

Ethane as an alternative solvent for supercritical extraction of orange peel oils

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Abstract

The objective of this study was to investigate the superiority of ethane in comparison to CO₂ as a supercritical extraction solvent for deterpenating citrus oils. A rigorous computer code was developed that optimized extraction column operating conditions to minimize solvent recirculation. The SRK equation of state was used as the thermodynamic model after globally optimizing its adjustable binary interaction parameters to a combination of different literature data sets consisting of binary isothermal P – x , y , ternary constant composition P – T , and ternary isothermal isobaric x – y data. An investigation of the effects of different process variables on the degree of extraction revealed complicated and interconnected relations among the variables and extraction efficiencies. However, since the process of deterpenation, in particular, benefits from higher solubility more than from higher selectivity, increases in temperature, pressure, solvent-to-feed ratio, and reflux rate all seem to favor the separation.

To compare the performance of ethane and carbon dioxide for orange oil deterpenation, selectivities of separation between the terpene and aroma fractions were calculated and compared for the two solvents. Compared to CO₂, ethane is the better solvent for citrus constituents. This results in decreased solvent/feed mass ratio for ethane when the processes are compared at the same reduced pressure. However, these are not the only benefits of ethane over CO₂. As the critical pressure of ethane is lower, the absolute operating pressures of ethane columns can be lower.

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1. Introduction

Citrus essential oils are specialty byproducts of the citrus processing industry and are used in a wide variety of applications such as the flavor, cosmetic, pharmaceutical, and chemical industries. However, these oils are usually not used in their raw form, but purified in a process called “folding” or “deterpenation” that removes large parts of the undesirable terpenes. The shortcomings of the conventional deterpenation processes have given rise to extensive research on alternatives for citrus oil deterpenation, especially with supercritical carbon dioxide. Such investigations have covered all aspects from fundamentals to practical process design, and employed different approaches from experimental (for example [1–11]) to mathematical model-

ing and optimization [5,7,10,12–20]. The separation approaches have covered various types of techniques from semi-batch to continuous, and from simple countercurrent extraction to more elaborate extraction with reflux and temperature gradients.

Such investigations have indicated that even though supercritical CO₂ extraction has both the advantages of low operating temperatures and solvent-free products, it is difficult to optimize the operating conditions. Low pressures lead to high selectivity at the cost of low extraction yield, whereas high pressures give high extraction yields, but with low selectivity. In addition, the process is expensive since vessels, columns, and equipment must withstand high pressures. Further investigations have been carried out aiming to overcome the problems of supercritical CO₂ extraction. One approach was to add to supercritical CO₂, a cosolvent such as ethanol. Preliminary investigations [21] indicated encouraging results. However with this method, the organic solvents have come back into the process, which must be separated with an additional separation step. In other attempts, researchers introduced adsorbent into the supercritical

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fluids system to achieve higher selectivity [22]. They successfully fractionated lemon oil, bergamot oil, and orange oil by using silica gel as an adsorbent [23]. However, since the desired oxygenated compounds are strongly adsorbed, a considerably high pressure is required to desorb the solutes, resulting in a requirement for higher investment and operating costs [22]. This study is a further attempt to increase separation yield of the supercritical extraction process by substituting carbon dioxide by an alternative solvent with higher extraction capabilities.

2. Phase equilibria

Previous studies on citrus oil constituents dissolved in supercritical CO₂ have proven the ability of the cubic equations of state in adequately correlating such systems. The Soave–Redlich–Kwong [24] equation of state (SRK EOS) together with the classical one-fluid van der Waals mixing rules has been selected as the thermodynamic model. The suitability of this thermodynamic model was also confirmed in this study by correlating binary P - x - y data of representative citrus oil component(s), limonene and linalool, with not only CO₂ as solvent but also with ethane. The experimental data points for the binary systems with CO₂ were taken from Iwai et al. [25,26], Chang and Chen [27], and Raeissi and Peters [28] and those with ethane were from Raeissi and Peters [29] and Raeissi et al. [30]. While these correlations were successful, the ternary data [31–33] could not be well replicated with binary-optimized interaction parameters. After comparing different modes of optimization, it was chosen to carry out all ternary calculations by using only k_{12} and k_{13} (where subscripts 1, 2, and 3 denote the supercritical solvent, limonene, and linalool, respectively).

