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Process Analysis and Phase Equilibria for the Removal of Chemicals from Fatty Oils Using Near-Critical Solvents

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The use of near-critical CO₂ and propane for the removal of chemicals—pollutants, undesirable or valuable products—from fatty oils is studied. The process conditions are discussed, on the basis of phase equilibrium predictions from a group contribution equation of state. The extension of the equation to cover systems with large differences in molecular size requires the use of revised parameters. With the new parameters, a good correlation of phase equilibrium data for all of the binaries involved in the process was achieved. Distribution coefficients of different chemicals between the oil and solvent phases were predicted, and optimum process conditions were explored. The extraction with propane requires the operation above the lower critical end-point temperature of the binary fatty oil–propane system, to have liquid–liquid or liquid–near-critical fluid phase immiscibility. The process analysis indicates that there are optimum operating pressures that minimize solvent requirements and fatty oil losses in the extract.

Introduction

Natural oils are prone to contamination with liposoluble pollutants. On the other hand, fatty oils may contain some valuable chemicals. The use of CO₂ for the removal of these compounds—hereafter referred as *solutes*—from natural oils is a promising approach. CO₂ is an environmentally benign solvent, and the solubility of fatty oils in liquid or near-critical CO₂ is very low. Propane has a greater solvent power than CO₂ for organic solutes but has the disadvantage of being flammable. Besides, the use of propane is restricted to a limited range of pressure and temperature to achieve oil–solvent immiscibility.^{1,2} Under these conditions the solubility of the oil in the propane phase is also very low. The use of mixtures of CO₂ and propane, even promising, is not discussed in the present work.

The low molecular weight of the solvent (CO₂ or propane) is beneficial in the extraction of solutes from high molecular weight material, because the solvent requirements are directly proportional to the solvent–raffinate (oil-phase) molecular weight ratio. The triglycerides or triacylglycerides (TAGs) have molecular weights on the order of 800; however, liquid or near-critical CO₂ or propane is soluble in the oil phase and, as a consequence, decreases the raffinate average molecular weight, making the process concept less attractive. The differences in densities of the oil and the extract phase for both solvents are adequate for countercurrent operation.³

Operating conditions that maximize the solute solubility in the near-critical phase and at the same time keep the TAGs solubility in the extract phase at very low values are selected in the present work. Optimum conditions have been identified with the assistance of the group contribution with association equation of state (GCA-EOS).^{4,5} This equation has been extended to describe systems with large molecular size differences.

Process Analysis

Several solutes are commonly present in vegetable oils. Paraffinic, chlorinated, or aromatic hydrocarbons may come from the process of extraction of oil from the seeds. Others may be natural oil constituents or may have originated in the use of herbicides or plaguicides.

The solute weight distribution coefficient (K_{iw}) between the oil and extract (CO₂ or propane) phases is the primary solvent property from an economic point of view. This property is related to the molar fraction y_i/x_i ratio as follows:

$$K_{iw} = \frac{y_i M_x}{x_i M_y} \quad (1)$$

where

$$M_x = \sum_{j=1}^N x_j M_j; \quad M_y = \sum_{j=1}^N y_j M_j \quad (2a,b)$$

x_i and y_i are the molar fractions of component i in the raffinate and extract phases, M_x and M_y are the respective average molecular weights, and N is the number of components.

The value of M_y is very close to the solvent molecular weight in most cases. On the other hand, the oil-phase molecular weight M_x is much lower than the oil molecular weight because of the solubility of the near-critical solvent in the oil. For instance, from the data of Kalra et al.⁶ the solubility of CO₂ in palm kernel oil is 38.6 wt % at 323 K and 20.8 MPa. Under these conditions, the relation between the molar fraction ratio and the weight distribution coefficient is $K_{iw} = 2.5(y_i/x_i)$. Figure 1 shows the data of Bharath et al.⁷ on the solubility of CO₂ in palm kernel oil as a function of temperature, for two different pressures. It is clear, from this figure, that higher temperatures and lower pressures reduce the solvent solubility in the oil phase. Propane has also a significant solubility in the oil phase. For example, the

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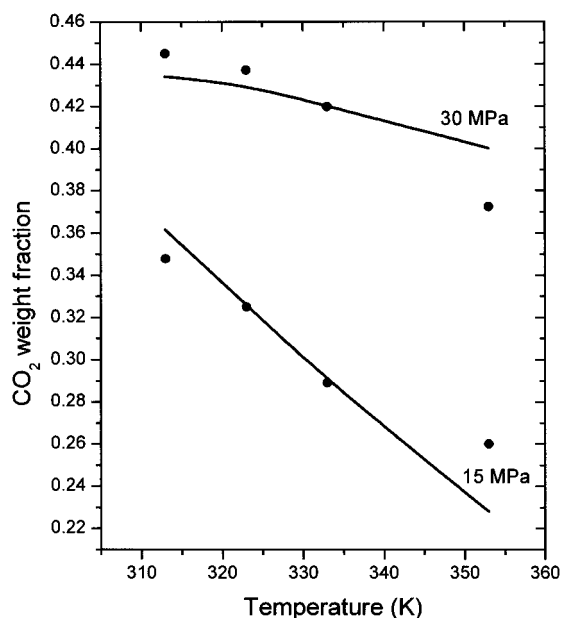


Figure 1. Solubility of CO₂ in palm kernel oil: (●) experimental data;⁷ (—) GCA-EOS predictions.

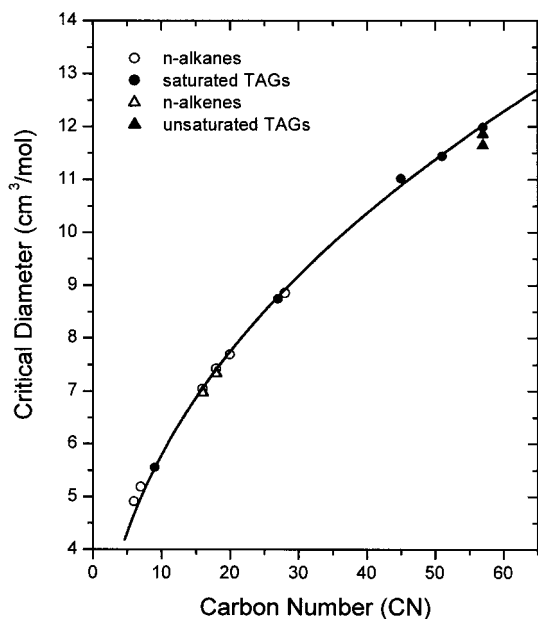


Figure 2. Correlation of critical diameters of *n*-alkanes and TAGs with carbon number.⁵

solubility of propane in palm kernel oil is about 50 wt % at 370 K and 6.6 MPa.²

The determination of suitable conditions for the purification of oils with near-critical solvents requires information about the effect of pressure and temperature on the solute distribution coefficient and on the oil solubility in the near-critical phase.

