Development of a New Process for Palm Oil Refining Based On Supercritical Fluid Extraction Technology

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Abstract

This work described the development of a new flowsheet model for palm oil refining using supercritical fluid extraction (SFE) technology. The first step was the synthesis of a new flowsheet structure to recover high purity palm oil which includes its minor components. Next, a thermodynamic model was developed to predict the phase equilibrium behavior of the crude palm oil (CPO)-supercritical CO_2 mixture. The process structure to recover high nutritional value palm oil using supercritical fluid was finally simulated by means of the commercial process simulation package Aspen Plus® release 10.2.1 based on the Redlich-Kwong-Aspen (RKA) thermodynamic model. The results obtained were in good agreement with the pilot plant data reported in the literature. It is envisioned that the development of the new, intensified and simpler palm oil refining process that is based on SFE technology can overcome the limitations of the existing technology for palm oil refining apart from making the refining process drastically simpler.

Keywords: Equation of state; palm oil refining; process simulation; supercritical fluid extraction; thermodynamic modeling.

Introduction

Palm oil belongs to the family of natural oils and fats which consist of major lipid components such as free fatty acids (FFA), monoglycerides (MG), diglycerides (DG) and triglycerides (TG). In addition to major lipid components, fats and oils also contain minor components such as vitamins, sterols, pigments and hydrocarbons, some of which have received increased attention due to the health benefits they bring. The removal of FFA, phospholipids and waxes from fats and oils constitutes an important part of vegetable oil processing prior to their use as foodstuffs. The process involves acid removal and deodorization and is normally accomplished in several steps which include neutralization with alkaline substances, distillation and steam distillation below atmospheric pressure.

Supercritical fluid extraction (SFE) of natural products using CO_2 has already been studied in an attempt to replace conventional processes in the oils and fats industry, which require high energy due to the high operating temperature. Some examples are the refining of palm oil [1], degumming of soybean oil [2], refining of olive oil [3, 4, 5] and deacidification of rice bran oil [6, 7]. In addition to that, SFE technique has also been investigated to recover oil fractions with high concentrations of vitamins, especially carotenes and tocopherols [8, 9, 10].

The commercial application of the SFE technology has been relegated to only special applications due to the high capital cost required. Besides that, the development of processes for natural fats and oils extraction based on supercritical fluid technology was hindered by the lack of suitable design tools and reliable thermodynamic data and models at high pressure. This has changed in the last few years with the advances in process equipment design and the development of robust simulation tools and optimization methods for process development.

This paper focused on the development of a complete new flowsheet model for palm oil refining using SFE technology to recover high purity palm oil which includes its minor components. We began by describing the steps involved in a conventional palm oil refining process. This was followed by the description of the newly developed flowsheet that was based on the SFE technique. In this work, a rigorous steady state equilibrium-stage model of supercritical fluid extractor was proposed and numerically simulated for the particular case of the production of refined quality palm oil using CO_2 as supercritical solvent. It is envisioned that the development of the new, intensified and simpler palm oil refining process that is based on SFE technology can overcome the limitations of the existing technology for palm oil refining apart from making the refining process drastically simpler.

Conventional Palm Oil Refining Process

Currently, CPO is refined through physical or chemical refining. Physical refining, which is the more popular and cheaper technique involves degumming, alkaline wash, and steam distillation at high temperature under vacuum. The refining processes remove FFA and deodorize the oil. However, it also reduces the tocopherol content and destroys all carotenes present in palm oil. The final product is the refined, bleached and deodorized (RBD) palm oil

The use of supercritical fluids in vegetable oil refining, with particular reference to the removal of FFA from oil and a simultaneous improvement of organoleptic characteristics, dates back to the patents registered by Zosel [12] and Coenen and Kriegel [13]. Drescher *et al.* [14] investigated on palm oil deacidification using supercritical fluids with dimethylether as co-solvent and concluded that supercritical CO_2 is suitable for the removal of FFA in palm oil. Ooi *et al.* [1] carried out a pilot plant study of the SFE process with CO_2 as supercritical solvent, using a continuous countercurrent packed column, and demonstrated that removal of FFA in order to produce a refined quality palm oil was feasible. Recently, Gast *et al* [9] demonstrated the feasibility of palm oil deacidification and vitamin recovery using supercritical CO_2 for a continuous pilot-plant packed column, and studied the effect of reflux ratio, solvent-to-feed ratio on the operation of the column.