In an attempt to optimize the overall performance of the SRK EOS, binary interaction coefficient optimization was not carried out with unilateral focus on achieving the best possible binary P - x , y fit. Instead, it was attempted to reach a compromise in acceptable predictions of binary data, as well as ternary constant composition P - T and ternary isobaric–isothermal x - y data. For this purpose, in addition to k_{12} and k_{13} , the critical temperatures and pressures, and also the acentric factors of limonene and linalool were treated as adjustable parameters within a narrow error-window surrounding the values calculated by conventional group contribution methods for calculating T_c , P_c , and ω . This was only possible since there are no experimental values available for the T_c , P_c , and ω of limonene and linalool, except for the T_c of limonene [34], and because the errors in such prediction methods can reach for example, 3% for T_c and up to as high as 100% for P_c [35]. In the case of limonene, the experimentally available value of T_c [34] was considered and the optimized value for ω happened to equal the value calculated in literature. These values, together with the optimized parameters, are presented in Tables 1 and 2.

The binary phase equilibria predictions with these optimized parameters are compared with the corresponding experimental values in Fig. 1. Fig. 2 compares predicted and experimental bubble and dew point compositions at constant temperature and pressure for the ternary system of CO₂ + limonene + linalool [31]. While the bubble point correlations show some errors, the

Table 1
Pure component properties used for modeling

Component	T_c (K)	P_c (MPa)	ω
Ethane	305.3 ^a	4.82 ^a	0.098 ^b
Carbon dioxide	304.2 ^c	7.38 ^c	0.239 ^c
Limonene	653.0 ^d	2.50 ^f	0.313 ^e
Linalool	625.5 ^f	1.87 ^f	0.700 ^f

^a Stahl et al. [36].

^b Schmitt and Reid [37].

^c Reid et al. [38].

^d Smith et al. [34].

^e Yaws [39].

^f Optimized.

Table 2
Optimized binary interaction coefficients

Interaction coefficient	Carbon dioxide	Ethane
k_{12}	0.123	0.040
l_{12}	0.000	0.000
k_{13}	0.085	0.080
l_{13}	0.000	0.000
k_{23}	0.000	0.000
l_{23}	0.000	0.000

The subscripts 1, 2, and 3 symbolize solvent, limonene, and linalool, respectively

dew point predictions of the graph on the right, are in particularly good agreement with the data.

One further check of the phase behavior predicting model is carried out against the selectivity data of Sato et al. [2] for a mixture of CO₂ and a model citrus oil (80 wt% limonene–20 wt% linalool). The separation selectivity is defined as

$$\alpha = \frac{y_2/x_2}{y_3/x_3}$$

The results (Fig. 3) comparing the experimental and predicted selectivities as a function of temperature, show an overprediction of separation selectivity but the deviations are not serious.

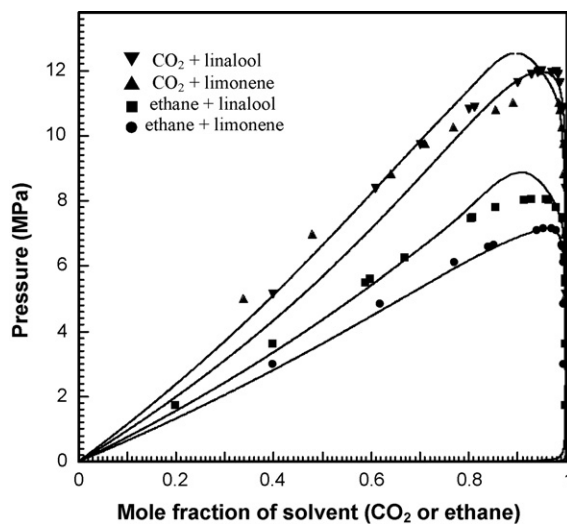


Fig. 1. SRK EOS correlated (curves) and experimental (points) bubble and dew point pressures for four binary systems at 333.15 K. Experimental or interpolated data taken from [25–30].