The estimation of distribution coefficients and oil solubilities is carried out by extending the GCA-EOS model to mixtures of TAGs with low to medium molecular weight compounds. This thermodynamic model supports a rigorous simulator–optimizer of the extraction process.⁸ The simulator–optimizer was applied to study the removal of different solutes. From these results, a better understanding of the process was obtained and optimum operating conditions were identified.

Table 1. New GCA-EOS Parameters

Pure Group Parameters					
group	T^* (K)	q	g^*	g'	g''
TG: triglyceride	600	3.948	346 350	−1.3460	0
ACCl: chlorinated aromatic	600	0.844	881 900	−0.8453	0
Binary Interaction Parameters					
i	j	k_{ij}	K_{ij}	α_{ij}	α_{ji}
CO ₂	CH ₃	0.898	0	4.683	4.683
	CH ₂	0.874	0	4.683	4.683
	TG	1.094	0.1120	−1.651	−1.651
	ACCl	0.986	0.1845	−0.488	−0.488
TG	CH ₃ /CH ₂	0.860	0	0	0
	CH=CH	0.883	0	0	0
AC	CH ₃ /CH ₂	0.8544	0	0	0
	CH=CH	1.100	0	0	0
ACH	TG	0.986	0	0	0
	CH ₃	0.937	0.0200	−0.794	−0.794
	CH ₂	1.136	0.0200	−2.678	−2.678
	ACCl	1.037	0.1210	3.440	3.440
ACCH ₃	CH=CH	1.100	0	0	0
	TG	0.986	0	0	0
	CH ₃ /CH ₂	1.012	0	0	0
	CH=CH	1.100	0	0	0
ACCl	TG	0.986	0	0	0
	CH ₃ /CH ₂	1.006	0	0	0
	CH=CH	1.286	0	0	0
	TG	1.233	0.1000	−19.201	−19.201

Thermodynamic Modeling

Natural oils are complex mixtures of TAGs with fatty acid chains of different length and degree of saturation. However, their molecular structure can be characterized with a few functional groups. This feature supports the selection of a group contribution procedure for the prediction and correlation of phase equilibria of mixtures containing natural oils. The development of near-critical processes for the removal of solutes from natural oils requires the prediction of phase equilibria in molecular size asymmetric nonideal mixtures.

The use of equations of state of the van der Waals family has been unsuccessful in representing simultaneously liquid–liquid and vapor–liquid equilibria of TAGs with propane or ethane.¹ Therefore, a revised version of the GCA-EOS model⁴ has been chosen to correlate and simulate the fatty oils processing with near-critical fluids.⁵ In this model there are three contributions to the residual Helmholtz energy of the mixture: repulsive or free volume (A^{fv}), attractive (A^{att}), and associative (A^{assoc}):

$$A = A^{\text{fv}} + A^{\text{att}} + A^{\text{assoc}} \quad (3)$$

The repulsive contribution is based on the equation of Carnahan–Starling⁹ for hard spheres. The attractive contribution is a van der Waals expression, with density-dependent local composition mixing rules, and the associating term is a group contribution Helmholtz function⁴ based on Wertheim's statistical association fluid theory.^{10,11}

The GCA-EOS size-related parameter in the repulsive term is the critical diameter d_c . For low molecular weight compounds, d_c is obtained from vapor pressure and critical data. For high molecular weight organic compounds, these data are not available. Therefore, the d_c values are estimated from data on infinite-dilution activity coefficients of *n*-hexane in the heavy com-

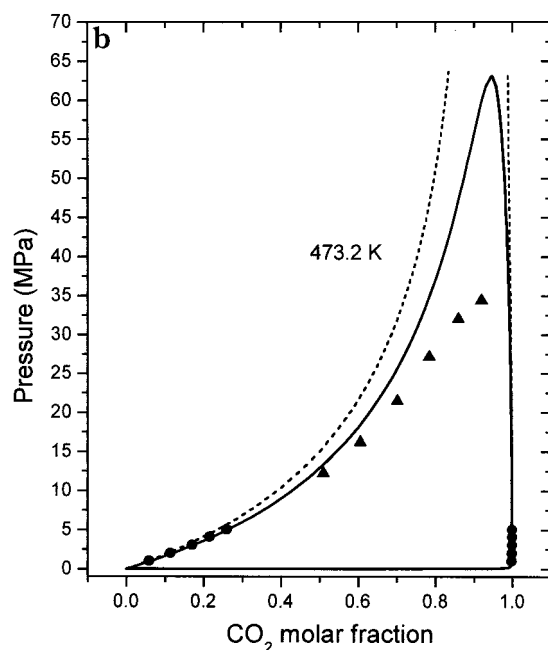
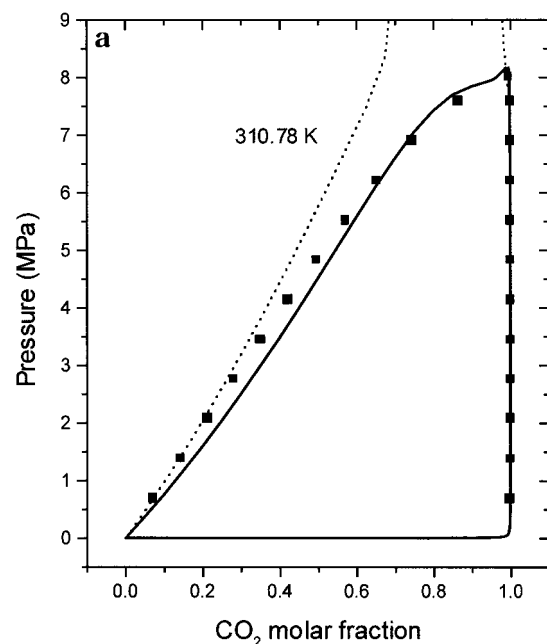


Figure 3. (a) Vapor-liquid equilibrium of the binary CO_2 -decane: (■) experimental data;⁴⁴ (---) GCA-EOS original parameters;¹⁴ (—) GCA-EOS new parameters.¹⁵ (b) Vapor-liquid equilibrium of the binary CO_2 -eicosane: (▲⁴⁵ and ●⁴⁶) experimental data; (---) GCA-EOS original parameters;¹⁴ (—) GCA-EOS new parameters.¹⁵

pounds.^{12,13} Bottini et al.⁵ presented a correlation of critical diameters as a function of the carbon number for TAGs and hydrocarbons (see Figure 2). The vapor-liquid and liquid-liquid equilibria predictions for mixtures of TAGs with ethane or propane⁵ demonstrate the capability of the GCA-EOS model to deal with systems highly asymmetric in molecular size.

