the measurements (±5%).
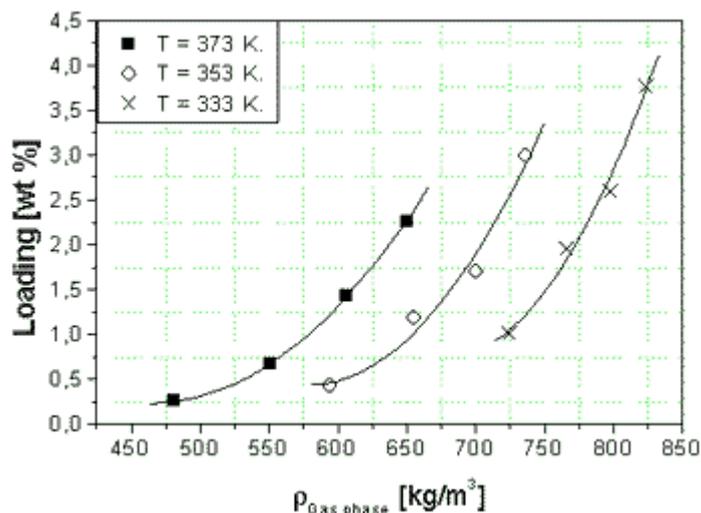


**FIGURE 3.** Loading in the gaseous phase as a function of the density in the supercritical phase.

*Figure 3* summarizes the loading in the gaseous phase calculated from VLE data for the system palm fatty acids distillates + carbon dioxide. The loading in the gaseous phase increases with increasing density (the solvating power of a supercritical fluid increases with increasing density). The solubility of the mixture in the gaseous phase gives information about the amount of solvent, and the energy requirements for the recycle of the solvent necessary to achieve a desired separation task in continuous multistage countercurrent columns [12].
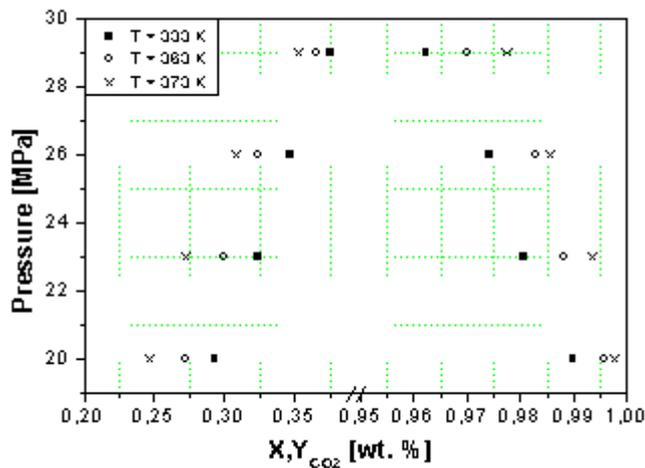
**FIGURE 4.** Vapor-liquid equilibria of the system palm fatty acids distillates-carbon dioxide.

*Figure 4* illustrates the vapor-liquid equilibria for the palm fatty acids distillates-carbon dioxide system. For all the isotherms, the solubility of palm fatty acids distillates in the gaseous phase and that of carbon dioxide in the liquid phase increases, as the system pressure increases (the solvating power of a supercritical fluid increases with increasing density). For all the isobars, the solubility of palm fatty acids distillates in the gaseous phase and that of carbon dioxide in the liquid phase decreases, as the system temperature increases. This is because the density of the supercritical phase decreases with increasing temperature for constant pressure, and this has a negative (diminution) effect on the solvating power of the supercritical fluid.