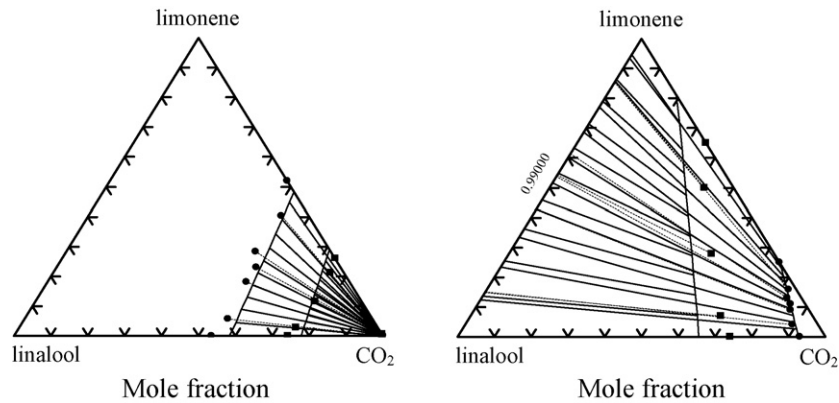


Fig. 2. SRK EOS correlated (curves) and experimental (points) bubble and dew point curves of the ternary mixture carbon dioxide + limonene + linalool at 333.2 K and (■) 10 MPa and (●) 6.9 MPa. The left side graph shows the bubble point behavior while the graph on the right is zoomed in on the dew point behavior. The data are taken from Morotomi et al. [31].

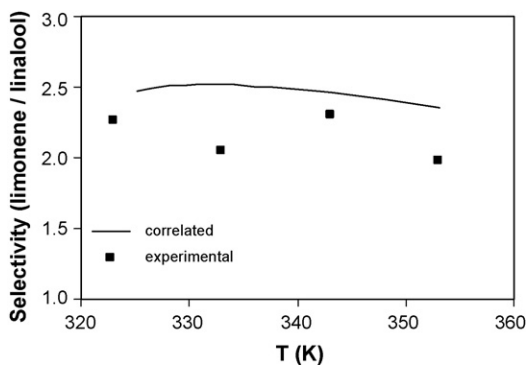


Fig. 3. Experimental and SRK EOS-predicted selectivities of limonene over linalool as a function of temperature at 8.8 MPa for an 80 wt% limonene–20 wt% linalool model mixture in CO₂, data from Sato et al. [2].

3. Process modeling and optimization

The supercritical separation scheme consists of a counter-current extractor with recycle and a separator tank. As shown in Fig. 4, the raw orange peel oil is introduced into the extractor on any desired stage and the supercritical solvent is fed at the bottom. The terpene fraction, represented by limonene, is solubilized by the supercritical solvent to a greater extent than the aroma/ flavor fraction, represented by linalool. This is because the terpenes are non-polar, and the vapor pressure of the terpene

fraction is larger than the aroma fraction. For this reason, it is the raffinate, which is the remaining oil partly stripped of terpenes and concentrated in aromas, that is the desired product. The limonene-rich byproduct is obtained at the top as extract. The extract is cooled, followed by depressurization in a separator. The solvent is compressed and recycled to the extractor.

The optimization of different operating conditions is solved as a non-linear programming (NLP) problem, with a successive quadratic programming (SQP) algorithm [40]. The model is composed of a series of equality constraints, as well as inequality constraints. With the search field defined by these equality and inequality constraints, optimization is carried out to approach a certain defined goal [41]. Inequality constraints include process specifications, operating bounds and bounds on capacity of units. Equality constraints represent the mathematical model of the process and they are solved within a sequential process simulator. This includes rigorous models for a high-pressure multistage extractor [42] and a multiphase flash [43]. The SRK EOS has been integrated as the thermodynamic support for these unit simulation routines.

Based on the explanations above, the optimization program considers as its optimization variables the extractor pressure, solvent flow rate, reflux ratio, and separator pressure. The objective is to minimize solvent recirculation. The non-linear inequality constraints include process specifications on limonene concentration in the extract. An additional equality constraint is to achieve a desired fixed level of oil folding, for example a fivefold oil, which indicates that the product oil is reduced to one-fifth the mass of the raw oil.

3.1. Prediction of column data

The process model was checked against the experimental countercurrent column data of Budich et al. [5], using carbon dioxide as the solvent and a raw orange oil consisting of 98.25 wt% terpenes. Operating temperature was fixed at 333 K while the pressure and reflux ratio were simultaneously adjusted in a way to result in a fivefold oil product that is an oil stripped of terpenes to one-fifth its original weight. Separator temperature and pressure were 303 K and 5 MPa, respectively.