Thermodynamic Modeling

For the design of a SFE process, the knowledge on phase equilibria is inevitable. In order to ensure the reliability of the phase equilibrium prediction for supercritical CO_2 and fatty oil components, pure component property parameter database and a thermodynamic model which can well represent the phase behavior of the mixture have been developed in our previous work [15].

Palm Oil Characterization

Palm oil contains various components such as monoglycerides (<1%), diglycerides (2–7%), triglycerides (>90%), free fatty acids (3–5%), phospholipids, pigmented compounds as well as several nutritionally beneficial bioactive compounds [16]. In the present study, CPO was modeled as a mixture consisting of principally TG (46.5% tripalmitin and 48.8% triolein), FFA (4.5% oleic acid) and valuable minor components (540 ppm of β-carotene and 1000 ppm of α-tocopherol), with an average molecular weight of 846.7 kg kmol^{-1}.

Physical Properties Estimation

The property estimation task is a pre-requisite for simulation modeling of SFE processes using Aspen Plus®. The development of palm oil physical property database in Aspen Plus® in has been enhanced using the built-in Property Constant Estimation System to perform the estimation of the property parameters required by physical property models [17]. The previously estimated thermo-physical parameters for palm oil components summarized in Table 1 were employed unchanged in all the following simulations of this work.

Phase Equilibrium Calculation

The Redlich-Kwong-Aspen (RKA) thermodynamic model implemented in the Aspen Plus® was chosen to calculate the phase equilibrium between the palm oil components and the supercritical CO_2. The RKA equation of state employs in the following form:

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

$$a = \sum_i \sum_j x_i x_j \sqrt{a_i a_j}\left(1 - k_{a,ij}\right) \quad (2)$$

$$b = \sum_i \sum_j x_i x_j \frac{(b_i b_j)}{2}\left(1 - k_{b,ij}\right) \quad (3)$$

For a_i, an extra polar factor (η_i) fitted from experimental data is used:

$$a_i = f\left(T, T_{ci}, P_{ci}, \omega_i, \eta_i\right) \quad (4)$$

$$b_i = f\left(T_{ci}, P_{ci}\right) \quad (5)$$

The RKA thermodynamic model requires the binary interaction parameters ($k_{a,ij}$ and $k_{b,ij}$) parameters specific for the mixture of components treated to account for interaction between the mixture of components. The RKA thermodynamic model makes use of temperature-dependent interaction parameters to improve the predicting capability of the model:

$$k_{a,ij} = k^0_{a,ij} + k^1_{a,ij}\frac{T}{1000} \quad (6)$$

$$k_{b,ij} = k^0_{b,ij} + k^1_{b,ij}\frac{T}{1000} \quad (7)$$

For the calculation of phase equilibrium, the CPO-supercritical CO_2 mixture is treated as a pseudo-binary system. The RKA model parameters were estimated on the basis of binary phase equilibria information for palm oil component -supercritical CO_2 system. The regressed parameters presented in the previous paper [18] were used to predict the phase equilibrium behavior for the model system treated in this work (see Table 2).

SFE Process Development

Multistage SFE process has emerged as an alternative to replace traditional separation processes, when the separation of thermally labile substances and the

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

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

of high purity products is the target [19]. Economically, a countercurrent SFE process is more advantageous since the saturation solubility of supercritical fluid can be maintained.

A two-step supercritical CO_2 extraction process was attempted by means of process simulation to remove FFA from CPO and simultaneously enrich tocopherols present in CPO. Such a processing scheme simplifies the refining process and improves the economic feasibility of the production through enrichment of valuable vitamin E.