The original group contribution equation of state¹⁴ was developed for low to medium molecular weight substances. The extension of the model to describe the removal of chemicals from fatty oils with CO_2 or propane requires the adjustment of the attractive term group interaction parameters. The number of methyl and

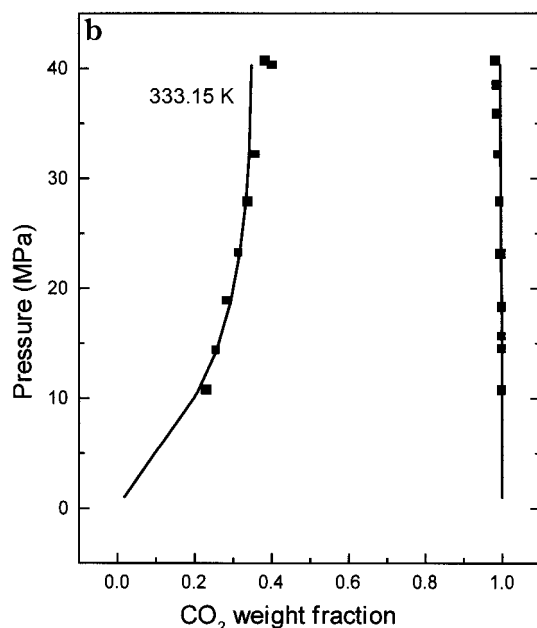
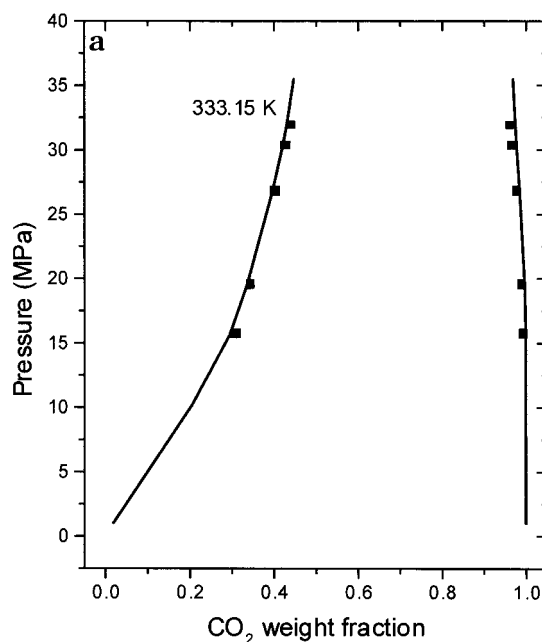


Figure 4. (a) Vapor-liquid equilibrium of the binary CO_2 -palm kernel oil: (■) experimental data;⁷ (—) GCA-EOS predictions. (b) Vapor-liquid equilibrium of the binary CO_2 -rape seed oil: (■) experimental data;⁴⁷ (—) GCA-EOS predictions.

methylene groups in oil molecules is in the range of 40–60. For molecules of this size, even with moderate interaction energies, it is very important to carefully evaluate the binary interaction parameters in order to avoid degeneration of the predictions with the increase in molecular size. This is the case of the interaction between CO_2 and CH_2 or CH_3 groups. Phase equilibrium predictions with the original parameters¹⁴ deteriorate for alkanes with a carbon number above 8. On the other hand, the solutes to be removed from the oil will be, in general, of medium to low molecular weight. Therefore, the model not only should perform well for high molecular weight compounds but also should give reasonable predictions in the low carbon number range.

In addition, the development of extraction processes requires the modeling of the distribution coefficients of

Table 2. References of the Experimental Phase Equilibria Data Used in the Regression and Test of the New GCA-EOS Parameters¹⁵

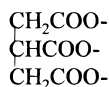
<i>i</i>	<i>j</i>	type of experimental data ^a	ref
CO ₂	CH ₃ /CH ₂	VLE of normal alkanes–CO ₂ mixtures	16–19
	TG	low-pressure solubility of CO ₂ in triacetin	20
	ACCl	vapor pressure of pure chlorobenzene and dichlorobenzene	21, 22
TG	CH ₃ /CH ₂	high-pressure VLE of chlorobenzene–CO ₂ and dichlorobenzene–CO ₂ mixtures	21, 23
	CH=CH	vapor pressure of pure triacetin; γ^∞ of alkanes in triacetin	23
AC	CH ₃ /CH ₂	γ^∞ of 1-hexene in triacetin	24
ACH	CH ₃ /CH ₂	VLE of naphthalene–tetradecane mixtures	25–28
	ACCL	VLE of normal alkanes–benzene mixtures	29, 30
ACCH ₃	TG	low- and high-pressure solubilities and VLE of benzene in chlorobenzene	12, 13
	CH=CH	γ^∞ of benzene in triacetin, tricaprylin, trimyristin, tripalmitin, and tristearin	31–33
	CH ₃ /CH ₂	VLE of mixtures of benzene with 1-hexene, 1-heptene, and 1-octene	34–38
ACCL	TG	VLE of mixtures of toluene with pentane, heptane, octane, decane, and octadecane	12, 13
	CH ₃ /CH ₂	γ^∞ of toluene in triacetin, trimyristin, tripalmitin, triolein, trilinolein, and tristearin	39–41
	TG	VLE of binary mixtures of chlorobenzene with pentane, hexane, and heptane	12, 13
	CH=CH	γ^∞ of chlorobenzene in triacetin, tripalmitin, trilinolein, and triolein	41
		VLE of 1-pentene in chlorobenzene	

^a VLE: vapor–liquid equilibria. γ^∞ : infinite-dilution activity coefficients.

solutes between the oil and near-critical phases. There is a lack of experimental data on the distribution coefficients of solutes between oils and near-critical solvents. Consequently, the predictions will be mainly based on experimental information on the respective binary systems (solute–near-critical solvent, solute–oil, and oil–near-critical solvent).

The model should be able to represent vapor–liquid, liquid–liquid, and liquid–near-critical fluid equilibria, in a wide range of pressure, temperature, and composition. In the present work, the GCA-EOS model is applied to study the removal of the following solutes from fatty oils: hexane, benzene, toluene, biphenyl, naphthalene, chlorobenzene, and dichlorobenzene.