*Table 3* shows the composition of the fatty acids in the liquid and gaseous phase for the vapor-liquid equilibria of the system palm fatty acids distillates-carbon dioxide.

| TABLE 3 | | | | | | | |
|---------|---|---|---|---|---|---|---|
| Composition of the fatty acids in the liquid and gaseous phase. | | | | | | | |
| P [MPa] | T [K] | Palmitic acid | | Oleic + Linoleic acids | | Carbon dioxide | |
| | | Vapor | Liquid | Vapor | Liquid | Vapor | Liquid |
| 20.04 | 333 | 0.005394 | 0.364077 | 0.004680 | 0.340111 | 0.98984 | 0.29290 |
| 23.05 | 333 | 0.011099 | 0.351244 | 0.008313 | 0.322204 | 0.98043 | 0.32340 |
| 26.00 | 333 | 0.014819 | 0.332584 | 0.010855 | 0.317174 | 0.97411 | 0.34630 |
| 29.03 | 333 | 0.021860 | 0.305372 | 0.015528 | 0.315138 | 0.96231 | 0.37510 |
| 20.12 | 353 | 0.002432 | 0.366508 | 0.001767 | 0.356791 | 0.99575 | 0.27220 |
| 23.03 | 353 | 0.006827 | 0.345255 | 0.004874 | 0.350740 | 0.98818 | 0.29990 |
| 26.07 | 353 | 0.010027 | 0.333511 | 0.006834 | 0.338882 | 0.98299 | 0.32310 |
| 29.20 | 353 | 0.01785 | 0.310016 | 0.011847 | 0.320669 | 0.97009 | 0.36530 |
| 20.07 | 373 | 0.001550 | 0.388670 | 0.000950 | 0.359958 | 0.99747 | 0.24650 |
| 23.05 | 373 | 0.004093 | 0.371370 | 0.002501 | 0.350661 | 0.99333 | 0.27250 |
| 26.00 | 373 | 0.008571 | 0.336195 | 0.005640 | 0.350471 | 0.98567 | 0.30840 |
| 29.03 | 373 | 0.013597 | 0.312555 | 0.008817 | 0.329057 | 0.97739 | 0.35310 |

**TABLE 3.** Composition of the fatty acids in the liquid and gaseous phase.

For the separation analysis it is of fundamental importance to calculate the $K_i$-values of all the components of the mixture. The $K_i$-values described in solvent-free basis provides information about the phase where the components are preferably enriched . Knowledge of the $K_i$-values is of special interest in separation processes using multistage countercurrent columns, because it indicates what components are preferably enriched in the extract ($K_i > 1$) and raffinate ($K_i < 1$). *Figure 5* shows the partition coefficients ($K_i = Y_i/X_i$), computed in solvent-free basis for the saturated (palmitic acid) and unsaturated (oleic+linoleic) fatty acids of palm fatty acids distillates. Squalen was not taken into account for the calculations, because palm fatty acids distillates consists mainly of fatty acids (» 99%). For all the isotherms, the Ki-values of palmitic acid increases and that of oleic+linoleic acids decreases, as the system pressure increases. Based on the $K_i$-values it is possible to reduce the mixture to a quasi-binary system and calculate the separation factor or selectivity ($a_{ij} = K_i/K_j$), as shown in the *Figure 6*.
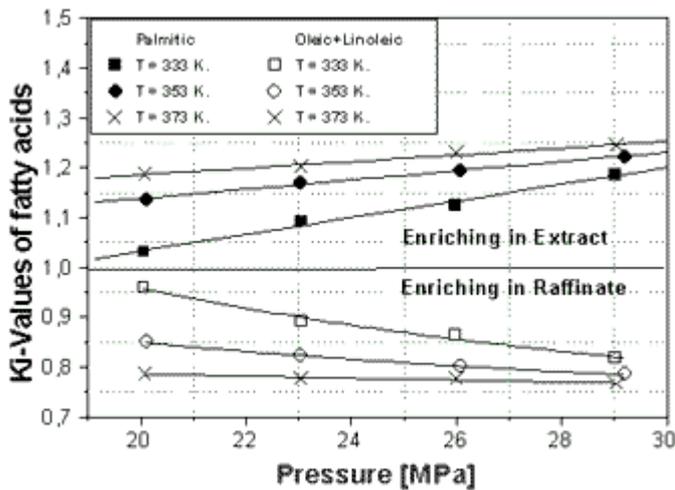