Synthesis of the SFE Process

In this study, the separation strategy to separate the high volatile component (free fatty acids and α-tocopherol) and low volatile component (TG and β-carotene) fractions was attempted first. Thermo-physically similar components (FFA and tocopherols) were then separated from each other. This strategy would determine the basic process structure and fix the appropriate process conditions. In order to maximize the recovery of refined palm oil in the raffinate phase, we proposed the use of external reflux and additional extraction stages during countercurrent extraction.

Hydrodynamics in Countercurrent SFE Columns

The viability of packed column fractionation of lipid mixtures, including palm oil, depends on there being sufficient density difference between the solvent and solute phases to avoid entrainment and flooding [20]. 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 [4].

Process Simulation

The design of countercurrent multistage SFE process requires rigorous calculation of stream flow rates, stream compositions, concentration profiles along the column, temperatures and pressures at each stage. A better insight into compositions of phases along the separation process is obtained through a multicomponent process simulation with the aid of commercial process simulator, Aspen Plus® version 10.2.1. Aspen Plus® is useful for observation of phase behaviors in chemical process in a steady state since one can rapidly conduct theoretical calculation of unit operations. 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 SFE process is performed using the concept of theoretical stages in which the extractor is 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 provide information on the number of theoretical stages depending on the purity of the products, and for different operating conditions.

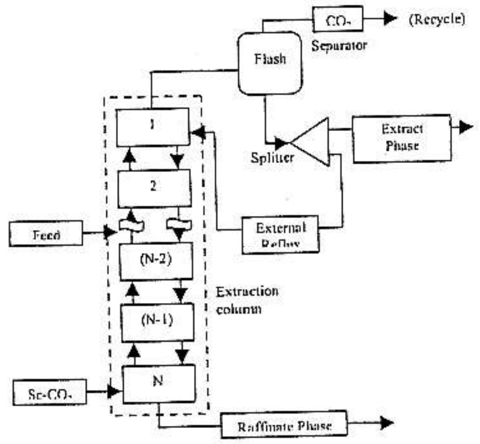
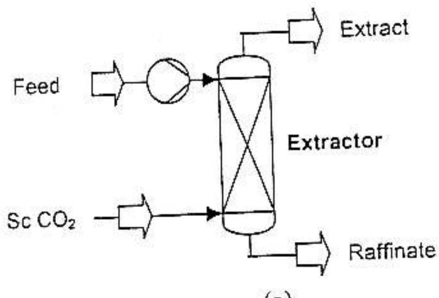


Figure 2: SFE Process flow diagram for deacidification column

Simple Countercurrent Extraction

In simple countercurrent extraction scheme, the column works as a stripping section where supercritical CO_2 is the continuous phase entering at the bottom of the column and feed oil is the dispersed phase entering at the top of the extraction column. Figure 3 shows the basic flow scheme of a countercurrent extraction column: CO_2 is the continuous phase entering at the bottom of the column and feed oil is the dispersed phase entering at the top of the extraction column.



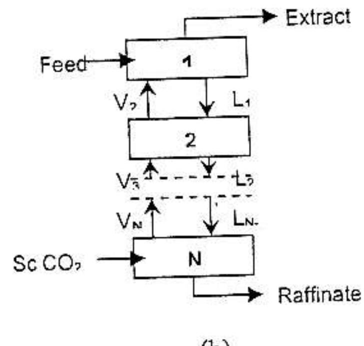


Figure 3:
Schematic diagram for SFE process model: (a) Basic flow scheme; (b) Equilibrium-stage model

Countercurrent Extraction with External Reflux

For large scale continuous SFE process, an external reflux is a more effective way to increase process efficiency [21]. The method requires that sufficient solvent be removed from the extract leaving the cascade to form a raffinate, part of which is returned to the cascade as reflux, the remainder being withdrawn from the plant as a product. Raffinate is withdrawn from the cascade as bottoms product, and fresh solvent is admitted directly to the bottom of the cascade. The proposed flow scheme is shown in figure 4.

