# Separation Performance of Supercritical Carbon Dioxide Extraction Column for Crude Palm Oil Processing: Observation Using Process Simulator

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## Abstract

*Separation behaviour of crude palm oil (CPO), which contains principally triglycerides, fatty acids and valuable minor components such as α-tocopherol and β-carotene, with supercritical carbon dioxide was observed using process simulator Aspen® Plus. Solubility of palm oil components in supercritical $CO_2$ was calculated by Redlich-Kwong –Aspen equation of state. Process flow diagram for the CPO processing by supercritical $CO_2$ extraction column was successfully constructed to evaluate the separation performance. The effects of reflux ratio, stage number of extraction column and solvent-to-feed (S/F) flow rate ratio on the extract and raffinate product purities as well as the recovery of palm oil TG were studied at 373K and 20 – 30Mpa.*

**Keyword:** Crude palm oil, process simulation, supercritical fluid extraction, sensitivity analysis.

## Introduction

The application of supercritical fluid technology for the extraction and purification has a number of processing advantages over conventional processing methods (i.e. chemical or physical refining): low-temperature operation, inert solvent, selective separation, and the extraction of high-value product or new product with improved functional or nutritional characteristics. There are several studies that demonstrate the feasibility and applications of this technique. One of the main applications of supercritical fluids is in the field of separation processes, particularly in the extraction of high-value substances from natural products. Some examples are the refining of palm oil [1], degumming of soybean oil [2], deacidification of rice bran oil [3], and refining of olive oil [4-6]. In addition to that, SFE technique has also been investigated to recover oil fractions with high concentration of vitamins especially carotenes and tocopherols [7-9]. With supercritical fluids. It is also possible to combine these operations into one step, which can be carried out under moderate conditions at low temperature. Crude palm oil (CPO) is a valuable source of high –value raw material for the chemical and nutriceutical industries.

It is now well established from numerous nutrition studies that some of minor components such as carotenes and tocopherols are destroyed or removed by the current refining technology, rendering them unavailable for recovery. The use of supercritical fluids in vegetable oil refining, with particular reference to removal of fatty acids from triglycerides and a simultaneous improvement of organoleptic characteristics, dates back to the patents registered by Zosel [11] and Cohen and Krigel [12]

To deacidify adible oils, supercritical $CO_2$ is able to separate TG and FFA since their vapour pressure and solubilities are different [13]. Supercritical $CO_2$ has been proven a viable solvent to deacidify the CPO in order to produce refined quality palm oil [1, 14]. The design of palm oil deacidification process using supercritical $CO_2$ requires fundamental data on phase equilibria, mass transfer and hydrodynamics of packed column. Published data on the phase equilibrium [15-16] and countercurrent extraction [1,9] of mixtures containing CPO and supercritical $CO_2$ is scarce and limited to certain operating conditions. In the absence of extensive experimental data, a modeling tool should be used to make educated predictions of the most promising conditions and solvent.

Thus, we have carried out a study on phase equilibrium of the binary mixture CPO-supercritical $CO_2$ by means of computer aided simulation [17]. In this work, we present the study of the deacidification of the model CPO mixture by supercritical $CO_2$ using process simulator Aspen® Plus release 10.2.1. The separation performance of the packed column was studied as a function of solvent-to-feed ratio, number of stages, and reflux ratio.

## Thermodynamic Modelling of CPO-supercritical $CO_2$ systems

The RKA model was applied to the SFE process since it is particularly suitable for modelling a mixture of polar components with light gases at medium to high pressures [18]. The RKA-EOS [18] is a cubic equation of state that is an extension of the Redlich-Kwong-Soave equation of state. The RKA-EOS was regressed using the Data Regression System module available in 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 modelling the phase equilibria of the CPO-supercritical $CO_2$ system:

$$P = \frac{RT}{v - b} - \frac{a}{v(v + b)} \tag{1}$$

where $P$ is pressure (in MPa), $R$ is universal gas constant (8.314 J mol$^{-1}$ K$^{-1}$), $T$ is temperature (in K), $v$ is molar volume (in m$^3$·mol$^{-1}$), $a$ (in m$^6$·MPa·mol$^{-2}$) and $b$ (in m$^3$·mol$^{-1}$) are the cross-energy and co-volume parameters for a mixture. 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. In our previous work [17], the RKA-EOS was validated as an appropriate means of predicting phase equilibrium for the model system treated in this paper. The parameters summarized in Table 1 and Table 2 were employed unchanged in all following simulations of this work.

