A Theoretical Model to Simulate Supercritical Fluid Extraction: Application to the Extraction of Terpenes by Supercritical Carbon Dioxide

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The ternary system CO_2−limonene−citral was chosen as a model system in order to study the extraction of terpenes from lemon oil using supercritical carbon dioxide. Extractions were performed at several pressures and temperatures to evaluate the influence of these parameters on the separation efficiency. Extract composition was monitored by capillary gas chromatography. A theoretical model, based on a modified Peng−Robinson equation of state, was used to simulate the thermodynamic and mass transfer aspects of the extraction column. The critical parameters and the acentric factors of limonene and citral were estimated by group contribution methods. The method developed by Abdoul et al., which allows the calculation of binary interaction parameters (k_{ij}), was applied to terpenic compounds. The extraction experiments were simulated using this model, and the extraction profiles were accurately reproduced.

Introduction

Extraction with supercritical (SC) fluids is a method frequently applied to the extraction and purification of essential oils. These oils contain thermolabile compounds, and their main applications are in the cosmetic, pharmaceutical, and food industries. The methods used in the processing of these oils must, therefore, have low operating temperatures and leave no toxic residues in the final product. Extraction with supercritical carbon dioxide fulfills those requirements, and the solvent properties of SC-CO_2 are adequate for the solutes involved.

In the last twenty years, a considerable number of publications report applications of supercritical CO_2 in the extraction and refining of terpene-rich oils such as lemon oil, orange oil, or grapefruit oil. All of the references can be found in the review recently written by Reverchon[1] on this topic.

For work with lemon oil, extraction conditions (temperature, pressure, solvent flow rate, feed composition, etc.) should be chosen in order to obtain an oil with a high content of oxygenated terpenes (responsible for the aroma of the oil) and a low content of terpene hydrocarbon (major components of the crude oils but with poor aromatic properties). The choice of the extraction temperature is limited by the carbon dioxide critical temperature and by the temperature above which thermal degradation of the feed can occur.

In this work, a model system composed of carbon dioxide, an oxygenated terpene (citral), and a terpene hydrocarbon (limonene) was chosen to study the pa-

rameters controlling the extraction of lemon oil by SC-CO_2. Discontinuous extractions were performed in a homemade apparatus at different pressures and temperatures. Moreover, we developed a theoretical model, based on a modified Peng−Robinson equation of state (PR-EOS) in order to simulate phase equilibrium and mass transfer inside the extraction column. A comparison is made between the experimental measurements and the simulation results. Our goal is to determine whether a theoretical model can or can not be used to predict the extraction column behavior (phase equilibrium, mass transfer, etc.) with new operating conditions (temperature, pressure, solvent flow rate, feed composition, etc.) by taking as an illustration the extraction of lemon oil by supercritical CO_2.

Experimental Section

Description of the Experimental Apparatus. Extractions were performed with the homemade apparatus depicted in Figure 1. It is composed of a CO_2 conditioning section, an extraction column, a high-pressure pump to feed the liquid solutes into the column, and a series of three separators where the solutes were recovered. A gas flowmeter and a gas totalizer are placed in series after the cyclones.

The CO_2 conditioning section is composed of a CO_2 cylinder, a heat exchanger (where the carbon dioxide is condensed), a liquid CO_2 storing tank, a high-pressure pump (Minipump, Dosapro Milton Roy, Pont Saint Pierre, France), a back-pressure regulator (Alphagaz, HBS 315/8), a pulse dampener, and another heat exchanger (where CO_2 is heated to the temperature of the experiment).

The extraction column has an internal diameter of 23 mm and a length of 400 mm and is packed with 261 g of glass beads with a medium diameter of 5 mm. The column empty volume (after packing) was measured by volume displacement with a calibrated buret (0.01 mL precision) and was found to be 68.2 mL.

