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SEPARATION OF SATURATED AND UNSATURATED FATTY ACIDS FROM PALM FATTY ACIDS DISTILLATES IN CONTINUOUS MULTISTAGE COUNTERCURRENT COLUMS WITH SUPERCRITICAL CARBON DIOXIDE AS SOLVENT: A PROCESS DESIGN METHODOLOGY[1]

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SUMMARY

In this work the separation of multicomponent mixtures in counter-current columns with supercritical carbon dioxide has been investigated using a process design methodology. First the separation task must be defined, then phase equilibria experiments are carried out, and the data obtained are correlated with thermodynamic models or empirical functions. Mutual solubilities, K_i-values, and separation factors a_{ij} are determined. Based on this data possible operating conditions for further extraction experiments can be determined. Separation analysis using graphical methods are performed to optimize the process parameters. Hydrodynamic experiments are carried out to determine the flow capacity diagram. Extraction experiments in laboratory scale are planned and carried out in order to determine HETP values, to validate the simulation results, and to provide new materials for additional phase equilibria experiments, needed to determine the dependence of separation factors on concetration. Numerical simulation of the separation process and auxiliary systems is carried out to optimize the number of stages, solvent-to-feed ratio, product purity, yield, and energy consumption. Scale-up and cost analysis close the process design. The separation of palmitic acid and (oleic+linoleic) acids from PFAD-Palm Fatty Acids Distillates was used as a case study.

Keywords: VLE, High pressure, Separation analysis, Hydrodynamics, Experiments, Multistage extraction, Process development, Fatty acids.

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1 □ PROCESS DESIGN METHODOLOGY

The design and evaluation of separation processes are commonly carried out to obtain optimal separation devices and operating conditions which satisfy some economical criteria. In counter-current gas extraction the trade-off between the energy, solvent and investment costs operates as the decision factor on the process design. In order to optimize the design of counter-current multistage supercritical gas extraction process, a hierarchical approach was suggested [1]. This process design methodology is presented in a systematic form as a logical sequence of procedures, which are described as follows

Process Design Methodology
Separation task
Phase equilibria
Separation Analysis
Hydrodynamic experiments
Separations experiments
Numerical Simulation
Scale-up
Cost Analysis

2 □ SEPARATION TASK

The separation task (component(s) to be enriched, product purity, and percentage recovery) can be completely defined before information concerning the knowledge of phase equilibria of the liquid and gas phases is available, but not the separation sequence. In general the separation task becomes very complex, if separation of multicomponent mixtures into several products is the target.

3 □ PHASE EQUILIBRIA

First, phase equilibria measurements for the multicomponent mixture + supercritical fluid system have to be carried out over a wide range of temperature and pressures in order to yield the mutual solubilities (especially that in the gaseous phase), the composition of the coexisting phases, the distribution coefficients, separation factor, as well as to ensure a two phase region (liquid, and gas), which is of fundamental importance in counter-current extraction. For vapor-liquid equilibrium, the so-called distribution coefficient is defined for each component i as follows

$K_i = Y_i/X_i$ (1)

where Yi is the mass or mole fraction in the gas phase, and Xi the mass or mole fraction in the liquid phase.

The two phase region can be determined observing the phase transitions in a high pressure equilibrium view cell by means of optical methods, or by extrapolating experimental data with thermodynamic models (equations of state). The correlation of experimental data using thermodynamic models is also important in order to provide a general view of the phase behavior of the system, and to diminish the number of experiments [1].

Once information concerning the distribution coefficients is available, it is usual to reduce the multicomponent mixture to a quasi-binary system in order to simplify the separation analysis, as well as to estimate quantitatively the component splits in the overhead and bottom products. After defining the pseudo components (LK = light component and HK = heavy component), a dimensionless parameter, called separation factor is defined as follows

$a_{ij} = K_i/K_j$ (2)

This factor characterizes the relative volatility of two chemical species [2]. Notice that no general rule exists, which can be applied to describe the mixture as a quasi-binary system. This simplification depends on the desired separation task, the Ki-values of each component, chemical structure of the major components, and on the molar composition of each component of the mixture, thus every system must be analyzed separately. In general compounds of homologous series can be simplified as pseudo components, and chemically different compounds are better treated as key components [1].

In multistage gas extraction using supercritical fluids, it is very important to find a compromise between the solubility in the supercritical phase, the separation factor, and the density of the supercritical phase, because these variables are directly related to the amount of solvent needed to assure a desired separation task (column diameter & compression cost), the number of stages (column height), and the flow capacity diagram (flooding) respectively. There are situations, where points on the P-XY diagram associated with a) high separation factor or b) high separation factor and high solubility have to be discharged. At a first glance, this decision seems to be inconsistent, because high separation factor and high solubility are important factors in counter-current multistage supercritical extraction. But, if the solubility of the mixture at the gas phase is very low in case a) or the density of the supercritical phase is too high to assure counter-current flow in case b) , then the decision is correct. Based on this two distinct situations, one can say that in multistage gas extraction conditions of state leading to high separation factor or high separation factor and high solubility do not have be selected in general as optimal points to further extraction experiments. Both constraints (solubility of the mixture at the gas phase, and density of the gas phase) may be used to select preliminary feasible extraction points or regions. These points must be determined before experiments with enriched mixtures are carried out. As a consequence a drastic diminution on the number of phase equilibria experiments can be achieved. This preliminary analysis is illustrated in *Figure 1*.

Figure 1 shows the existence of two constraint lines (flooding and solubility ® dot lines). Solubilities lower than 2% [wt] may be avoided if the development of an industrial process is the target, because the process would need a large amount of solvent (high compression cost) to assure the desired separation task, and a column with higher internal diameter would be necessary. The solubility can be enhanced by increasing the density of the solvent, but this limits the counter-current flow in the column, so that the density differences Dr = (r_L-r_G) must always be higher than 150 kg/m3 [2] in order to avoid flooding (the density of the liquid phase varies in the range r $_L$@ 850-900 kg/m^3). Another way to avoid flooding is to increase the operating temperature. It is easy to conclude by analyzing figure 1, that there is only a small region of possible operating conditions which leads to economical process.