Results and Discussions

Using the developed RKA thermodynamic model and the proposed steady-state equilibrium-stage extractor model in the previous sections, different SFE schemes were applied to explore the feasible operating domain for the production of refined quality palm oil using supercritical CO_2. The simulation results were compared with the pilot plant data published in the literature to validate the developed process model.

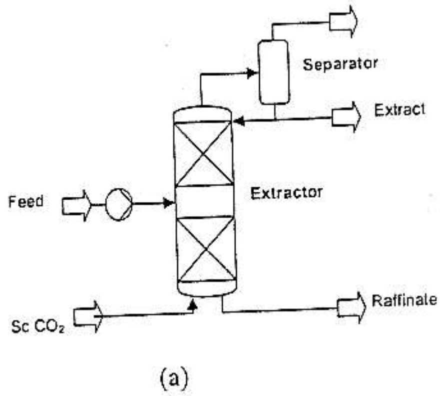
Removal of FFA from Palm Oil

Prior to the simulation of palm oil deacidification column, both the fluid dynamic properties and the phase equilibria were taken into consideration to obtain process conditions that allow the desired separation.

The separation of FFA from TG was conducted in countercurrent column without reflux. Extraction with external was applied particularly for the concentration of high volatile component such as FFA in extract phase product. In this case, the objective of deacidification column was to reduce the FFA content of the palm oil or in other way, concentration of low volatile component in raffinate phase product.

Hydrodynamic in Deacidification Column

The study of the fluid dynamic behavior of the palm oil-supercritical CO_2 system determines the range of temperature and pressure of which countercurrent extraction is feasible. Density differences of the coexisting phases of CPO-CO_2 system determined by [22] at temperature 333-373 K are shown in figure 5. In this study, temperature range of 353-373 K and pressure range of 20-30 MPa was considered



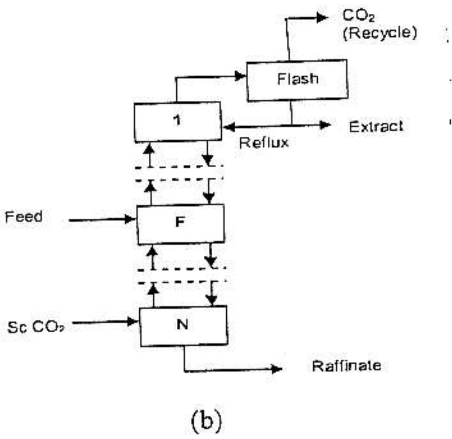


Figure 4: Schematic diagram for SFE process: (a) Countercurrent with reflux; (b) Equilibrium-stage model

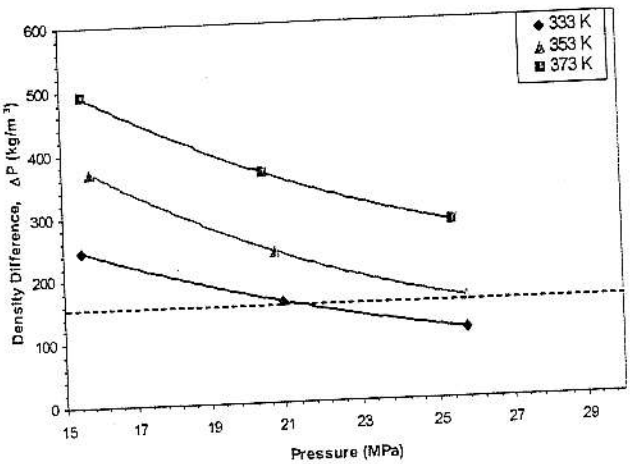


Figure 5: Density difference between CPO and supercritical CO_2 phases

Solubility of CPO in Supercritical CO_2

Solubility in the supercritical phase is most important for the separation and the amount of solvent required; a high loading is thus desirable [23]. Figure 6 shows the calculated solubility of palm oil components in supercritical CO_2 (under equilibrium condition) at various operating conditions. It was observed that at all temperatures, the solubilities of palm oil were found to increase with pressure, which is consistent with the findings of [24].