*Table 1: Predicted physical properties of pure components in palm oil*

| Component | $T_b$ (K) [a] | $T_c$ (K) [a] | $P_c$(kPa) [a] | $\omega$ [b] | $V_{L20}$ [c] (m$^3$/kmol) |
|---|---|---|---|---|---|
| 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 | 1250.19 | 0.8104 | 0.3172 |
| $\alpha$-tocopherol | 794.52 | 936.93 | 838.45 | 1.1946 | 0.4533 |
| $\beta$-carotene | 908.58 | 1031.06 | 678.41 | 1.6255 | 0.5348 |

[a] Estimated by the method of Dohrn and Brunner [19]
[b] Estimated using the Pitzer method [20]
[c] Liquid molar volume data (at 20 °C) obtained from open literature: tripalmitin, triolein, oleic acid [21] $\alpha$-tocopherol [19]; $\beta$-carotene [22]

## Multistage countercurrent SFE Process simulation

Multistage supercritical fluid extraction has emerged as an alternative to replace traditional separation processes, when the separation of thermally labile substances and the attainment of high purity products is the target [23]. Economically, a countercurrent SFE process is more advantageous since the saturation of supercritical fluid can be maintained.

In this study, the objective of deacidification column was to reduce the FFA content of the palm oil or in other way, to increase the concentration of low volatile component in raffinate phase product. Prior to the simulation of palm oil deacidification column, both the fluid dynamic properties and the phase Equilibria for CPO- $CO_2$ system were taken into consideration to obtain process conditions that allow the desired separation.

*Table 2: Temperature-dependent polar factors and binary interaction parameters for palm oil components supercritical $CO_2$ systems [17]*

| | Polar factor ($\eta$) | Binary interaction parameters |
|---|---|---|
| Tripalmitin-$CO_2$ | $0.0281\ T - 11.765$ | $k_a = 0.0007\ T - 0.2117$<br>$k_b = -0.0006\ T + 0.2021$ |
| Triolein-$CO_2$ | $0.0186\ T - 9.7848$ | $k_a = 0.0005\ T - 0.1428$<br>$k_b = 0.0004\ T - 0.1632$ |
| Oleic acid-$CO_2$ | $0.0044\ T - 2.5779$ | $k_a = 0.0004\ T - 0.0622$<br>$k_b = 0.0004\ T - 0.1349$ |
| $\alpha$-tocopherol-$CO_2$ | $0.0427T - 4.6165$ | $k_a = 0.0017\ T - 0.5082$<br>$k_b = 0.0059\ T - 2.0272$ |
| $\beta$-carotene-$CO_2$ | $0.0206\ T - 8.0155$ | $k_a = 0.0004\ T + 0.0895$<br>$k_b = -0.0005\ T + 0.0501$ |

## Hydrodynamic of Countercurrent SFE Process

The study of the fluid dynamic behaviour of the palm oil – supercritical $CO_2$ system determines the range of temperature and pressure of which countercurrent separation is feasible. The density difference of co-existing phases is crucial as a limiting factor to assure countercurrent flows and it must always be higher than 150 kg/m$^3$ in order to avoid flooding [9]. For palm oil-supercritical $CO_2$ system, the density of coexisting phases of CPO-$CO_2$ system was measured by Kalra *et al.* [15], Mochado [24] and Tegetmeier *et al.* [25].

Figure 1 shows the density differences between the coexisting $CO_2$-rich and oil-rich phases at temperature 333–373 K. As shown in the figure, the required density difference at a temperature of 333 K is not complied above pressure of 22 MPa which is within the pressure range of interest. Thus, only temperature range of 373 K and pressure range of 20–30 MPa were considered for the SFE process as the differences in density are high enough for the operation of a countercurrent process.