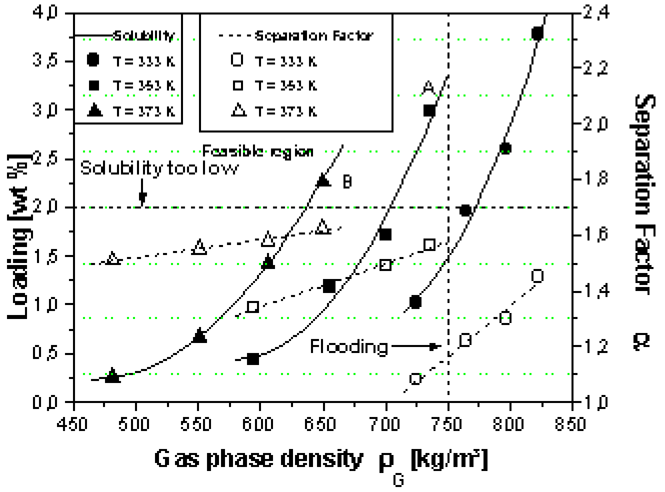

FIGURE 1. Loading and separation factor as a function of the density in the gaseous phase for the system PFAD/SC-CO2.

After determining the region in *Figure 1* containing the feasible points (A, and B) new phase equilibria experiments have to be carried out covering a large concentration spectrum (0-100%) of the key or pseudo components. This enables the description of the separation factor as a function of the composition of the major components in the liquid phase. The information above is useful to analyze the separation process by means of the Ponchon-Savarit method. There are two ways to produce mixtures enriched in one or more target components:

I. Separation experiments are carried out in a counter-current column in order to obtain top and bottom products enriched in one or more pseudo components.

II. Model mixtures can be synthesized if possible. This procedure can only be applied for mixtures containing few components. These components with purity higher than 98%, must also be available at the market.

4 □ EVALUATION OF SEPARATION PROCESS PARAMETERS BY USING GRAPHICAL METHODS

Once the feasible points a, and b) are determined, and information on the concentration dependence of the separation factor a_{ij} is available, separation analysis or preliminary evaluation of separation process parameters such as, number of theoretical stages, solvent-to-feed ratio, reflux ratio, product purity, and percentage recovery or yield can be performed using chemical engineering methods such as McCabe-Thiele (solvent-free basis) and Ponchon-Savarit (solvent basis) without carrying out separation experiments.

4.1 – McCabe-Thiele Method

The application of the McCabe-Thiele method in multistage supercritical gas extraction involves only the simultaneous solution of one equilibrium relation and material balance equations for the light pseudo component. This method considers the mixture as a pseudo-binary system. The operating lines are obtained without considering the solvent (solvent-free basis) as follow

Equilibrium line:

$$Y^{*} = a_{ij} X^{*} /(1+(a_{ij}-1) X^{*}) \quad (3)$$

Enriching section:

$$Y = [1/(v+1)] X+[v/(1+v)] X_{E} \quad (4)$$

Stripping section:

$$Y = [(F+r)/(E+r)] X-R X_{R}/(E+r) \quad (5)$$

where X* and Y* are the equilibrium concentrations of the light component, F the feed, E the extract, R the raffinate, n the reflux ratio, r the reflux, X_E and X_R the mass or mole fraction of the light component in the extract and raffinate respectively. The assumption of constant molar overflow and constant solubility of the mixture at the gas phase contributes to the low accuracy of the McCabe-Thiele method [3]. The first assumption is valid if the solubility of the mixture at the gas phase is low, which is reasonable in gas extraction using supercritical fluids. The second assumption can be overcome writing the separation factor as a function of the concentration of the light component at the liquid phase.

4.2 – Ponchon-Savarit Method

The application of the Ponchon-Savarit method for stage-to-stage calculations is restricted to binary distillation, and ternary extraction systems (solvent + pseudo-binary mixture) [3]. To construct a Ponchon-Savarit diagram for extraction problems it is convenient to use the *Jänecke coordinates* (N_E, N_R, Y_1, and X_1), which are defined as follows

$N_E = (Y_{Solvent}/Y_{Mixture})_{Gas\ Phase}$ (6)

$N_R = (X_{Solvent}/X_{Mixture})_{Liquid\ phase}$ (7)

$Y_{Mixture}+Y_{Solvent} = 1$ (8)

$X_{Mixture}+X_{solvent} = 1$ (9)

$Y_{Mixture} = Y_{LK}+Y_{HK}$ (10)

$X_{Mixture} = X_{LK}+X_{HK}$ (11)

$Y_1 = Y_{LK}/(Y_{LK}+Y_{HK})$ (12)

$X_1 = X_{LK}/(X_{LK}+X_{HK})$ (13)

First the mass of solvent per unit mass of solvent-free material for the extract and raffinate N_E, N_R are plotted as the ordinate versus the concentration Y_1, X_1 as abscissa on a solvent free basis. After that, the net flow points P_E and P_R have to be determined. This two points are calculated using the same procedure as in distillation process.

$P_E = (R/E)\ (N_E-N_R)+N_E$ (14)

$P_R = (N_R)-S/R$ (15)

where S is the solvent flow rate.

Notice that phase equilibrium data on the region near Y_1 @ 0 and Y_1 @ 1 has to be carefully analyzed, because the curvature at the end points of this diagram has a great influence on the number of theoretical stages. Curves at both ends of the Jänecke diagram are associated with a jump on the number of theoretical stages [4]. Therefore, It a product of high purity is the target, many experimental points must be available in the region near Y_1 @ 0 and Y_1 @ 1.

4.3 – Calculation of the number of stages N_{th}

For a given separation task, it is normally known the feed flow rate, and the mass fraction of the light pseudo component in the feed, extract and raffinate products. Therefore, the only remaining free design variables are the number of theoretical stages , the solvent flow rate, and the reflux ratio. Determining the values of N_{th} (number of theoretical stages) and S (the solvent flow rate) is an economic decision. A high value of N_{th} (more equilibrium stages) leads to a low solvent flow rate, thus reducing the operating cost and keeping the subsequent investment cost at maximum. However, the extraction column itself will need more stages to offset the lower solvent flow rate. Conversely, a low N_{th} leads to high S, so that columns with higher nominal diameter are needed. A smaller column reduces the investment cost, but keeps the operation cost (compression cost) at maximum.