**FIGURE 5.** Partition coefficients of fatty acids as a function of the system pressure.
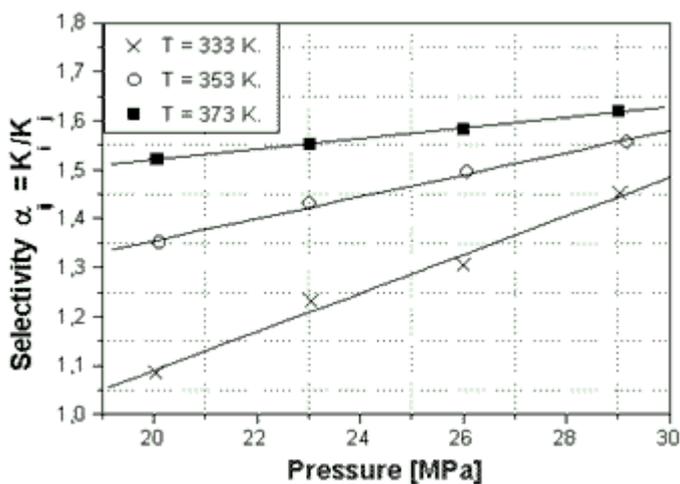


**FIGURE 6.** Selectivity $a_{ij} = K_{palmitic}/K_{oleic+linoleic}$ as a function of the system pressure.

For all isotherms the selectivity increases, as the system pressure increases. This unusual phenomena (normally $a_{ij}$ decreases with increasing solubility) was also reported by Stoldt [10]. The selectivity must decrease at higher pressures (> 30 MPa) to reach one at the critical point.

## 8 —ESTIMATION OF CRITICAL DATA OF PURE COMPONENTS

In order to compute the vapor-liquid phase equilibria of multicomponent mixtures using equations of state, it is necessary to estimate the critical data of all the pure components constituting the mixture such as: critical temperature $T_{ci}$, critical pressure $P_{ci}$, and the acentric factor $w_i$. Knowledge of critical data of all the components of the mixture makes possible to predict its critical properties. Unfortunately, many natural products degrade before the critical temperature is reached, as a consequence the critical data of those substances have to be predicted.

The critical data and the acentric factor of fatty acids were estimated using the physical property package available in the commercial simulator Aspen Plus [11], and the results are presented in *Table 4*. Information about the chemical structure and the boiling temperature of the substance is needed, in order to perform the computations. Experimental data available in the literature for the boiling temperatures of fatty acids reported by Araujo [13] were used as input parameter to predict the critical properties of fatty acids.

| TABLE 4. Estimation of critical data and acentric factor of fatty acids using the physical property package of Aspen Plus. | | | | | |
|---|---|---|---|---|---|
| Fatty Acids | Method | Tb [K] | Tci [K] | Pci [bar] | w |
| Palmitic acid | | 622.30 | | | |
| | Joback | | 783.95 | 12.87 | |
| | Lyndersen | | 780.41 | 14.19 | |
| | Ambrose | | 791.86 | 14.17 | |
| | Fedors | | 771.72 | | |
| | Lee-Kessler | | | | 0.8508 |
| Oleic acid | | 646.00 | | | |
| | Joback | | 791.06 | 13.69 | |
| | Lyndersen | | 790.83 | 14.42 | |
| | Ambrose | | 823.81 | 15.13 | |
| | Fedors | | 826.47 | | |
| | Lee-Kessler | | | | 0.8780 |
| Linoleic acid | | 644.20 | | | |
| | Joback | | 789.38 | 14.24 | |
| | Lyndersen | | 788.63 | 14.69 | |
| | Ambrose | | 824.07 | 15.48 | |
| | Fedors | | 827.27 | | |
| | Lee-Kessler | | | | 0.8651 |

**TABLE 4.** Estimation of critical data and acentric factor of fatty acids using the physical property package of Aspen Plus.