Generally, the solubility of palm oil in the equilibrium state is higher than that of under continuous processing conditions [1]. Thermodynamic equilibrium cannot be reached in an industrial extractor owing to the finite contact time between the solvent and the solute. 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

$$\eta_E = \frac{\text{Solubility (Continuous processing)}}{\text{Solubility (Equilibrium condition)}} \times 100\% \qquad (8)$$

[25] and [26] suggest a constant extraction efficiency of 60 % with respect to equilibrium value in their work involving a soybean oil–supercritical CO_2 system. In this study, extraction efficiency was defined as a function of S/F ratio. Figure 7 shows the computed extraction efficiency based on the experimental solubility data of [27] for edible oil-CO_2 system. An increase in the solvent- to-feed (S/F) ratio (higher gas flow rates and / or lower liquid feed flow rates) resulted in a decrease in the extract phase loading due to the fact that lower mass of liquid available for complete saturation of gas phase as S/F increases [27].

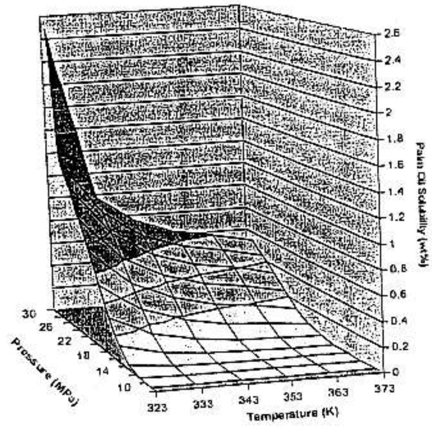


Figure 6: Effect of temperature and pressure on the solubility of palm oil in supercritical CO_2 (S/F ratio of 40)

Figure 8 compares the experimental solubility data of CPO in supercritical CO_2 determined by [1] to that predicted in this work. Extraction efficiency of 60 % was assumed for countercurrent extraction process with S/F ratio of 40. Supercritical CO_2 flow rate required under continuous operation was less, in which 60 % of the solvent that was required under equilibrium condition.

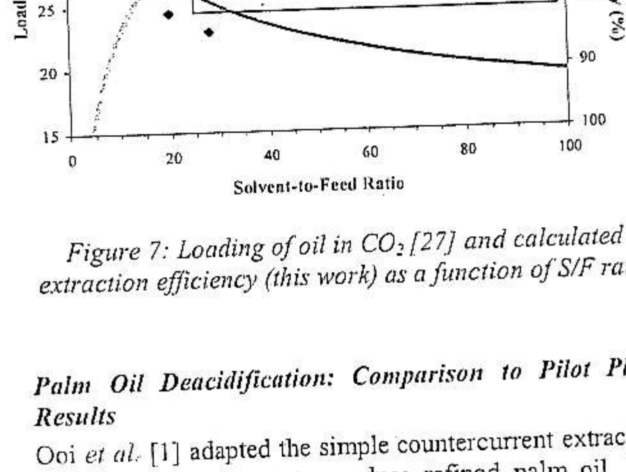


Figure 7: Loading of oil in CO_2 [27] and calculated extraction efficiency (this work) as a function of S/F ratio

Palm Oil Deacidification: Comparison to Pilot Plant Results

Ooi *et al.* [1] adapted the simple countercurrent extraction scheme in an attempt to produce refined palm oil. The countercurrent process was performed, in which the CPO was continuously fed into the top of the extractor at a rate of 60 g/h and supercritical CO_2 was pumped into the bottom of the column at a rate of 2400 g/h. A simple extractor was rigorously simulated for the conditions of pilot plant studies reported by Ooi *et al.* [1]. An extraction efficiency of 58 % was assumed. In the simulation run, the

FFA content of CPO is assumed as 2.35 wt% in order to obtain conceptually consistent and reliable results for comparison. Table 3 shows the comparison between simulation results and experimental work by Ooi *et al.* [1]. These results show that a rather low raffinate recovery is obtained using simple countercurrent scheme without reflux stream. The numerical results are in good agreement with experimental data except at 27.4 MPa and 323 K. This might be due to the flooding in the studied packed column as the required density difference of the co-existing phases for the CPO-supercritical CO_2 system was not complied above pressure of 25 MPa at temperature of 323 K, as shown in figure 5.