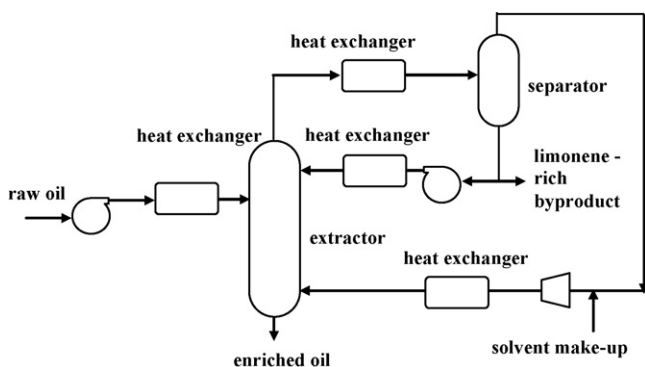


Fig. 4. Flow sheet of the supercritical deterpenation process.

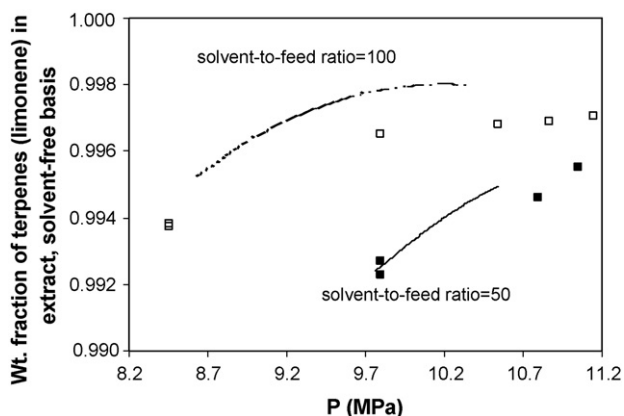


Fig. 5. Experimental (points) and modeled results (curves) for countercurrent CO_2 extraction at constant solvent-to-feed ratios (kg/kg) producing fivefold-oil at 333 K. Experimental data taken from Budich et al. [5].

The results shown in Fig. 5 indicate a slight overprediction of limonene extraction by CO_2 . However, the extent of disagreement between model and data is not surprising as the column was represented by a fixed number of plates in the calculations. This number of theoretical plates was calculated by Budich and coworkers using the short-cut stage calculation method based on the Jänecke diagram [5], which has its own simplifying assumptions and, therefore, has errors. In addition, in any column, the number of theoretical plates varies depending on operating conditions, and hence, taking a fixed number of plates for the experimental setup is not free of errors. Also, the complex raw oil composed of numerous components was modeled as a mixture of only limonene and linalool. Considering these limitations inherent with using this set of experimental data, one may conclude that the model is able to simulate the extraction column over this range of conditions.

Another experimental study by Reverchon et al. [4] presented supercritical CO_2 extraction data for a model mixture of four key components in a packed continuous countercurrent column. The column operated at a solvent-to-feed ratio of 80 kg/kg with no reflux. Separation of CO_2 was achieved at 2 MPa and 273 K. The model mixture consisted of 60 wt% limonene, 10 wt% γ -terpinene, 20 wt% linalool, and 10 wt% linalyl acetate. In our calculations, the two terpenes were lumped together as one terpene fraction and represented by 70 wt% limonene, while the two oxygenates together made up the 30 wt% oxygenate fraction represented by linalool. The results of these calculations are compared with the corresponding experimental values in Fig. 6. Considering the range of the data, the simulations are representative of the real process. The model simulations for yet another experimental column study [23] indicated comparatively similar error values as the previous two studies.

3.2. Effect of process variables

Process operation at optimal conditions requires the understanding of the effects of different process variables. The influence of pressure is illustrated in Figs. 5 and 7. As pressure increases, so does the fluid density, and thus solubility. However,

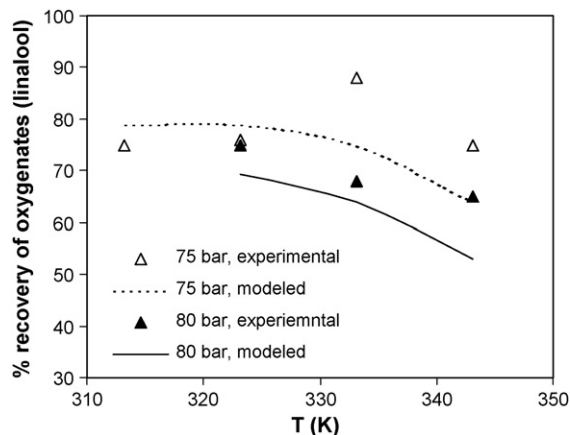


Fig. 6. Experimental and modeled results for countercurrent CO_2 extraction at a constant solvent-to-feed ratio of 80 kg/kg, experimental data from Reverchon et al. [4].