Equation of State Parameter Estimation. Triglycerides contain a functional nucleus (CH₂COO)₂–CHCOO to which the fatty acid chains are attached. The development of a group contribution approach for dealing with TAGs requires the introduction of a new group, the triester of glycerol (TG) group:



The TG pure group parameters as well as the interaction parameters between TG and propane were taken from Bottini et al.⁵ The binary interaction parameters between CO₂, TG, paraffinic (CH₃ and CH₂), olefinic (CH=CH), aromatic (AC, ACH, and ACCH₃), and chlorinated (ACCl) groups are given in Table 1.¹⁵ References to the experimental data used to fit each binary interaction parameter are given in Table 2.

The interaction parameters between the aromatic and TG groups were determined from experimental information on infinite-dilution activity coefficients of benzene and toluene in triacetin, tricaprylin, trimyristin, tripalmitin, and tristearin.¹³ A reparametrization of the paraffinic–aromatic interaction was required to achieve good correlation of vapor–liquid equilibrium of aromatic compounds with heavy paraffins.¹⁵ The interaction parameters between CO₂ and aromatic groups were taken from Bamberger et al.,⁴² and those between olefinic groups and paraffinic and aromatic groups were taken from Pusch and Schmelzer.⁴³

Parts a and b of Figure 3 compare, for the original¹⁴ and the new parameter set, deviations between predictions and experimental vapor–liquid equilibrium data

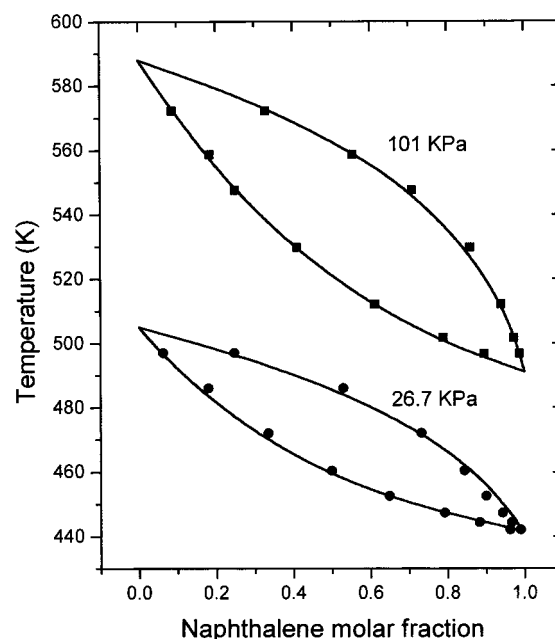


Figure 5. Vapor–liquid equilibrium of the binaries naphthalene–alkenes. Experimental data: (●) naphthalene–1-hexadecene;⁴⁸ (■) naphthalene–1-octadecene;⁴⁹ (—) GCA-EOS predictions.

for CO₂–decane and CO₂–eicosane mixtures. Parts a and b of Figure 4 show results for natural oil–CO₂ mixtures. In these comparisons, the recommendation¹⁴ to limit the application of the GCA-EOS model to 30 MPa should be taken into account.

The prediction of vapor–liquid equilibrium for binary mixtures of naphthalene with alkenes is shown in Figure 5. Figure 6 gives the results of the correlation of experimental vapor–liquid equilibrium data for chlorobenzene–CO₂ mixtures.

Analysis of Supercritical Processes for the Removal of Chemicals from Natural Oils

A preliminary selection of the process operating conditions can be made on the basis of the binodal curve of liquid–liquid or liquid–near-critical fluid equilibria for the ternary system solute–solvent–oil. Examples of binodal curves computed with the GCA-EOS model for the ternary systems palm kernel oil–CO₂–hexane and palm kernel oil–propane–benzene are shown in Figures 7 and 8, respectively.

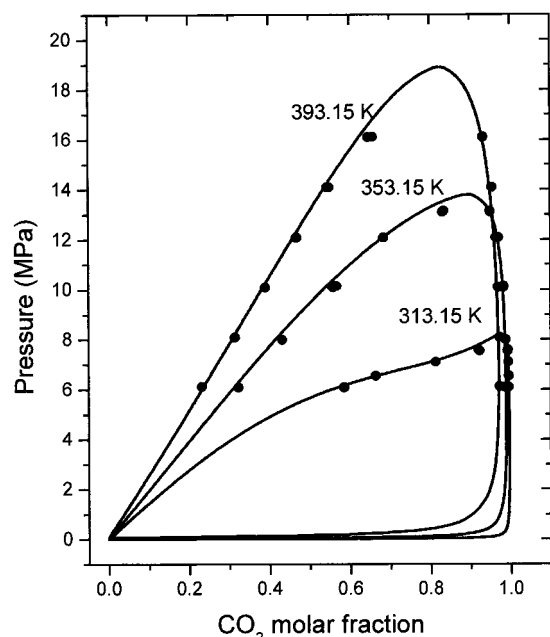


Figure 6. Vapor-liquid equilibrium of the binary chlorobenzene- CO_2 : (●) experimental data;²² (—) GCA-EOS correlations.

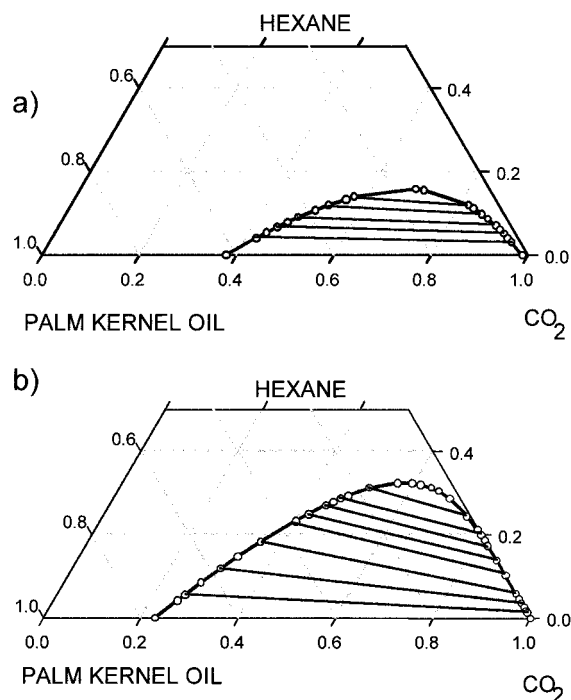


Figure 7. Phase equilibrium (weight fractions) for the ternary system CO_2 -hexane-palm kernel oil at 10 MPa and (a) 293.15 K and (b) 323.15 K.