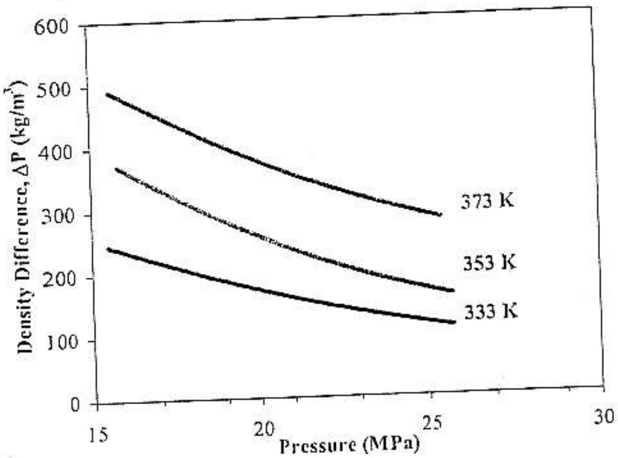


*Figure 1: Density difference between coexisting phases of palm oil- $CO_2$ system*

## Process Modeling and Simulation

Commercial process simulation software, Aspen Plus® release 10.2.1 was used to solve flowsheet modeling problems encountered in this work to obtain a better insight into compositions of phases along the separation process. Aspen Plus® process simulator includes thermodynamic and physical properties, unit operations, hydrodynamics, cost analysis, optimization, which makes the process simulator a powerful numerical tool to perform complete process design analysis. Simulations were performed on a stand-alone PC with a Microsoft® Windows operating system running with a Pentium III/1.0 GHz processor.

The calculation for countercurrent SFE process was performed using the concept of theoretical stages in which the extractor was split into cascade of flash modules. Each stage of the column was assumed as a single flash at fixed temperature and pressure. Using the modular structure of the Aspen Plus®, a rigorous sequential simulation for the process was implemented using flash separator (FLASH2) unit to model the cascade of flash modules in accordance with theory of a theoretical separation unit. The process flow diagram of the supercritical $CO_2$ extraction column is shown in figure 2. A variation of the number of theoretical stages and other process variables provides information on the purity of the products with different number of theoretical stages and operating conditions.

## Results and Discussion

Once the feasible operating conditions were determined, preliminary evaluation of separation process parameters such as number of stages, S/F ratio, product purity and yield was performed using the Aspen Plus® 10.2.1 process simulator. Separation analysis generally resulted in a preliminary estimation for optimum operating condition taking into account that a higher solvent density often yields in a higher loading and a decreased selectivity.

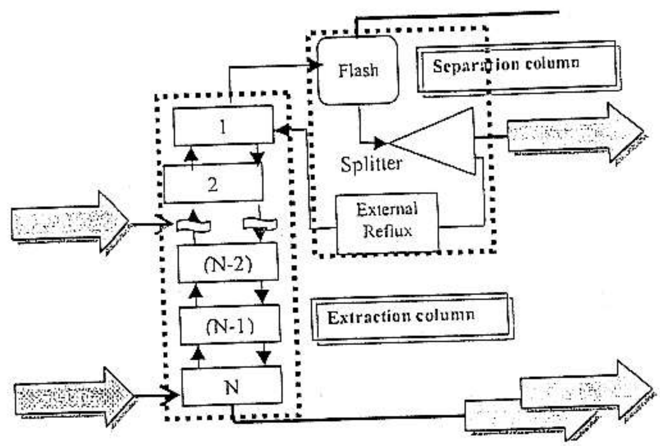


*Figure 2: SFE process flow diagram for deacidification column*

### Effect of Stage Number

The removal of FFA from CPO in a continuous countercurrent extraction column can be enhanced by increasing the number of equilibrium stages as well as multistage operation. For operation with different stage number, feed was introduced into the top of the column (Stage 1). In this case, the influence of stage number on the process parameters for the production of 0.1wt % FFA palm oil was considered.

Figure 3 shows the effect of stage number on the separation behaviour without external reflux at 373 K and 20-30 MPa. For a given operation, the separation performance of CPO deacidification process was improved with increase in the stage number. As the number of stages increases, the contacting time and contacting area between the coexisting phases of $CO_2$-palm oil system are increased. Due to this reason, the mixture separability and hence the purity of FFA in extract phase of the extraction column increases with the number of stages.

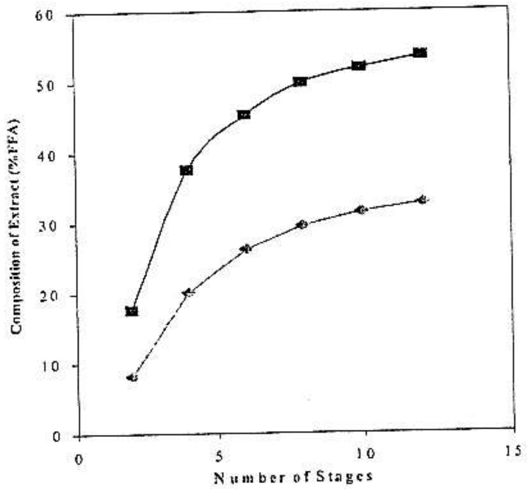


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*Figure 3: Effect of stage number on the separation behaviour for CPO- $CO_2$*

Figure 4 shows the effect of equilibrium stage on the product recovery in the raffinate phase. Recovery of refined palm oil was found gradually increased with an increase in the stage number. Consequently, the removal of FFA was achieved without decrease in oil recovery. It can be concluded that increase in the number of stages increases the separability subject to the economic constraint as the optimum number of stages is a trade-off between the column capital and the operating cost.