the increased solvent power caused by an increase in density applies to both solutes, and in being so, can reduce the separation selectivity. The choice of optimum pressure for a specific separation task would in general require careful optimization to make a rational compromise between yield, selectivity, and feasibility of operation.

The effect of temperature is somewhat more complicated as there is a competing solubility effect caused by the increase in vapor pressure and the decrease in density upon the increase of temperature. At low temperatures, the high solvent densities result in high solubilities. However, near the critical point, the increase of temperature strongly reduces solvent density, and consequently, the solubility. At pressures well above the critical value and temperatures higher than critical, the increase of solute vapor pressure becomes the predominant factor in affecting solubility and, therefore, solubility increases slowly but steadily with temperature. A minimum in solubility is therefore established near the critical temperature (Fig. 8a). Its precise location depends on the solute-solvent affinity and the pressure. Generally the higher the pressure and the solute-solvent affi-

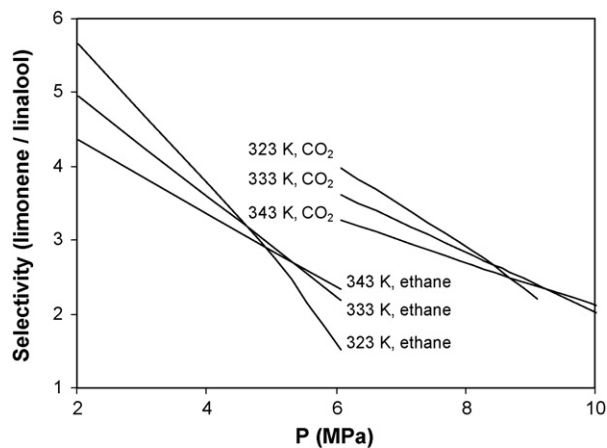


Fig. 7. Flash-calculated selectivities of limonene over linalool as a function of pressure for a mixture of 98.00 mol% solvent, 1.98 mol% limonene, and 0.02 mol% linalool.

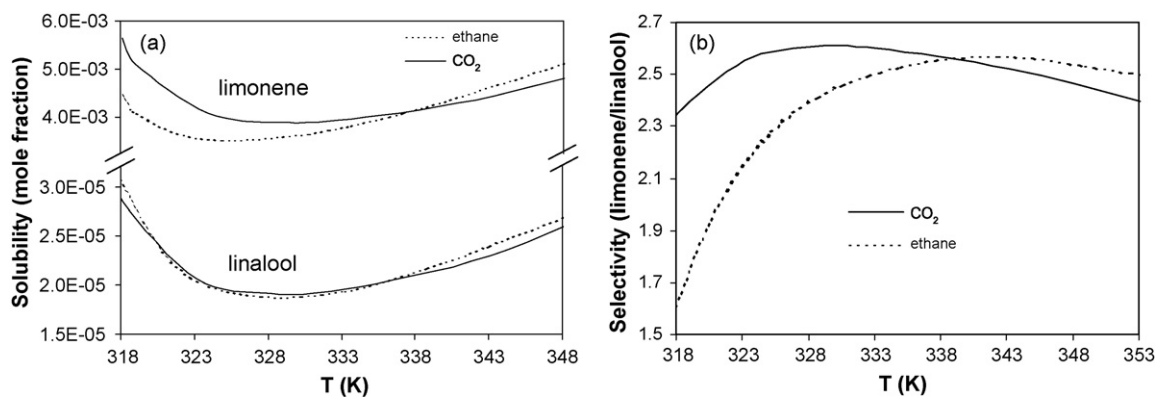


Fig. 8. (a and b) Flash-calculated solubilities and selectivities as a function of temperature for a mixture of 98.00 mol% solvent, 1.98 mol% limonene, and 0.02 mol% linalool at a reduced pressure (relative to pure solvent) of 1.15.

ity, the higher are the minimum solubility temperature and the corresponding solute concentration values [4].