The extraction conditions for the removal of paraffinic and aromatic pollutants were studied using a multi-component extraction subroutine EXTRAC, supported by the GCA-EOS model, available in the PROSYD process simulator.⁵⁰ The program is based on the GC-EXTRACT program developed by Andersen.⁵¹ The removal of chemicals from the vegetable oil with the near-critical solvent is analyzed for a countercurrent operation. An isothermal extractor of 15 stages was chosen. The extraction cycle is completed with a solvent recovery system as shown in Figure 9. The removal of low concentrations of pollutants was studied: 1 wt % of hexane and 0.01 wt % of aromatics and other solutes.

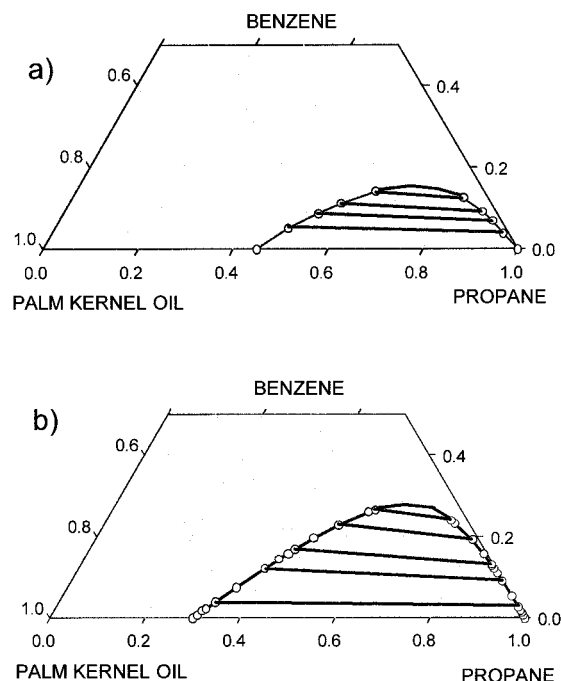


Figure 8. Phase equilibrium (weight fractions) for the ternary system propane-benzene-palm kernel oil: (a) 365.15 K, 4.5 MPa; (b) 390.15 K, 6 MPa.

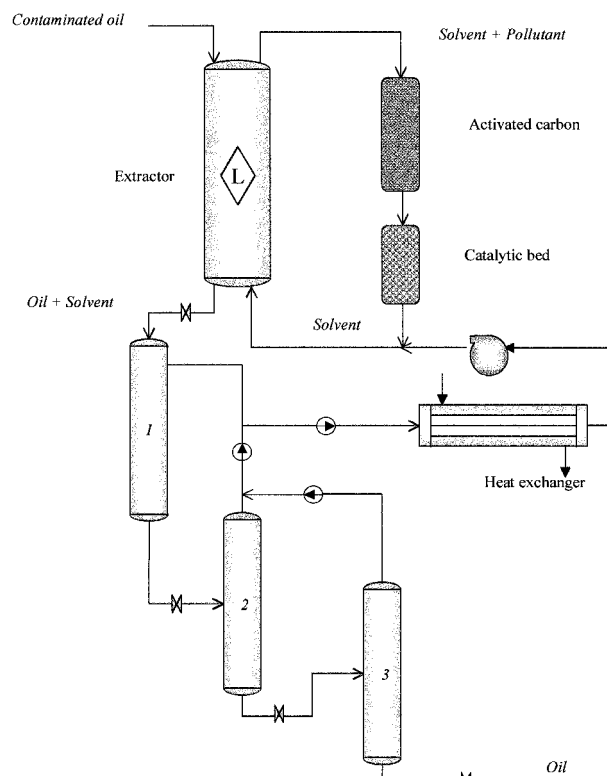


Figure 9. Flow diagram of a near-critical fluid extraction process. 1-3: solvent recovery units.

The maximum value of contaminants allowed in the treated oil was 5 ppm of hexane and 0.01 ppm of benzene and other aromatic pollutants.

Selection of Extraction Conditions

Extraction with CO_2 . The system vegetable oil- CO_2 shows phase immiscibility under CO_2 sub- and super-critical conditions. For example, Figure 4a shows that

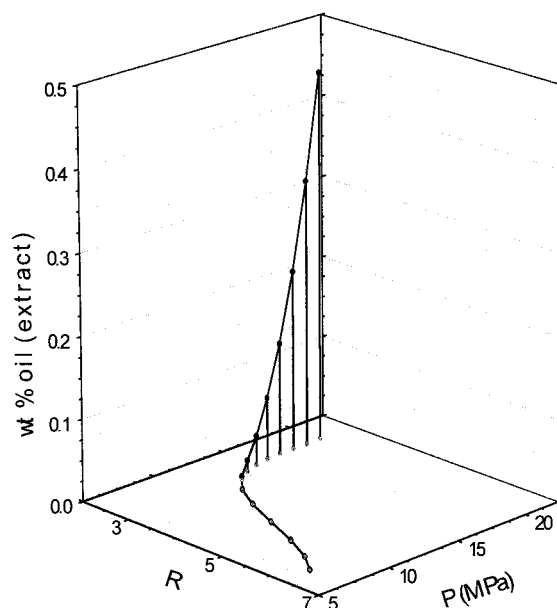


Figure 10. CO_2 -feed weight ratio and oil loss vs operating pressure, in the removal of hexane from palm kernel oil at 330.15 K. Inlet hexane concentration 1 wt %. Outlet hexane concentration 5 ppm. R : solvent-feed weight ratio.

at 10 MPa and 333 K there is liquid–fluid phase equilibrium for concentrations of CO_2 in palm kernel oil higher than 20 wt %. This immiscibility region extends to very high pressures. Therefore, the two-phase behavior required for countercurrent removal of pollutants with CO_2 is observed over all foreseeable operating conditions.

The simulation of the removal of *n*-hexane from palm kernel oil using CO_2 was studied for temperatures in the range $303 \leq T/\text{K} \leq 330$ and pressures from 7 to 20 MPa. These simulations had the objective of studying the effect of pressure and temperature on (a) the required solvent–feed ratio (R) and (b) the concentration of oil in the extract (oil loss).