The critical properties and the acentric factor of palm fatty acids distillates were predicted by using the Kay rule [14]. This rule uses a linear combination of the critical properties of the pure components, with the mass fraction as a weighting function.

$$T_{c,Mixture} = \sum_i x_i T_{ci} \; ; \; P_{c,Mixture} = \sum_i x_i P_{ci} \; ; \; \omega_{Mixture} = \sum_i x_i \omega_i \tag{4}$$

The critical temperature $T_{ci}$ and the critical pressure $P_{ci}$ were predicted using the methods of Ambrose and Joback respectively, based on the results of a comparative analysis of the different methods used to estimate critical properties data of fatty acids performed by Mello [15]. The acentric factor w was predicted with the Lee-Kessler method.

## 9 — THERMODYNAMIC MODELING

Modeling of phase equilibria data for the palm fatty acids distillates + carbon dioxide system have been performed using the Redlich-Kwong-Aspen equation of state with the Mathias and Boston-Mathias alpha functions [11], based on the results of a comparative analysis of the different models (EOS) used to correlate the vapor-liquid equilibria for the system palm fatty acids distillates + carbon dioxide performed by Stoldt [10].

**Redlich-Kwong-Aspen**

$$P = \frac{RT}{v - b} - \frac{a}{v(v+b)} \tag{5}$$

where a and b are fundamental mixture parameters whose composition can be obtained from any number of mixing rules available in the literature. The Redlich-Kwong-Aspen equation of state applies the classical quadratic mixing rule, with the conventional corrected geometric mean combining rule.

$$a = \sum_i \sum_j x_i x_j \left[ a_i(T) a_j(T) \right]^{0.5} (1 - k_{a,ij}) \tag{6}$$

In addition an interaction parameter is introduced in the mixing rule for b.

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

The interaction parameter $k_{ij}$ is associated with the inability of the geometric mean combination rule in equation (6) to describe the molecular interactions between the different species i and j. The Redlich-Kwong-Aspen equation of state makes use of a temperature-dependent interaction parameters to improve the accuracy of the model.

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

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

The pure component parameters for the Redlich-Kwong-Soave equation of state are given by

$$a_i(T) = \alpha_i(T_{ri})0{,}42747\frac{R^2 T_{ci}^2}{P_{ci}} \quad (10)$$

$$b_i = 0{,}08664\frac{RT_{ci}}{P_{ci}} \quad (11)$$

the Mathias alpha function $a_i(T_{ri})$ used for the subcritical component (palm fatty acids distillates) is given by the equation

$$\alpha_i(T_{ri}) = \left[1 + m_i(1 - T_{ri}^{1/2}) - \eta_i(1 - T_{ri}^{1/2})(0{,}7 - T_{ri})\right]^2 \quad (12)$$

where $T_{ri}$ is the reduced temperature, and $h_i$ is a pure component parameter, which takes into account the polarity. The Boston-Mathias alpha function $a_i(T_{ri})$ is used for the supercritical component (carbon dioxide)

$$\alpha_i(T_{ri}) = \left[\exp\left[c_i(1 - T_{ri}^{di})\right]\right]^2 \quad (13)$$

with $c_i$ and $d_i$ given as follow

$$c_i = 1 - \frac{1}{d_i} \ ; \ d_i = 1 + \frac{m_i}{2} + 0{,}3\eta_i \quad (14)$$

The parameter $m_i$, necessary to compute equation (12) and (14) can be correlated with the acentric factor as follow

$$m_i = 0{,}48 + 1{,}57\omega_i - 0{,}176\omega_i^2 \quad (15)$$

The objective function minimized for the parameter estimation relating to equations (8) and (9) was the Maximum-Likehood, which is given as follow

$$Obj.Func = \sum_i \left[\left[(P^{calc} - P^{exp})/W_P\right]^2 + \left[(y^{calc} - y^{exp})/W_y\right]^2 + \left[(x^{calc} - x^{exp})/W_x\right]^2\right] \quad (16)$$

where $W_P$, $W_y$, and $W_x$ are weighting functions related to the standard deviation of the pressure, the gaseous phase composition, and the liquid phase composition respectively. The results are expressed in terms of the absolute average deviation (AAD) as follow

$$AAD = \frac{1}{N}\sum_i \left|f^{exp} - f^{cal}\right| \quad (17)$$

where N is the number of experimental points, $f^{exp}$ and $f^{cal}$ are the experimental and calculated values of the variables (pressure, gas and liquid phases compositions) minimized in equation (16).