While the concentrations of solutes in the vapor phase as function of temperature show a concave behavior having a minimum, within the same temperature range the corresponding solute concentrations in the liquid phase exhibit a monotonous increase with temperature for both CO₂ and ethane (not shown). The combination of solute concentrations in the two phases results in a maximum in the selectivity curve as a function of temperature. This can be seen in Fig. 8b where the flash-calculated selectivities of CO₂ are compared with those of ethane for separating limonene from linalool as a function of temperature. Or more interestingly on a pressure coordinate, the “crossover” of the isotherms in Fig. 7 indicates that up to a certain pressure, lower temperatures have higher selectivities but this trend switches to the opposite after the crossover pressure is reached.

The influence of solvent-to-feed ratio and reflux ratio are shown in Figs. 9 and 10 for the deterpenation process with either carbon dioxide or ethane. In these calculations a 98.73 wt% limonene oil mixture was introduced on the eleventh stage of a 25-staged column operating at 333 K. Both CO₂ and ethane extractors were simulated at the same reduced pressure of 1.35 relative to pure solvent critical pressure, while the separation vessels were both operated at a pressure 2.1 MPa lower than the

critical pressure of the solvent being used. The temperature of the separation vessel was 303 K in both extraction setups. In the case of Fig. 9, reflux was set to 50% for both extractors while in the calculations leading to Fig. 10, solvent-to-feed ratio was kept at a constant value of 38.5 while the reflux ratio was varied.

Extraction ratio, the y-coordinate of Figs 9a and 10a, is defined as the mass flow rate of limonene in the extract to that in the feed. As expected, the extraction ratio increases with solvent-to-feed ratio (Fig. 9) for both solvents, having higher values for ethane. Fig. 10 indicates that when part of the extract is returned to the top of the column as reflux, the net effect is an increase in the amount of raffinate (desired product), a decrease in the yield of extract, and a large increase in selectivity of separation. This shows that great benefits can be obtained by applying an appropriate ratio of reflux to deterpenation processes.

3.3. Comparison of carbon dioxide and ethane

The previous section indicated the complicated and interconnected dependence of extraction yields and separation selectivities on different process variables. The importance of process optimization was thus highlighted. In the comparative calculations that follow, certain process variables were deliberately kept constant to form a comparative basis, while the

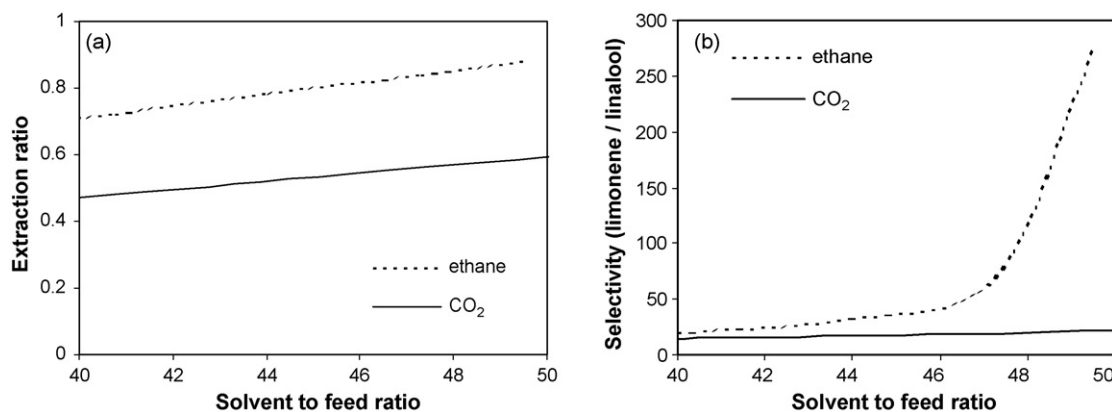


Fig. 9. (a and b) Predicted countercurrent extraction performance at varying solvent-to-feed ratios (kg/kg) for a feed of 98.73 wt% limonene introduced at the 11th stage of a 25-staged column operating at 333 K, reduced pressure of 1.35, and reflux ratio of 50%. The extraction ratio is the mass flow rate of limonene in the extract to that in the feed.