Simulations of an extraction at 330 K for a feed concentration of 1 wt % of hexane are shown in Figure 10. In this figure the concentration of oil in the extract and the solvent–feed ratio required to achieve the purity specifications are plotted as a function of pressure. It can be seen that the value of R is almost constant (2.7) for pressures above 15 MPa. However, there is a drastic increase in the oil concentration in the extract when the pressure increases from 15 to 20 MPa. Therefore, the optimum conditions of extraction (higher selectivity) at 330 K are obtained at pressures of around 15 MPa. At this pressure, the solvent–feed ratio is only 10% higher than that at 20 MPa but the oil loss is negligible. Reverchon et al.⁵² have reported recently pilot-plant results for the extraction of hexane from vegetable oil using CO_2 . In this study a solvent–feed ratio of about 5 was needed in order to decrease the hexane concentration from 10 wt % to 20 ppm working at 313 K and 12 MPa. For these conditions, our simulator gives a 5.4 solvent–feed ratio for a column with 7 theoretical stages. This is in good agreement with the pilot-plant results.

Parts a–c of Figure 11 show the results of simulations at different temperatures, for the same specifications. In these plots it is found that the pressure required for a limiting oil loss of 0.05 wt % represents a characteristic “optimum” value for each operating temperature.

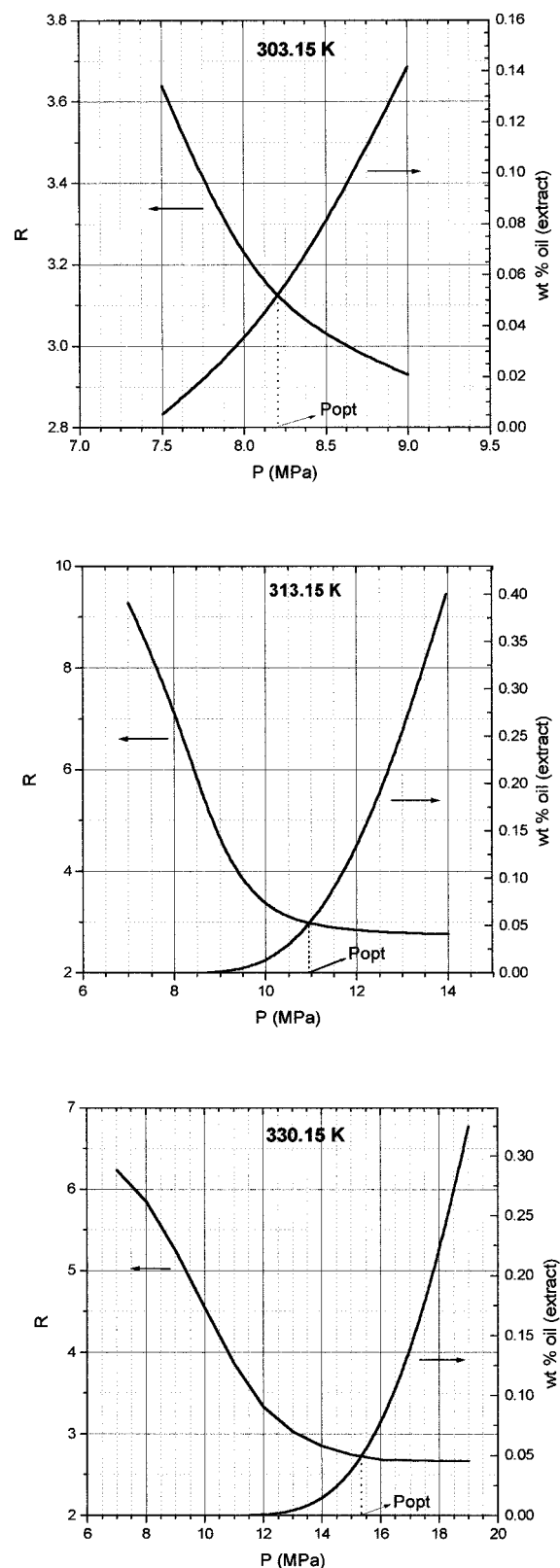


Figure 11. Effect of temperature on the optimal pressure and minimum solvent rate for the removal of hexane from palm kernel oil using CO_2 .

Working at higher temperatures increases the required pressure but decreases the value of R . It is clear that the operating pressure has a significant effect above the “optimum” value. Beyond this point there is little gain in the reduction of the solvent–feed ratio but a large increase in the oil loss.

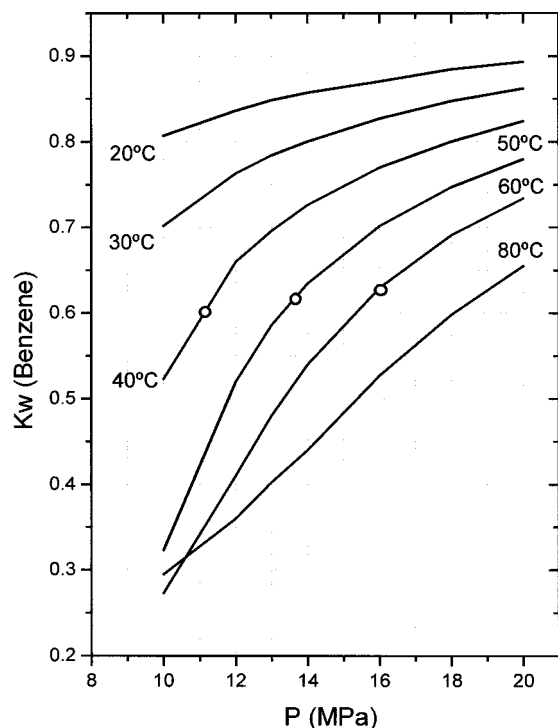


Figure 12. Effect of pressure on the distribution coefficient of benzene between palm kernel oil and CO₂. Open circles indicate optimal conditions for an oil loss ≤ 0.05 wt %.

For other solutes, the solvent–feed ratio required will be a function of the value of the distribution coefficient of that particular solute between the oil and CO₂ phases. Figure 12 illustrates the effect of pressure and temperature on the distribution coefficient of benzene. It can be seen that the higher distribution coefficients are obtained for liquid CO₂ at the highest pressure studied: 20 MPa. However, the optimum extraction pressures are lower in order to keep the oil loss below 0.05 wt %. Open circles in Figure 12 indicate the optimum operating pressures for the range of temperatures covered in the simulations. The extraction of chlorinated and polycyclic aromatic compounds requires higher solvent–feed ratios.

An important property in the operation of the countercurrent extraction with CO₂ is the density difference between the raffinate and the extract. The density of the extract can be considered to be that of pure CO₂. The density of the raffinate can be obtained from experimental data on densities of vegetable oils⁵³ and CO₂ + vegetable oil mixtures.⁵⁴ Figure 13 shows the differences in density between the raffinate and the extract, at optimum extraction conditions. The differences in density are high enough for the operation of a countercurrent extraction process.³

Extraction with Propane. For the type of solutes studied in the present work, propane is a better solvent than CO₂. In this case the operating temperature should be above the lower critical end point (LCEP) of the propane–TAG mixture, so that the process takes place in the two-phase region. LCEP for propane–TAG mixtures have been reported by Straver et al.² Typical values are 349 K for tripalmitin⁵⁵ and 341 K for tristearin.⁵⁶ LCEPs predicted by the GCA-EOS model are shown in Table 3.