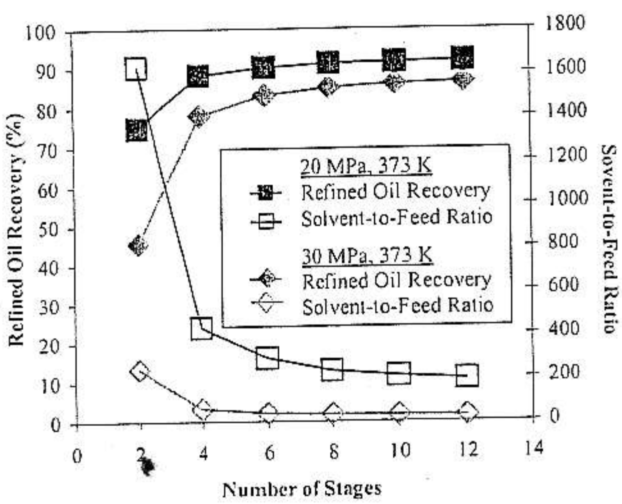


*Figure 4: Effect of stage number on the product recovery*

**Effect of Solvent-to-Feed Ratio**

The flow rate of supercritical $CO_2$ solvent is an important factor to design the extraction process. Countercurrent extraction for the production of refined palm oil was performed using 12-stage column without external reflux. For each operation, CPO feed was introduced into the top of the column (Stage 1).

Figure 5 shows the effect of S/F flow ratio on the on the FFA content of the extract phase and raffinate phase was evaluated at 370 K and 20-30 MPa. At lower S/F flow ratio, higher FFA content was obtained in the extract due to higher solubility of fatty acids in supercritical $CO_2$. In contrast, as S/F value increases, the TG content in the extract increases as more of the feed dissolves in the $CO_2$-rich supercritical fluid phase. Simultaneously, the raffinate phase also becomes richer in TG as the S/F ratio increases due to an increase in the selectivity of the supercritical $CO_2$ solvent as S/F flow ratio increases. According to Simões *et al.* [26], the variation of solvent and feed stream flow rates with S/F ratio kept constant did not significantly affect the compositions of the extract and raffinate phases.

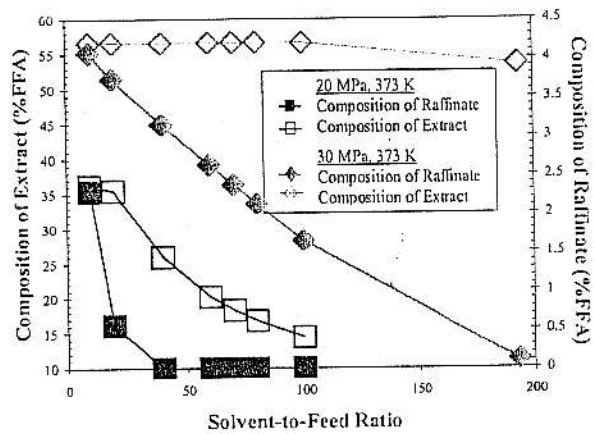


*Figure 5: Effect of S/F ratio on the separation behaviour: CPO-$CO_2$ system*

Figure 6 shows an increase in S/F flow ratio causes a decrease in the recovery of palm oil in the raffinate phase. As the S/F flow ratio increased, some of the TG initially present in the feed is dissolved in the supercritical fluid phase, that is, the mass ratio between the raffinate and extract flow decreases. The product quality increased with an increased in the S/F ratio whereas the recovery of product decreased. For a given calculation, it is concluded that effective separation is achieved by removal of FFA from the bottom product with higher S/F ratio. However, optimal condition in terms of both the selectivity and the recovery could not be decided easily.

**Effect of Reflux Ratio**

The influence of reflux flow on countercurrent extraction of CPO mixtures was investigated at 373 K and 30 MPa with a fixed S/F flow ratio and a range of reflux pump-rates for a 12-stage column. For each operation, the reflux stream was introduced into the top (stage 1) of the column.