Figure 2 illustrates the relationship between the number of stages N_{th}, the reflux ratio n, and the solvent-to-feed ratio S/F for the separation of palmitic and (oleic+linoleic) acids from PFAD in counter-current columns with SC-CO_2 for the defined separation task: (LK ® palmitic acid (C16); $X_{F,LK} = 0.48$; $X_{E,LK} = 0.90$ and 0.99; and $X_{R,LK} = 0.01$). With increasing reflux ratio, decreases the number of stages, and increases the solvent-to-feed. The influence of the product purity of palmitic acid on the number of stages is also presented in *Figure 2*. The results show that the number of stages increases with increasing product purity (90% ® 99%) holding the reflux ratio costant.

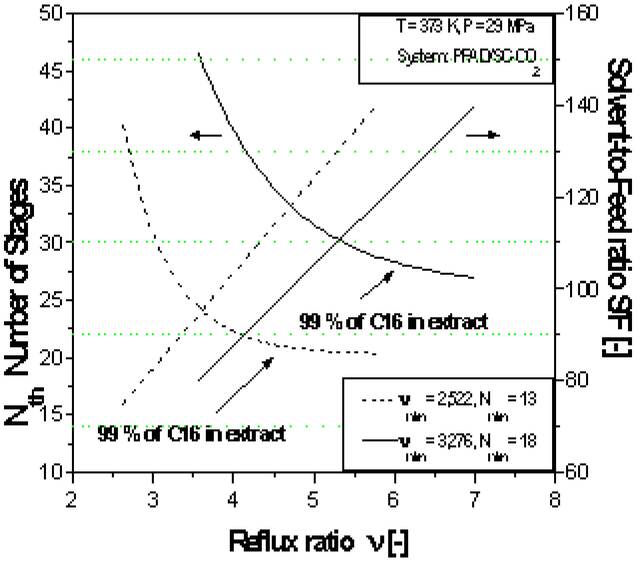

FIGURE 2. Number of stages and solvent-feed ratio as a function of reflux ratios of point B. P = 29 MPa, T = 373 K.

Figure 3 illustrates the evaluation of process parameters for both feasible points A and B. The results show that the minimum reflux ratio n_{min} and minimum number of theoretical stages $N_{th,min}$ of both points are equivalent. Thus a cost analysis must be performed in order to chose what operating conditions provide the optimal point.

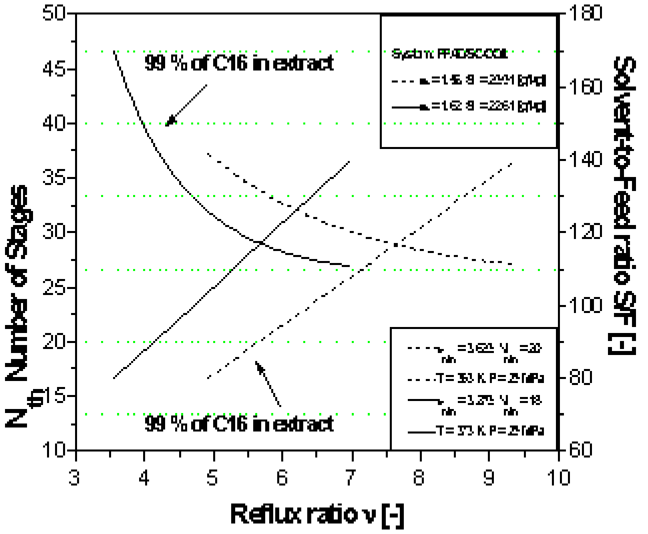

FIGURE 3. Evaluation of separation proces parameter of both points A and B. P = 29 MPa, and T = 353-373 K.

Figure 4 illustrates the graphical calculation of the number of stages by using the McCabe-Thiele method for the same conditions of state of point A, and 99% purity of palmitic acid in the extract.

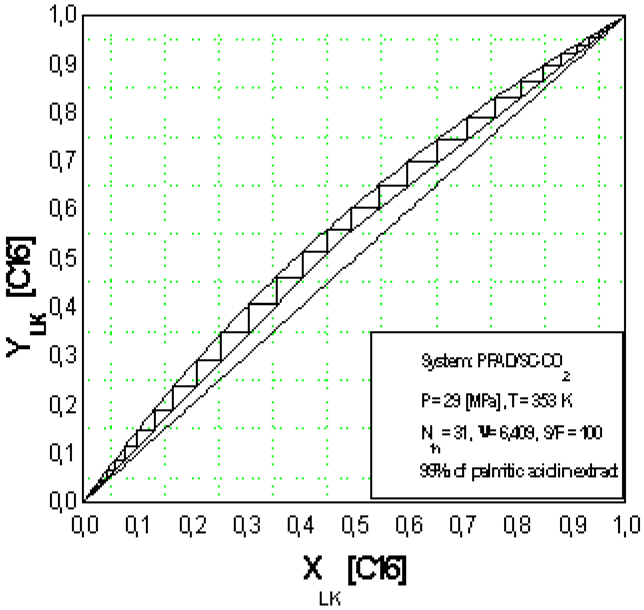

FIGURE 4. Graphical multistage calculations of the number of stages by the McCabe-Thiele method. P = 29 MPa, and T = 353 K.

As discussed on the McCabe-Thiele method, the assumption of constant solubility of the mixture in gas phase contributes to the low accuracy of the method. In real separation problems the separation factor has to be described as a function of the concentration of the light component in the liquid phase. This problem can be analyzed by determining the sensitivity of the number of stages (N_{th}) to changes in the separation factor along the column [5]. Let a^* be defined as a vector of the changes of the separation factor of the key components of the mixture for a wide range of values:

$$a^* = [a_1, a_2, a_3, a_4, \ldots\ldots, a_n]^{1/n} \quad (16)$$

where 1, 2, 3, .., n are the 1st, 2nd, .., nth stage on the column and a_i the respective separation factors. Then graphical calculation applying the McCabe-Thiele method is performed using the same conditions of *Figure 4*.

Figure 5 illustrates the sensitivity of the number of stages to the reduction in the separation factor. Thus a small reduction in the separation factor leads to a large variation on the number of stages. In real separation processes, the separation factor varies along the column, so that this analysis was carried out to show the importance of correlating the separation factor as a function of the light component composition in the liquid phase.