At temperatures below the LCEP, propane and oil are completely miscible. However, when the liquid phase

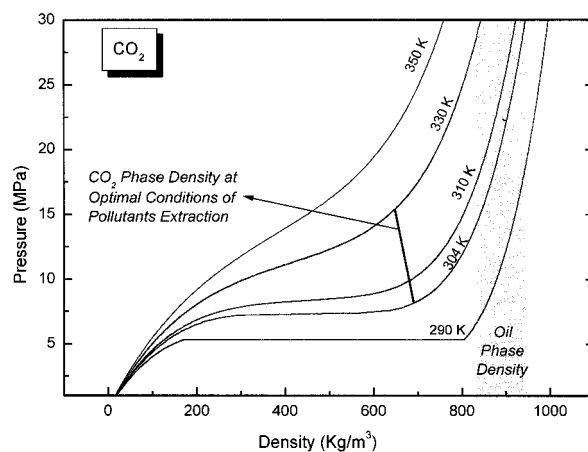


Figure 13. Density differences between oil and CO₂ phases.

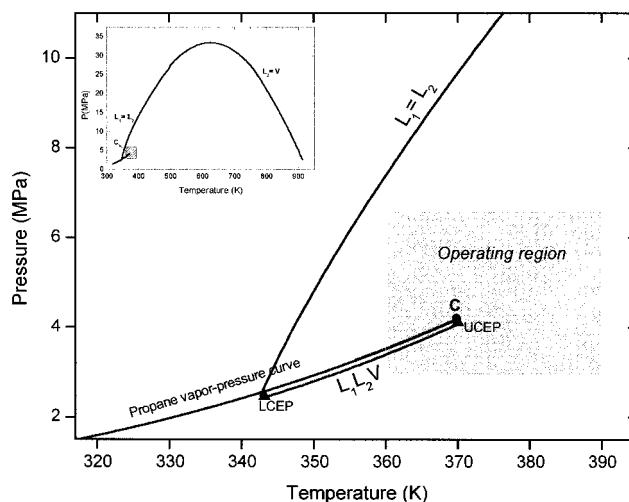


Figure 14. Pressure–temperature projection of the palm kernel oil–propane phase equilibrium surface.

Table 3. Comparison between Experimental LCEP and GCA-EOS Predictions for Propane–Triglyceride Mixtures

compound	carbon number	lower critical end point (LCEP)				ref of expt data
		experimental data		GCA-EOS predictions		
		<i>T</i> (K)	<i>P</i> (MPa)	<i>T</i> (K)	<i>P</i> (MPa)	
palm kernel oil	46	343.2	2.577	339.7	2.46	2
tripalmitin	51	348.9	2.876	345.3	2.72	55
tristearin	57	341.1	2.477	344.6	2.67	56

splits in two, the solubility of the oil in the propane phase decreases sharply. Under these conditions, propane is a feasible extraction solvent for the purification and refining of fatty oils. The temperature of the upper critical end point (UCEP) of these systems is very close to the critical temperature of propane (370 K). Therefore, in the temperature range 340–370 K, liquid–liquid equilibria are observed at pressures above the propane saturation pressure. At supercritical temperatures, a dense gas phase and an oil phase are obtained.

Figure 14 shows a typical pressure–temperature (*P*–*T*) projection of the operating region for the removal of solutes with propane. The heterogeneous region of the oil–propane binary mixture decreases at all temperatures with increasing pressure, and for each isotherm, there is a maximum pressure at which complete miscibility is obtained. Therefore, for each isotherm the

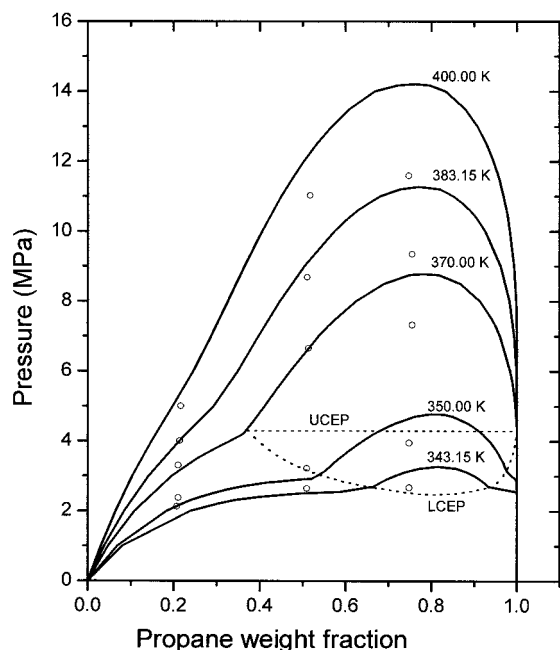


Figure 15. Phase equilibrium of the palm kernel oil–propane system: (○) experimental data;² (—) GCA-EOS predictions.

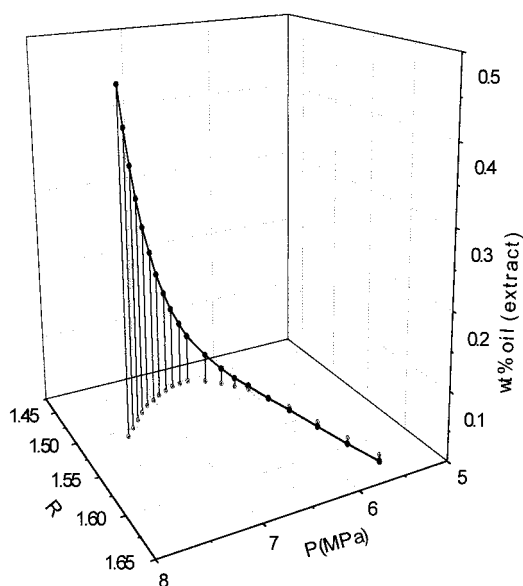


Figure 16. Propane–feed weight ratio and oil loss vs operating pressure, in the removal of hexane from palm kernel oil at 390.15 K. Inlet hexane concentration 1 wt %. Outlet hexane concentration 5 ppm. R : solvent–feed weight ratio.

operating pressure should be well below the maximum pressure, to keep the solubility of the oil in the propane phase very low. This behavior is illustrated for the system palm kernel oil–propane in Figure 15.