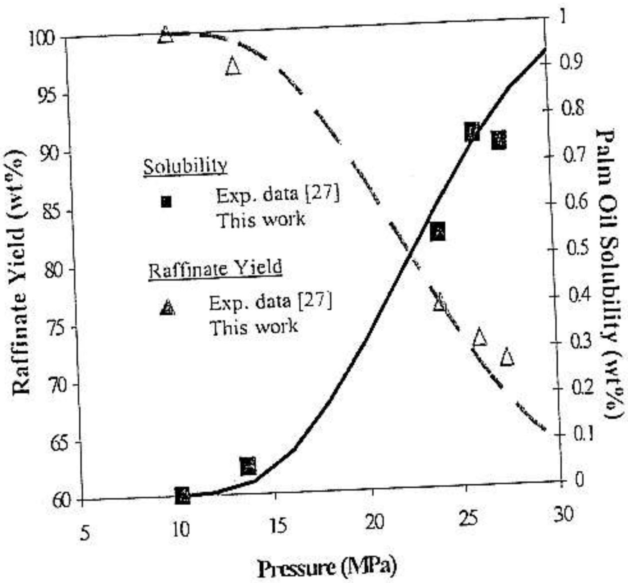


Figure 8: Effect of pressure on the yield of raffinate and solubility of palm oil in supercritical CO_2 at 50 °C (S/F ratio of 40 ± 5)

Gast *et al[9]* performed a pilot study on the separation between the palm oil components in a pilot-plant countercurrent packed column, which consists of both enriching and stripping section. In the experiment carried out by Gast *et al[9]*), CPO feed flux was kept between 71 and 82 g/h and the mass flow rate of supercritical CO_2 was varied between 2.0 and 4.5 kg/h. The same operating conditions as those studied by Gast *et al.* [9] were rigorously simulated for the extractor. A comparison of countercurrent extraction (without reflux) process simulation and experimental results as those obtained by Gast *et al.* [9] at 370 K and 25 MPa, is shown in figure 9.

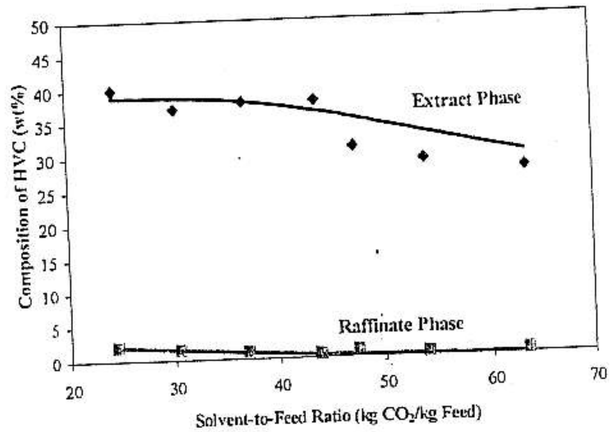


Figure 9: Countercurrent extraction (without reflux) of crude palm oil: Experimental [9] and simulation results (this work)

The content of high volatile components (i.e. FFA and tocochromanols) in the extract and the raffinate were shown in dependence of the solvent-to-feed ratio, respectively. Fatty acids rich fraction was recovered from the top of the column and deacidified palm oil was obtained from the bottom of the column. The predicted behavior of the studied SFE process agrees well with the previous pilot-plant study for the palm oil processing. For the extraction column used in the work of Ooi *et al.* [1], 4-stage column was used in the simulation while a column height of 0.61 m was used in the experiment. It was estimated that the HETS (height equivalent to the theoretical stage) for extraction column was around 0.15 m. In the work of Gast *et al.* [9], 8-stage was required for the simulation which corresponds to a HETS of 0.5 m, as a column height (stripping section) of 4 m was used in the pilot study.