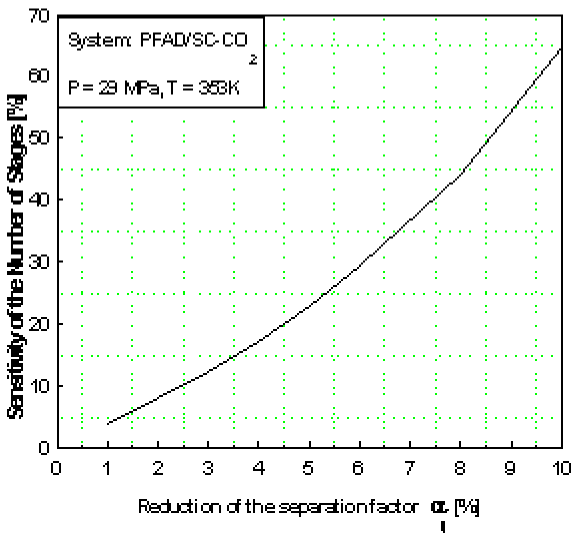

FIGURE 5. Sensitivity (increasing) of the number of stages on the reduction of the separation factor a_{ij} for the same conditions of *Figure 4*.

Figure 6, illustrates the graphical calculation of the number of stages by using the Ponchon-Savarit method for the same conditions of *Figure 4*.

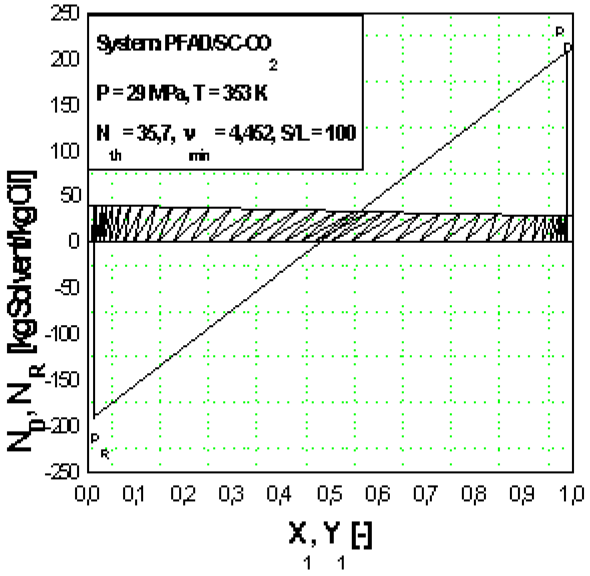

FIGURE 6. Graphical multistage calculations of the number of stages by the Ponchon-Savarit method. P = 29 MPa, and T = 353 K.

As discussed on the Ponchon-Savarit method, determination of phase equilibria on the regions near Y_1 @ 0 and Y_1 @ 1 is of fundamental importance, because a great number of stages are present between the regions $0 < Y_1 < 0{,}1$ and $0{,}90 < Y_1 < 1$, as can be seen in *Figure 6*.

5 □ HYDRODYNAMIC IN COUNTER CURRENT COLUMNS

The process of flooding in counter-current extraction devices is an interesting and important phenomena. It occurs for counter-current flow of gas and liquid where the liquid flows downward and the gas upwards, so that for each gas flow rate a maximum value of the liquid film flow rate exists that can move downward counter-current to the gas flow [6].

The range between the loading and flooding points is of fundamental importance in the design and operation of counter-current multistage devices. For the determination of the flow capacity diagram, experiments concerning the hydrodynamics of the counter-current process must be carried out.

Knowledge of the flow capacity diagram (loading and flooding regions) for the system multicomponent mixture + SC-CO_2 allows to predict for specific S/L ratios, if counter-current flows still exists or not for a desired separation task. The flow capacity diagram is determined by plotting the flow capacity factor C as a function of a dimensionless flow parameter y given by the equations

$$C = U_G \sqrt{\frac{\rho_G}{(\rho_L - \rho_G)}} \qquad (17)$$

$$\psi = \frac{L}{S}\sqrt{\frac{\rho_G}{\rho_L}} \qquad (18)$$

where r_L and r_G are the coexisting liquid and gas phase densities, L the feed flow rate (feed+reflux), S the solvent flow rate, and U_G the solvent superficial velocity.

Flooding, pressure drop, and densities of the coexisting phases have been determined in a hydrodynamics apparatus, for more information see [2].

5.1 – Experimental determination of the densities of the coexisting phases

Among the most important hydrodynamic variables such as solvent flow rate, liquid flow rate, densities of the coexisting phases, and others, the density difference of the coexisting phases plays a central role as a limiting factor to assure counter-current flows.

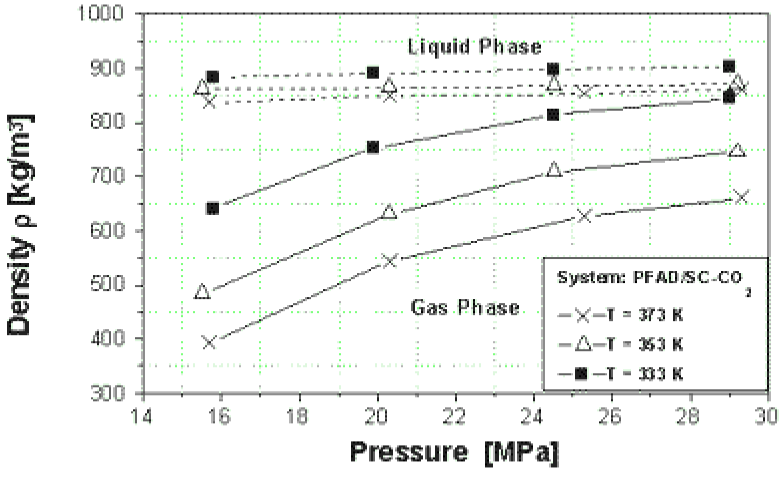

FIGURE 7. Densities of the coexisting phase for the PFAD/SC-CO_2 system.

Figure 7 illustrates the behavior of the densities of the coexisting phases over a wide range of temperatures and pressures.