Results from the simulation of the removal of hexane from palm kernel oil, for the same initial and final concentrations as specified before (1 wt % to 5 ppm of hexane in oil), are shown in Figure 16. There is a minimum value for the solvent–feed ratio as a function of pressure. The presence of this minimum is due to the fact that the solubility of propane in oil increases markedly with pressure. As a consequence, the actual raffinate flow rate in the extractor increases and a higher solvent flow rate is required. In other aspects, the process behavior with propane is similar to that using CO_2 and an optimum value for the extractor

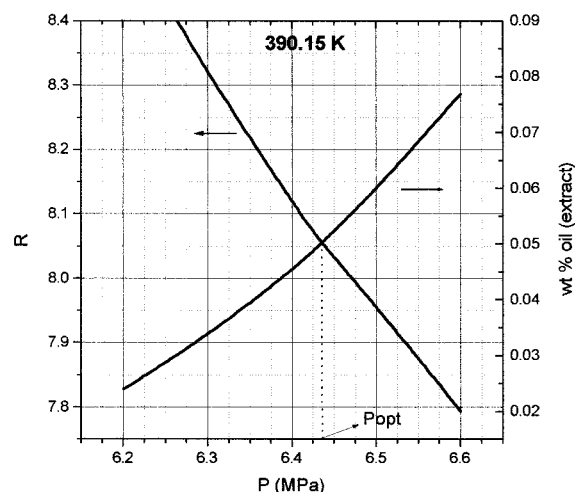
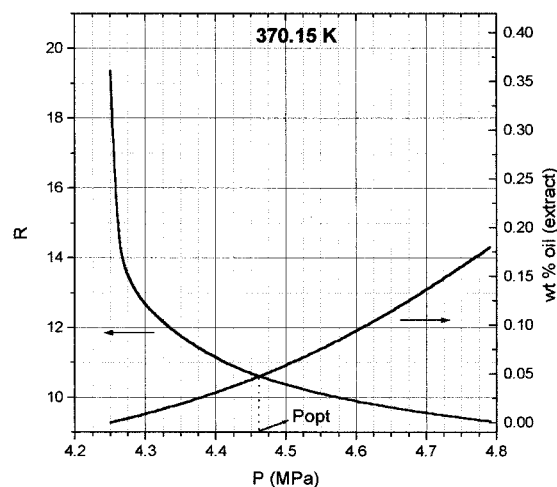
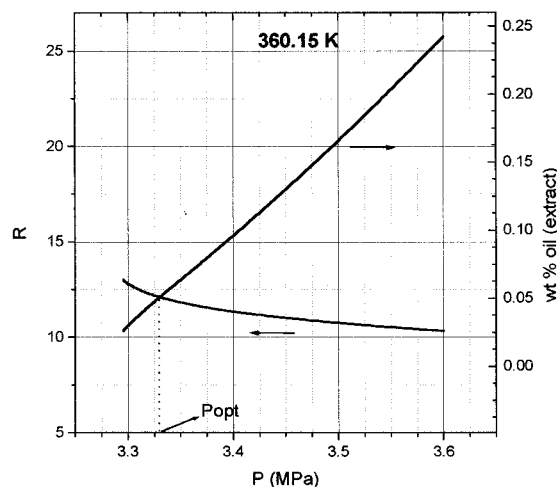


Figure 17. Effect of temperature on the optimal pressure and minimum solvent rate for the removal of chlorobenzene from palm kernel oil using propane.

operating pressure can be selected at each temperature. This behavior is illustrated for the extraction of chlorobenzene from palm kernel oil in parts a–c of Figure 17.

In Figure 18 a comparison is given for the removal of different solutes with propane or CO_2 at the optimum

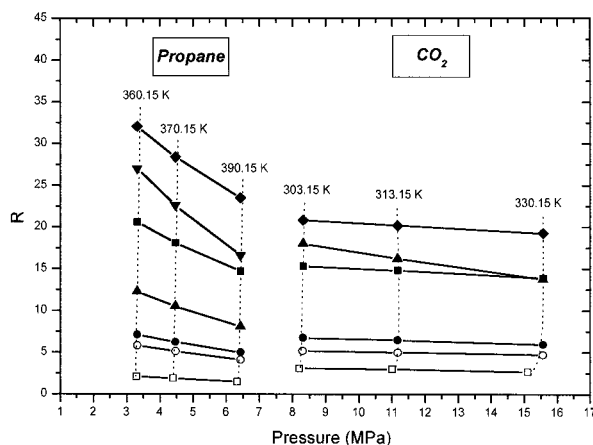


Figure 18. Optimal conditions for the removal of pollutants from fatty oils using propane and CO_2 as solvents: (\square) hexane, (\circ) benzene, (\bullet) toluene, (\blacktriangle) chlorobenzene, (\blacksquare) naphthalene, (\blacktriangledown) 1,2-dichlorobenzene, (\blacklozenge) biphenyl.

pressures. It can be seen that, for each solvent, the optimum pressure is the same at a given temperature and almost independent of the extracted solute. This is a consequence of the low concentration of solute in the feed and the restrictions imposed on the oil losses in the extract. The variation of solvent requirements with temperature at the optimum conditions is small for both solvents. The observation that the solvent requirements are insensitive to the operating temperature is due to the fact that the restriction of the oil solubility in the extract (0.05 wt %) is always active at the optimum operating pressure. This means that at higher temperatures the pressure, which favors the solvent power, is increased until the solvent power of the near-critical fluid is recovered. Therefore, the solvent requirements remain relatively constant for the range of temperatures studied. This result can also be explained in terms of the relation between solvent power and density, characteristic of supercritical fluids. Figure 13 shows that the density of the CO_2 phase is kept at a narrow range around 0.65 kg/m^3 at the optimum conditions for all temperatures. The results of this study are being applied by the authors to other problems of purification and refining of fatty oils, such as the removal of cholesterol from butter and milk fat.

Conclusions

Optimum operating conditions for the purification and refining of fatty oils with near-critical CO_2 or propane are identified with the help of reliable predictions of phase equilibria using the GCA-EOS model. This model is also used to determine the region of liquid-liquid equilibrium for mixtures of propane with TAGs. The study shows that, for each solvent, there is an optimum pressure that minimizes solvent requirements and gives maximum selectivity. The thermodynamic model applied in the present work can be used to study a great variety of problems in the processing, refining, and purification of natural oils with high-pressure gases. A better understanding of the effect of phase equilibrium on process conditions can be gained in this way.

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