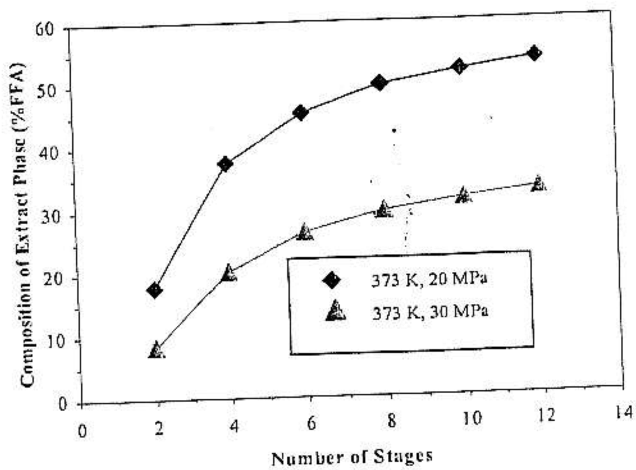


Figure 10: Effect of stage number on the separation behavior as a function of S/F ratio

Table 3: Comparison of experimental [1] and simulation results (this work) for countercurrent palm oil processing at 50 °C

	FFA Content of the Raffinate							
Pressure (MPa)	27.4		24.0		13.7		10.3	
S/F Ratio	62.8		58.2		88.7		40.0	
	Experimental Data	Simulation	Experimental Data	Simulation	Experimental Data	Simulation	Experimental Data	Simulation
FFA (%)	0.25	0.13	0.19 ± 0.01	0.23	1.21	1.43	2.02	2.33
Carotene (ppm)	-	865	690 ± 10	735	-	549	-	540
Yield (%)	72.0	50.45	68.5 ± 3.0	64.26	98.0	98.2	99.5	99.98
Extraction Efficiency* (%)	-	57	-	58	-	53	-	63

Evaluation of Separation Performance

Once the feasible operating conditions phase equilibria were determined, preliminary evaluation of separation process parameters such as number of stages, solvent-to-feed ratio, product purity and yield was performed using the Aspen Plus® 10.2.1 process simulator. The primary function of deacidification column is to produce a refined quality palm oil (in the raffinate phase) with FFA content of less than 0.1 wt%. 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.

The proposed SFE process was rigorously simulated for the operating condition of 370 K and 20-30 MPa. Figure 10 shows the effect of stage number on the separation behavior for the CPO mixture as a function of S/F ratio for the production of refined palm oil. CPO feed was introduced into the top of the column. For a given operation, the separation performance of FFA removal was improved with increase in the stage number. Figure 11 shows the effect of S/F ratio on the product recovery in the raffinate phase. Recovery of refined palm oil was found gradually decreasing with increase in the S/F ratio.

Proposed Palm Oil Deacidification Process

In this study, the removal of FFA from CPO with supercritical CO_2 was studied using simple countercurrent column without reflux. This is due to the fact that the objective of deacidification column is to produce refined quality palm oil with maximum recovery of palm oil. A 12-stage deacidification column was simulated based on equilibrium stage model with the aid of Aspen Plus® 10.2.1. Table 4 shows the input and results of the simulation.

Flow Scheme of An Integrated SFE Process for Palm Oil Processing

Summarizing the results of the previous section, the basic conceptual structure of an integrated extraction-separation process can be outlined as presented in figure 12. CPO (FFA content of 4.5 wt %) was introduced into deacidification column with partial extract reflux. The raffinate phase from deacidification column consists of refined palm oil with FFA content less than 0.1 wt %. The extract phase, which contains mainly FFA and tocopherols, was treated in a similar column, enriching column to produce enriched tocopherol fraction.