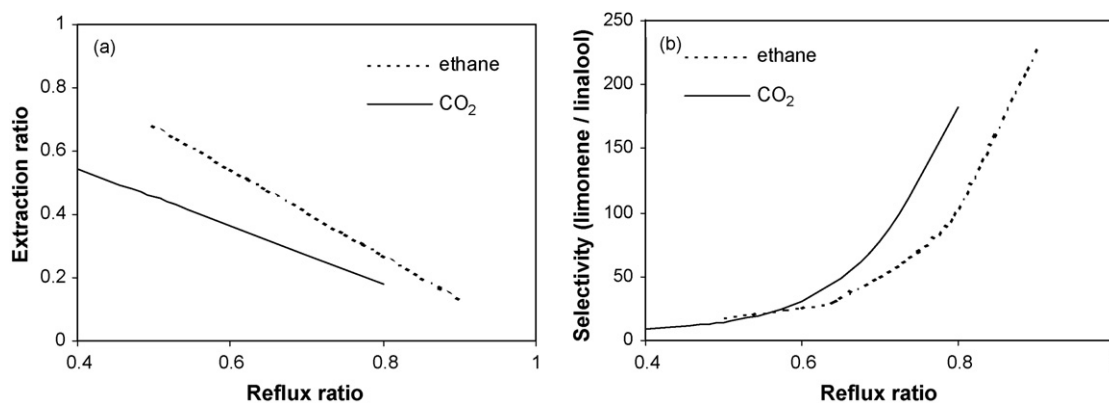


Fig. 10. (a and b) Predicted countercurrent extraction performance at varying reflux ratios for a feed of 98.73 wt% limonene introduced at the 11th stage of a 25-staged column operating at 333 K, reduced pressure of 1.35, and a solvent-to-feed ratio of 38.5. The extraction ratio is the mass flow rate of limonene in the extract to that in the feed.

others were optimized in order to minimize the required solvent circulation. Since supercritical extractions perform based on “closeness” to criticality, to make a fair comparison in the solubility performances of CO₂ and ethane, extractions were compared at the same reduced pressures. Fortunately, the critical temperatures of CO₂ and ethane are very close and, therefore, the same operating temperatures correspond to nearly the same reduced temperatures as well. The operating temperature of the extractor was chosen as 333 K, in order to avoid any risk of thermal degradation of the oil.

To comply with actual conditions of the orange oil industry, the feed and product compositions were chosen corresponding to commercial raw and vacuum-distilled oils from literature. For example, in the case of fivefold oils, the raw oil was chosen as 1.27% linalool–98.73% limonene, corresponding to the 1.27 wt% oxygenate containing raw oil of Auerbach [44] and a fivefold oil product of 5.68 wt% (5.05 mol%) linalool, corresponding to the commercial fivefold oil of 5.68 wt% oxygenates [44]. The number of plates was 25, with the oil entering at stage 6 in both models with carbon dioxide and ethane.

3.3.1. Fivefold oil, optimized process

The different operating conditions and constraints considered in making process comparisons are listed in the top part of Table 3. The bottom part of this table lists the most significant process optimization results for the two solvents. These results show some of the advantages of ethane over CO₂ for the supercritical deterpenation of orange peel oil with the constraints of replicating a commercial vacuum-distilled fivefold oil [44]. Ethane is capable of carrying out the same extraction task as CO₂ at a considerably lower pressure (6.5 versus 10.0 MPa), and also with a lower solvent-to-feed ratio (60 versus 69). In addition to operating at a lower absolute pressure, the pressure head of the recycle compressor is also considerably lower for ethane (3.05 MPa versus 6.69 MPa).

3.3.2. Tenfold oil, optimized process

In addition to fivefold oil, the citrus oil industry also commonly produces the more concentrated 10-fold orange oils. The results of simulations at the same reduced pressure to produce

a 10-fold oil product with the same aroma (linalool) concentration are given in Table 4. In this case, however, it was not possible to obtain a 10-fold oil with the corresponding commercial vacuum-distilled aroma concentration of 5.19 mol% [44].