Figure 7 shows the effect of reflux ratio on the composition of the product (refined palm oil) for the CPO mixture at 373 K and 30 MPa with S/F ratio of 40. The FFA content in the refined palm oil and top product increased with increased in the reflux ratio. These results show that the reflux of the top product is a rewarding technology not for the fractionation of CPO but for the concentration of high volatile component such as FFA.

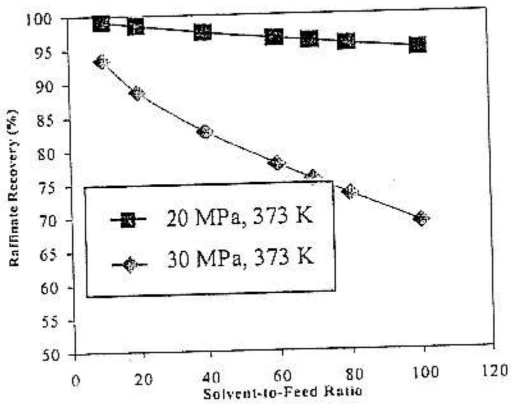


*Figure 6: Effect of S/F ratio on the product recovery*

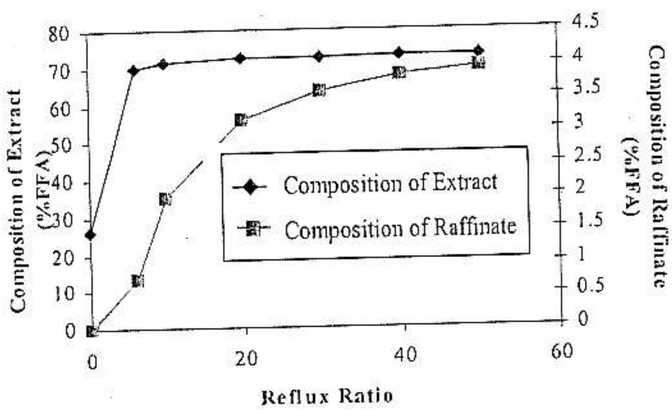


*Figure 7: Effect of reflux ratio on the composition of top and bottom products at 373 K and 30 MPa S/F ratio of 40*

Figure 8 shows the effect of reflux ratio on the recovery of refined palm oil in the raffinate phase. Recovery of refined palm oil increased in the reflux ratio, whereas decreased with increase in S/F ratio.

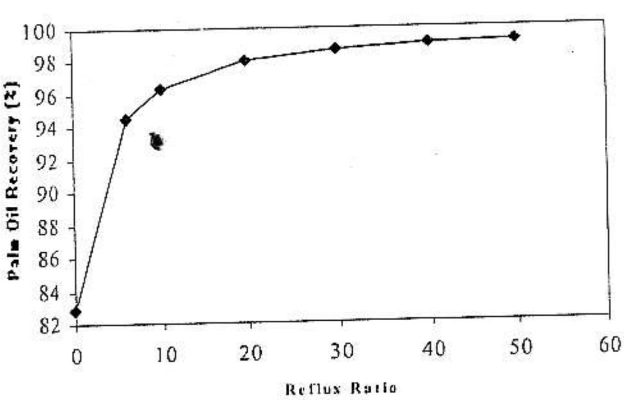


*Figure 8: Effect of reflux ratio on the palm oil recovery (S/F ratio of 40)*

## Conclusions

Pure component parameters for thermally labile palm oil components were estimated using the method proposed in our previous work [17]. Phase equilibrium calculation for palm oil components-supercritical $CO_2$ mixtures is possible by introducing mixing rules for pure component parameters and by using the binary interaction parameters. Binary phase equilibrium data and solubility data for palm oil components with supercritical $CO_2$ in the literature were used for binary interaction parameters correlation. High pressure equilibrium data between the oil components were not available in the literature, therefore only the interaction parameters between the palm oil components and $CO_2$ were considered in the calculation procedure.

The use of computer simulation techniques is particularly advantageous for the design of SFE processes, since it allows a broad range of operating conditions and process configurations to be explored quickly and easily. Using the developed RKA thermodynamic model and the proposed steady-state equilibrium-stage extractor model, SFE process simulations were applied to explore the feasible operating domain for the production of refined quality palm oil using supercritical $CO_2$.

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