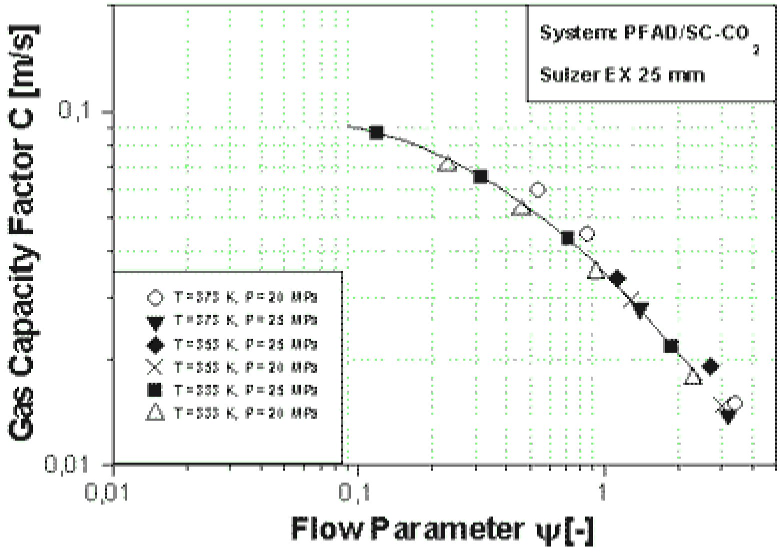

FIGURE 8. Flow capacity diagram for the PFAD/CO_2 system.

Figure 8 illustrates the flow capacity diagram for the PFAD/SC-CO_2 system over a wide range of temperatures and pressures. The flooding line depends mainly on the packing geometry, and on the density difference of the coexisting phases. In this experiments a structured packing of the type EX (Sulzer, Chemtech) with 25 mm internal diameter and »1730 m^2/m^3 specific area was used.

Once the flow capacity diagram is available, it is possible to transpose the experimental data from the diagram of *Figure 8* to columns with different cross sectional areas, but not for different packings.

5.2 – Calculation of column diameter

If, for a desired separation task, the calculated solvent-liquid ratio assures counter-current flow, than is easy to determine the column internal diameter. In general counter-current column operates at 75-80 % of flooding conditions. The internal diameter of a packed column is calculated following the procedures below [8]

$C_{\text{Operation}} = 0.75\text{-}0.8\ C_{\text{Flooding}}$ (19)

where C_{Flooding} is obtained from the diagram of *Figure 8*.

$$C_{Flooding} = \frac{S}{A\rho_G}\sqrt{\frac{\rho_G}{(\rho_L - \rho_G)}} \quad (20)$$

where A = $pfc^2/4$, and p f_c the colum diameter

$$\phi_c = \sqrt[4]{\frac{\rho_G}{(\rho_L - \rho_G)}}\sqrt{\frac{3S}{3600C_{operation}\pi\rho_G}} \quad (21)$$

6 □ SEPARATION EXPERIMENTS

Based on the optimization of process parameters by means of graphical methods and hydrodynamic experiments (flow capacity diagram), separation experiments in a laboratory countercurrent column can be planned in order to obtain first estimates of the HETP values, to provide new enriched mixtures for further phase equilibria measurements, to predict process performance, and to validate the simulation results by using graphical methods.

HETP values are determined based on the height of the column H and the number of theoretical stages N_{th} obtained from separation experiments.

$HETP = H/N_{th}$ (22)

The height of an equivalent theoretical stage can also be determined by using the NTU-HTU method. In this case the overal mass transfer coefficient of both liquid and gas phases K_L and K_G must be available. The accuracy of the NTU-HTU method is inferior compared to those of the McCabe-Thiele and Ponchon-Savarit methods, because the K_L and K_G values are determined by empirical correlations, and the equilibrium line is assumed to be linear.

Experiments were performed in a ladoratory column with 17,5 mm internal diameter and 7000 mm height, that accommodate metal gauze-type packing (Sulzer EX, specific area » 1730 m^2/m^3) at T = 353 K and P = 26 MPa.

Figure 9, shows the dependence of the number of stages on the reflux ratio for differents (LK/HK) ratios in the feed, where palmitic acid is the light component and oleic+linoleic acids the heavy component. The number of stages decreases with increasing reflux ratios. Lower (LK/HK) ratios in the feed lead to higher number of stages.

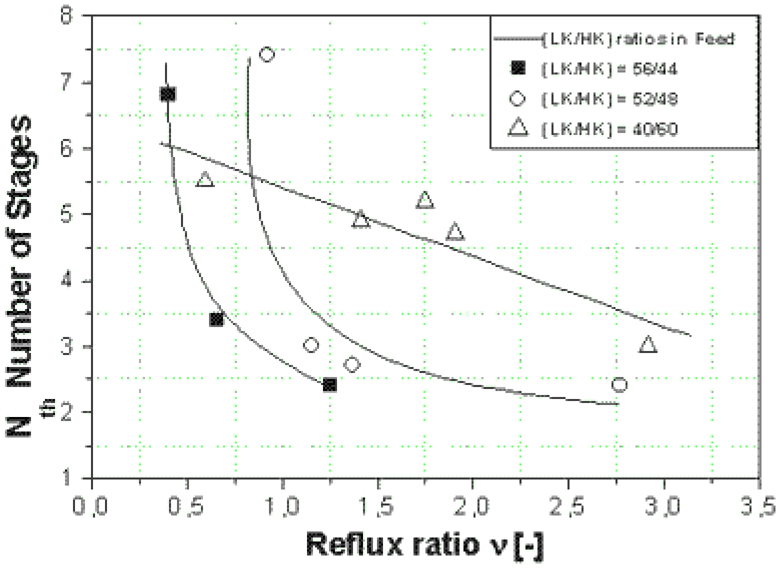

FIGURE 9. Number of stages as a function of reflux ratio for different (LK/HK) ratios in the feed.

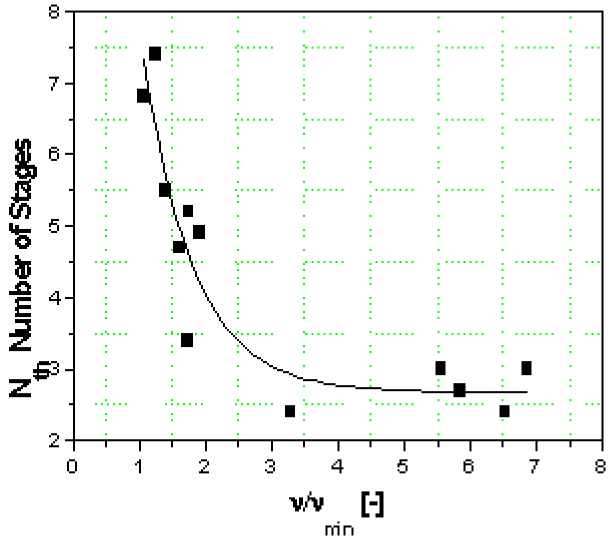

FIGURE 10. Number of stages as a function of the ratio (n/n_{min}) for all experimental points.