Table 3

Comparison of optimized supercritical extraction processes with CO₂ and ethane at the same reduced pressure to produce commercial [44] fivefold oil

Process variable	CO ₂	Ethane
Variables kept the same in both extractions		
Extent of concentration	fivefold	fivefold
Raw oil, mol% linalool	1.12	1.12
Product, mol% linalool	5.06	5.05
Temperature (K)	333.15	333.15
Reduced pressure (absolute pressure) (MPa)	1.35 (10.0)	1.35 (6.5)
Separator temperature (K)	295	295
Variables calculated by the optimization program for the two extractions		
Solvent to feed ratio (kg/kg)	69	60
Reflux ratio	0.53	0.63
Separator pressure (MPa)	3.31	3.45
ΔP for solvent recycle compressor (MPa)	6.69	3.05
Molar recovery of linalool in raffinate (%)	89.5	89.6
Molar recovery of limonene in extract (%)	80.9	80.9

Table 4

Comparison of optimized supercritical extraction processes with CO₂ and ethane to produce 10-fold oil at the same reduced pressure

Process variable	CO ₂	Ethane
Variables kept the same in both extractions		
Extent of concentration	10-fold	10-fold
Raw oil, mol% linalool	0.88	0.88
Product, mol% linalool	6.70	6.71
Temperature (K)	333.15	333.15
Reduced pressure (absolute pressure) (MPa)	1.26 (9.32)	1.26 (6.08)
Separator temperature (K)	295	295
Variables calculated by the optimization program for the two extractions		
Solvent to feed ratio (kg/kg)	74	56
Reflux ratio	0.27	0.32
Separator pressure (MPa)	3.77	3.48
ΔP for solvent recycle compressor (MPa)	5.55	2.60
Molar recovery of linalool in raffinate (%)	75.2	75.2
Molar recovery of limonene in extract (%)	90.7	90.7

The purification level is even better with supercritical solvents, for example, 6.7 mol% in the calculated examples of Table 4. Although this is just one example, it may well be that in general, supercritical extraction produces citrus oils of higher quality than conventional vacuum distillation.

Here again, higher solvent-to-feed ratios with higher compressor pressure heads and higher absolute pressures are necessary for CO₂ to produce the same product, as compared to ethane. As one may expect, since a greater degree of terpene separation is desired for tenfold oils, even a greater difference in solvent loading is necessary. For example, in the extraction of the fivefold oil of Table 3 the ratio of CO₂ to ethane loading was 1.2, while for the 10-fold extraction of Table 4, this ratio increases to 1.3. It is expected that higher order foldings will show even further benefits of ethane over CO₂. Nevertheless, from the industrial point of view, it is the 5- and 10-fold oils that have the most significance. Deterpenation in excess of 25-fold is rarely done. However, one important issue that must be pointed out is the extra safety provisions required for ethane-operating equipment due to the potential explosion hazards of ethane. This will of course add to the investment costs of ethane extraction plants. In addition, if the oil is to be used in foods, some countries may find the use of ethane as solvent to be unacceptable, while CO₂ has no such issues.

4. Conclusions

In an attempt to verify the hypothesis that the replacement of supercritical CO₂ with supercritical ethane will result in an improved deterpenation process, a numerical modeling and optimization program was developed. Phase equilibria was predicted using the SRK equation of state, having its binary interaction coefficients optimized to available binary and ternary experimental data in different space coordinates.

The rigorous stage-by-stage computational procedure predicting the extraction process was checked against available supercritical CO₂ column data. Upon the validation of the process simulator, the effect of different operating conditions on the performance of the extractor such as temperature, pressure, solvent-to-feed ratio, and reflux rate were investigated. It was shown that there is a rather complicated relationship among the variables and the extraction efficiency.

The processes of supercritical deterpenation of orange peel oil with either carbon dioxide or ethane were then numerically optimized using a non-linear programming algorithm. Different system variables including extractor pressure, solvent-to-feed ratio, reflux ratio, and separator pressure were treated as adjustable parameters and optimized in such a way that the rate of solvent recirculation was minimized.

The numerical results indicated ethane as having greater solvent power over CO₂, while no general statement could be drawn regarding selectivity. Anyhow, although solvent selectivity is a determining factor in many extraction tasks, this is not the case in citrus peel oil deterpenation. In this industry, obtaining a high purity product is not the main goal of extraction. It is simply desired to partially remove the terpenes to concentrate the oil from about 1% aroma constituents to only about 5%. This goal

is achieved better by ethane than by CO₂. If the two processes are compared at the same reduced pressures, the ethane-operated extractor requires much lower operating pressure (for example, by a factor of 0.7), as well as a much lower pressure difference to be accomplished by the compressor (for example half).

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