*Table 6* shows the regression of the binary interaction parameters and the deviations from the correlation of equilibrium data of the system palm fatty acids distillates-$CO_2$ using the RK-Aspen equation of state.

| TABLE 6 | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Binary interaction parameters and deviations from experimental equilibrium data. | | | | | | | | |
| $\eta CO2$ | $\eta PFAD$ | $k^0_{a,ij}$ | $k^1_{a,ij}$ | $k^0_{b,ij}$ | $k^1_{a,ij}$ | AADP | AADy | AADx |
| 0.3209 | -1.7389 | -0.0532 | 0.3200 | -0.0792 | 0.1595 | 0.4947 | 4.2E-5 | 2.0E-3 |

The AAD values for the pressure, and composition of carbon dioxide in the gas and liquid phases indicates a good agreement with experimental data. The correlation of experimental data using thermodynamic models is very important in order to provide a general view of the phase behavior of the system, and to diminish the number of experiments [16]. The pressure-composition diagram P-XY showing the experimental and predicted values for the quasi-binary system palm fatty acids distillates + carbon dioxide is illustrated in *Figure 7*. The modeling shows good agreement with experimental data for the quasi-binary system palm fatty acids distillates + supercritical carbon dioxide within the investigated pressure range.
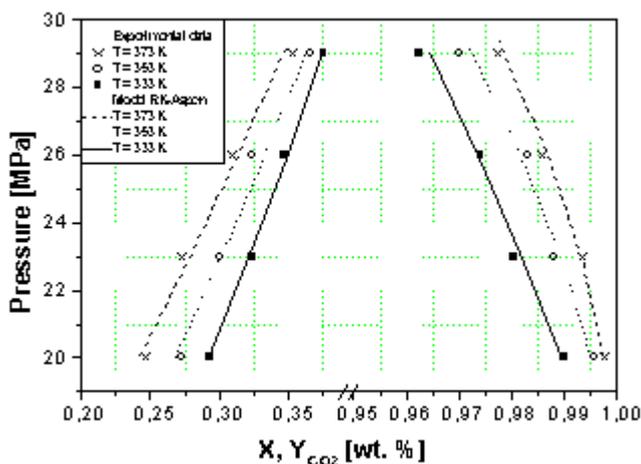


**FIGURE 7.** Regression of VLE experimental data for the quasi-binary system palm fatty acids distillates + carbon dioxide using the Redlich-Kwong-Aspen equation of state.

10 —CONCLUSIONS

Phase equilibria of the system palm fatty acids distillates has been measured by the static method. The partition coefficients $K_i$ were computed in solvent-free basis, and the results shows that the palmitic acid is preferably enriched in the gas phase, whereas the oleic + linoleic acids in the liquid phase. The multicomponent mixture was reduced to a quasi-binary system (Light component ® palmitic acid, Heavy component ® oleic + linoleic acids) in order to compute the selectivity. A thermodynamic analysis shows that supercritical carbon dioxide can be used as a solvent for separating saturated (palmitic acid) and unsaturated (oleic+linoleic acids) fatty acids from palm fatty acids distillates in a continuous multistage countercurrent column. The Redlich-Kwong-Aspen equation of state with the Mathias and Boston-Mathias alpha functions, quadratic mixing rules, and binary interaction parameter dependent of the temperature provides a good prediction for the vapor-liquid equilibria of the quasi-binary system palm fatty acids distillates + carbon dioxide.

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