Figure 10 gives information on the dependence of the number of stages on the ratio (n/n_{min}) for all experiments. It is easy to observe that the number of stages decreases with increasing (n/n_{min}) ratios. The separation parameter (n/n_{min}) ratio is an absolute variable which has been used in this separation analysis, because some process conditions such as mass flow rate of feed, solvent flow rate, and reflux ratio were not hold constant. In addition feed with different (LK/HK) ratios has been used.

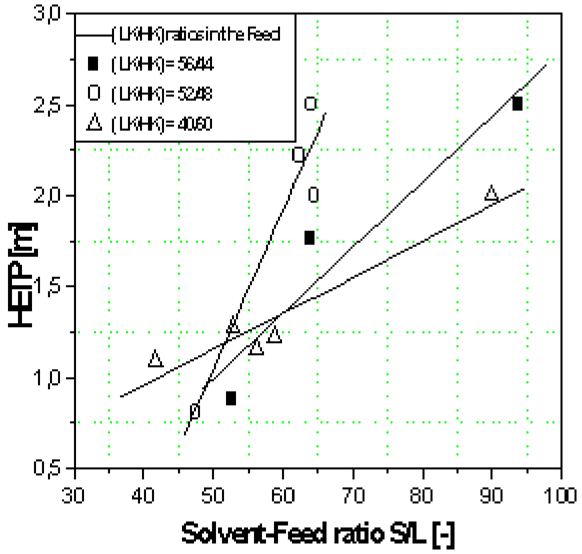

FIGURE 11. HETP values as a function of the solvent flow rate for different (LK/HK) ratios in the feed.

Figure 11, shows the dependence of the HETP on the solvent flow rate. The results show that the HETP increases with increasing solvent flow rate. HETP values stay within the range (1 ® 2,5). High values of HETP obtained by experiments depends not only on process conditions, but also on transport properties, particularly the viscosity. Palm fatty acids distillates is a very viscous fluid (PFAD is solid at temperatures lower than 38°C), and high viscous fluids inhibits and diminish the mass transfer of palmitic acid molecules within the gaseous phase. HETP is strongly dependent on the system under investigation, the method used to determine the number of stages (McCabe-Thiele, Ponchon-Savarit, NTU-HTU, Approximate methods: Fenske, Gilliland), operating conditions, and the type of the separation equipament [1].

Figure 12 illustrates the variation of the yield or percentage recovery of component i in the extract and raffinate with the extract-raffinate ratio. The yield or percentage recovery is defined as follow

$\text{Yield}_{\text{Extract}}$ [%] = 100 ($D\, X_{D,i}/F\, X_{F,i}$) (23)

$\text{Yield}_{\text{Raffinate}}$ [%] = 100 ($R\, X_{R,i}/F\, X_{F,i}$) (24)

The results show that the yield in the extract increases, while that in the raffinate decreases with increasing extract-raffinate ratio. It is easy to conclude by means of an overal and a component balance for the light component that $\text{Yield}_{\text{Extract}} + \text{Yield}_{\text{Raffinate}} = 100$.

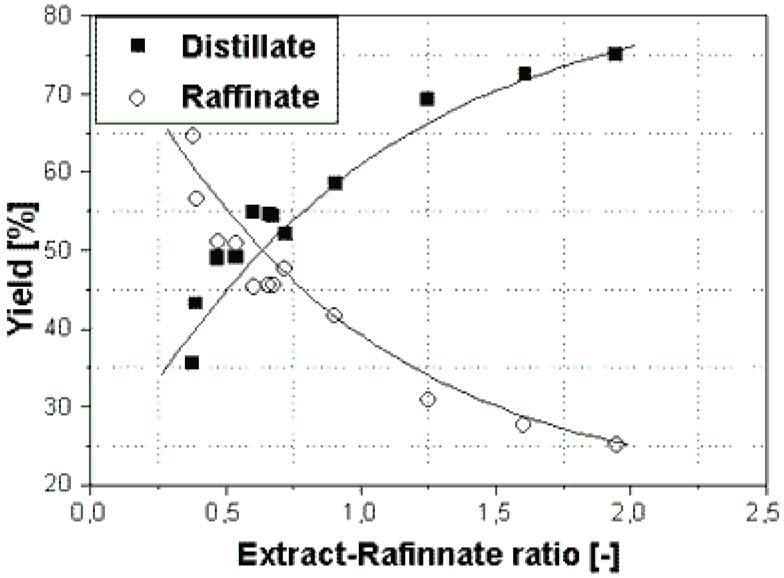

FIGURE 12. Yield or percentage recovery as a function of the extract-raffinate ratio for all experimental points.

Figure 13 shows the variation of the yield or percentage recovery and the enriching of the light component with the distillate-raffinate ratio. The enriching of the light component (palmitic acid ® C16) which is defined as follow

Enriching of LK[%] = 100 $X_{D,LK}/X_{F,LK}$ (25)

decreases with increasing extract-raffinate ratios, while the yield or percentage recovery increases with increasing extract-raffinate ratio. We have introduced this separation parameter, because experiments were carried out with different (LK/HK) ratios in the feed, and the product purity is a function of the (LK/HK) in the feed, but the enriching grad of the light component is not a function of the (LK/HK) in the feed. Notice that the intersection of lines in the *Figure 13*, generates a point of optimum, where the yield and the enriching exhibits its maximum values. After the intersection point, an increasing on the yield leads to a decreasing on the enriching of palmitic acid in the extract, and before the intersection point, an increasing on the enriching of palmitic acid in the extract leads to a decreasing on the yield.