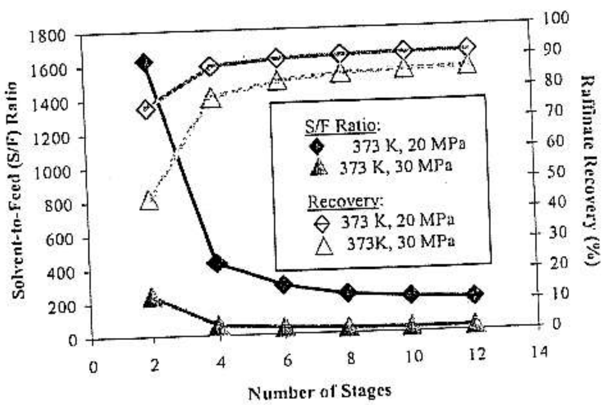


Figure 11: Effect of S/F ratio on the product recovery

Table 4: Simulation results of countercurrent deacidification column based on equilibrium stage model

	PALM-OIL	SC-CO2	EXTRACT	RAFINATE
Mass Frac				
TRIPALM	.4652885	0.0	.4542821	.4602703
TRIOLEIN	.4881715	0.0	4.95739E-3	.5313843
TOCOPHRL	1.00000E-3	0.0	4.61564E-3	6.76626E-4
CAROTENE	5.40000E-4	0.0	1.47698E-4	5.75082E-4
FFA	.0450000	0.0	.5359971	1.09366E-3
CO2	0.0	1.000000	0.0	0.0
Total Flow kmol/sec	.0774187	118.1555	.0122001	.0652195
Total Flow kg/sec	60.00000	5200.000	4.925500	55.07478
Total Flow cum/sec	.0438504	9.976305	4.57875E-3	.0385093
Temperature K	373.0000	373.0000	383.2644	369.4678

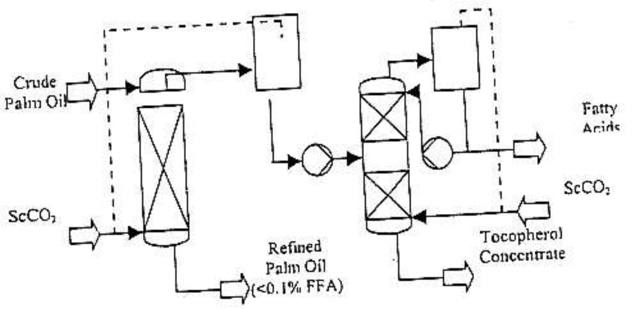


Figure 12: Conceptual process flowsheet for the integrated deacidification-enrichment process with supercritical CO_2

Conclusions

The great variety of separation problems calls for suitable modeling and simulation tools for process synthesis and design. The development of a new flowsheet model for palm oil refining using SFE began with the synthesis of a conceptual flowsheet structure to recover high purity palm oil and its minor components. Next, phase behavior of palm oil with supercritical CO_2 was observed using the RKA equation of state thermodynamic model available in the Aspen Plus® process simulation package. The application of temperature-dependent interaction parameters extended the predicting capability of the developed thermodynamic model. The preliminary process design for the production of refined palm oil using supercritical CO_2 had been successfully constructed and simulated using Aspen Plus® to evaluate the separation performance.

The steady state simulation successfully demonstrated the conceptual feasibility of the alternative method for the recovery of refined quality palm oil while maintaining the high value β-carotene, and at the same time, recovering tocopherols. A two-stage process was found to be suitable in order to enrich tocopherols and to remove the FFA from CPO using supercritical CO_2 as solvent. In the first extraction column, α-tocopherol and FFA were separated from palm oil TG and β-carotene. The content of FFA of palm oil was reduced from 4.5% to 0.1%. β-carotene generally remains in the oil phase. The extract phase consisting mainly FFA and α-tocopherol was found to be suitable for additional processing. Subsequently, the

It is envisioned that the development of the new, intensified and simpler palm oil refining process that is based on SFE technology can overcome the limitations of the existing technology for palm oil refining apart from making the refining process drastically simpler along with the realization of the potentially profitable opportunities in the production of high added value products from oils and fats.

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