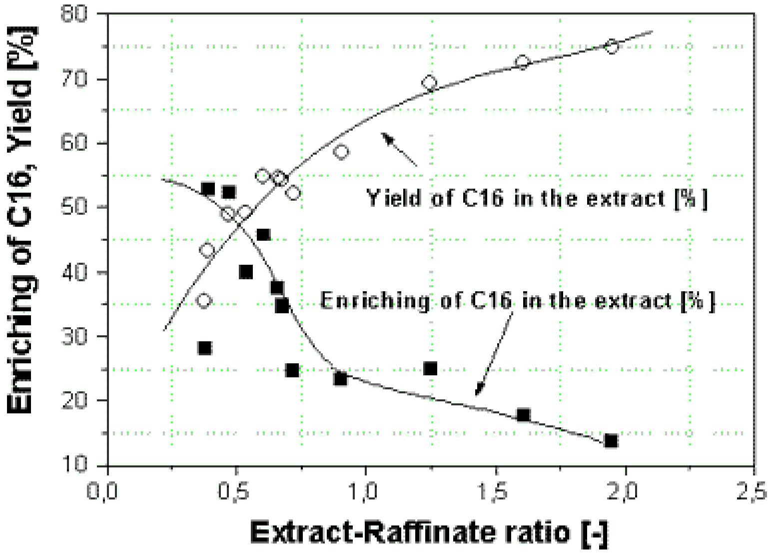

FIGURE 13. Yield and enriching of the light component in the extract as a function of the extract-raffinate ratio for all experiments.

Figure 14 gives the dependence of the product purity of the extract and raffinate as a function of the reflux ratio. The results shows that, the product purity in the extract increases smoothly with increasing reflux ratio, and that of the raffinate decreases in the same fashion with increasing reflux ratios. This is because of the small variation in the reflux ratio (0,3 < n < 2,8)

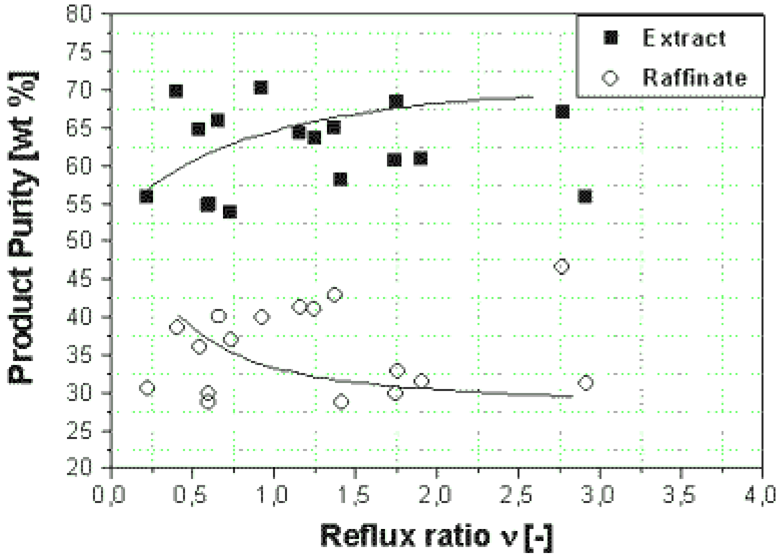

FIGURE 14. Product purity as a function of the reflux ratio for all experiments.

Figure 15 illustrates the variation of the HETP values as a function of the liquid flow rate , holding the solvent flow rate constant. The results show that HETP values decreases with increasing liquid flow rates. At low liquid flow rates the packing surface is not completely wetted which worsens the mass transfer process, conversely an increasing on the liquid flow rate improves the wetting, and therefore the mass transfer process.

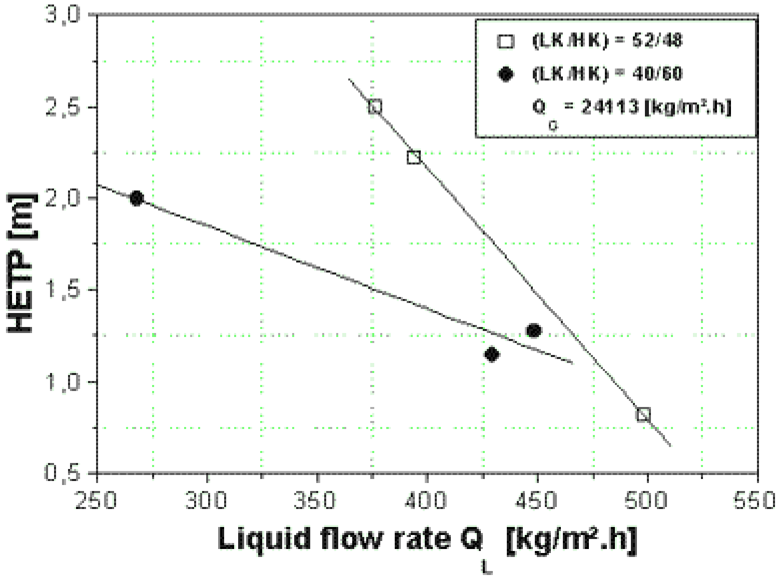

FIGURE 15. HETP as a function of the liquid flow rate.

7 □ NUMERICAL SIMULATION OF SEPARATION PROCESS

Graphical methods are suitable only for preliminary design analysis [2]. The final design of counter-current multistage supercritical gas extraction processes requires rigorous determination of stream flow rates, stream compositions, concentration profiles along the column, temperatures, and pressures at each stage. Unfortunately these relations are nonlinear algebraic relations, that interact strongly, which cannot be achieved by simple methods.

New process simulators (e.g. Aspen plus) include thermodynamic and physical properties, unit operations, hydrodynamics, cost analysis, optimization, and user models, among others. It is the flexibility of connecting different models, that makes process simulators a powerful numerical tool to perform complete process design analysis.

For multistage supercritical gas extraction a user-defined model must be implemented, in order to perform numerical simulations [10]. This user-defined model has an input-file, that needs information about the number of stages, process and operating conditions, empirical correlation for the K_i values as a function of the major components in the liquid phase, the flow rates of extract and raffinate in order to recalculate the feed flow rate ratio, the reflux ratio, and the composition of the product streams. The high performance solution algorithms is based on numerical methods, so that the separation parameters are continuously refined to produce results more confident with the reality, compared to stage calculations by using graphical methods.

8 □ SCALE-UP OF COUNTER-CURRENT MULTISTAGE GAS EXTRACTION COLUMNS

In general laboratory scale plants are used to provide preliminary information about the feasibility of the process. Scale-up in chemical process technology makes possible to transpose experimental data obtained in laboratory scale equipment to larger process plants.

Bravo et all [9], proposed a model that can be used to scale-up distillation column containing structured packing. The model is described as follow

$$\frac{HETP_1}{HETP_2} = \psi \frac{a_1}{a_2} \left(\frac{U_{G,2}\phi_2}{U_{G,1}\phi_1}\right)^{0,2} \qquad (26)$$

where subscript 1 and 2 are related to the large and small column respectively, U_G is the superficial gas velocity, f is the specific area of the packing, f the internal diameter, and Y is a geometric parameter defined by

$$\psi = (\frac{\varepsilon_2}{\varepsilon_1})^{0,8}(\frac{\sin\theta_2}{\sin\theta_1})^{0,8} \qquad (27)$$

where e is the void fraction of the packing, and q is the angle of inclination of the packing channels with the horizontal. If packing of the same type are to be used, equation (26) can be simplified to give

$$\frac{HETP_2}{HETP_1} = (\frac{S_2\phi_1}{S_1\phi_2})^{0,2} \qquad (28)$$

where S is the solvent mass flow rate. Riha [10] has used the relation below to scale-up the HETP

$$HETP_2 = HETP_1 \exp(0,5(\phi_2 - \phi_1)) \qquad (29)$$

where subscript 1 and 2 are related to the large and small column diameter respectively The correlation proposed by Bravo et all [9] is superior, because not only geometric parameter (diameter) are analyzed, but also the hydrodynamic (solvent mass flow rate).

Figure 16 shows the dependence of the HETP on the column diameter using equations (29). An average value of 1,5 m has been used to illustrate the application of equation on the correlation given by equation (29). The HETP has almost a linear dependence with the column diameter for the Sulzer EX packing.

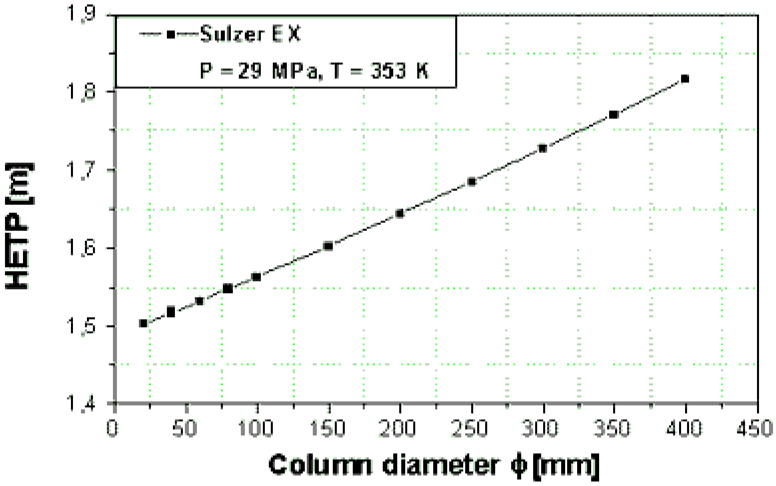

FIGURE 16. HETP as a function of column internal diameter. System:PFAD/SC-CO_2. P= 29 MPa, T = 353 K.

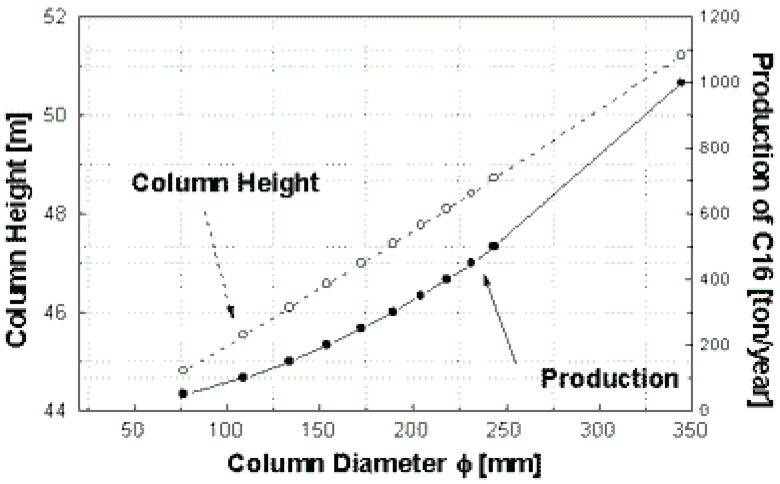

FIGURE 17. Column height and production of palmistic acid as a function of column internal diameter. System: PFAD/SC-CO_2. P = 29 MPa, T = 353 K.

Figure 17 illustrates the project of a large scale process plant to produce palmitic acid of high purity 99 % from palm oil fatty acid distillates using multistage counter-current extraction with supercritical carbon dioxide as a solvent.

Process Plant Scale-up
Process Design Data
Loading: 2.26 [wt%]
Reflux ratio: 7.6
Separation factor: 1.62
$HETP_1$ = 1.5 m
f_1 = 17.5 mm
$HETP_2 = HETP_1 \exp[0,5(f_2\text{-}f_1)$ variable
Product Purity: 99 [wt%]
N_{th}: 29.2
H = N_{th} HETP2 variable
S/L: 118
365 days/year * 24 hours/day

9 □ PROCESS COST ANALYSIS

Cost analysis is a critical step in chemical process design and development. The cost analysis provided information for further decisions, it also predicts if a novel process is feasible from a economical point of view. In countercurrent multistage extraction with supercritical fluids determining the cost of equipment installation, the cost of solvent regeneration, and compression costs is of fundamental importance. Among those, the energy requirement for the recycle of the solvent (operation cost) plays a important role on the investment cost. A cost analysis has been done by Woerlee [11]. Woerlee proposed for the total cost of a column the following relation

$$CF = C_1(C_2 + PV_c) + C_4 a(C_5 + \frac{C_6}{\phi_c})V_c \qquad (30)$$

where P, V_c and f are the column pressure, volume and diameter, $C_1..C_6$ are constants related to the process cost, a the specific area. Equation (30) makes possible to compare SFE with traditional separation process as distillation, liquid-liquid extraction and others.

10 CONCLUSIONS

The increasing interest on processing natural products and severe environmental protection polices has been contributing to the development of novel separation processes. Multistage supercritical gas extraction has been emerged as an alternative to replace those traditional separation process, if separation of thermally labile substances and obtaining of high purity products is the target. Therefore, the systematic engineering analysis presented here can contribute to the consolidation of multistage supercritical gas extraction as a standard separation method in the future.

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