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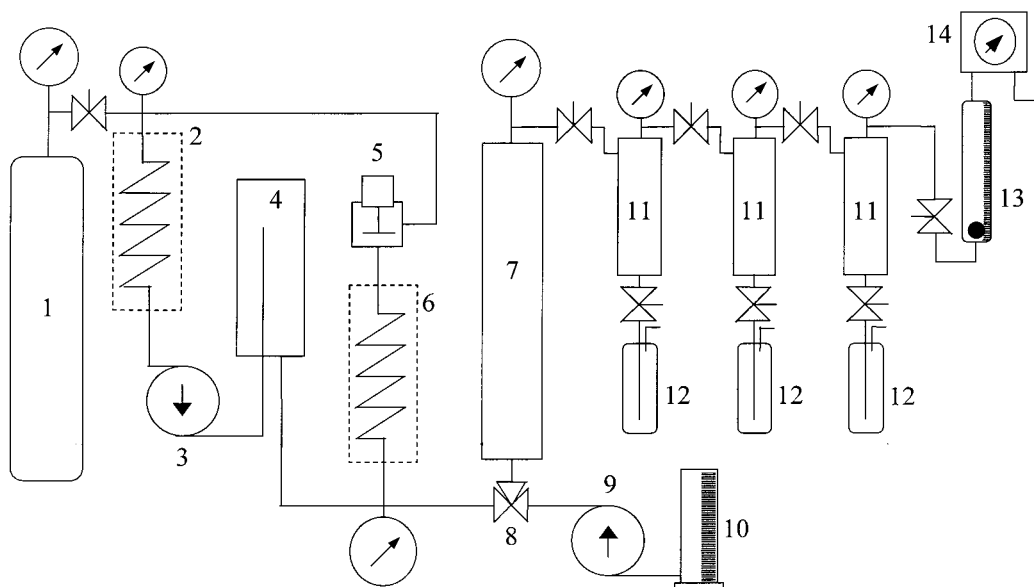
Legend: **1.** CO_2 cylinder **2.** Heat exchanger **3.** CO_2 pump **4.** Liquid CO_2 reservoir **5.** Back pressure regulator **6.** Heat exchanger **7.** Extraction column **8.** Three way valve **9.** Liquids pump **10.** Liquid solutes container **11.** Separators (cyclones) **12.** Solutes recovery vials **13.** Gas flowmeter **14.** Gas totaliser

Figure 1. Apparatus flow sheet.

The separators used in this work were high-performance cyclones. The CO_2 volume exiting the apparatus was measured using a gas totalizer, with a precision of 0.1 dm³ (at room pressure and temperature).

Extraction Procedure. A typical extraction run starts by feeding the extraction column with the liquid solutes at atmospheric pressure. After this operation, the pump is washed with an appropriate solvent to recover the solutes left inside the pump volume. The resulting solution is treated by gas chromatography using an internal standard. Carbon dioxide is then pumped into the column until the pressure of the experiment is reached. Extraction starts after an equilibration period of 15 min. The fluid exiting the column is progressively expanded and cooled as it flows through the separators. The precipitated solutes can be recovered by opening the valves at the bottom of the cyclones. At the same time that a sample is recovered, the amount of gas passed through the system is registered. Each sample is weighed and analyzed by gas chromatography.

Pressure and temperature were measured with an accuracy of ±0.1 MPa and ±0.5 K, respectively.

Chromatographic Procedure. Samples were analyzed in a Carlo Erba Fractovap 2900 instrument equipped with an SE-54 capillary column and a flame ionization detector. The oven temperature was initially 90 °C, and the temperature was then raised to 160 °C at a heating rate of 20 °C/min, followed by a second heating period up to 180 °C at a heating rate of 10 °C/min. The carrier gas flow was 30 mL/min. The hydrogen flow was 1 mL/min, and the air flow was 100 mL/min. The oil samples were dissolved in an appropriate volume of ethanol and injected (injection volume was of 2 μL). Quantification of the amounts of limonene and citral present in the samples was achieved by using *m*-xylene as an internal standard.

Materials. Limonene (99% pure) and citral (97% pure) were purchased from Fluka. The *m*-xylene had a purity of 97% and was obtained from Merck. Carbon dioxide was supplied by Carboxyque Française and was of industrial grade (99.998% purity).

Modeling Section

Thermodynamic Model. To model the extraction column, it is necessary to know the phase behavior of the system CO_2−limonene−citral over the entire range of operating conditions.

Equation of State. In this paper, the Peng−Robinson equation of state[2] (PR-EOS) was used

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)+b(v-b)} \quad \text{with}$$

$$b = 0.07780 \frac{RT_c}{P_c} \quad \text{and} \quad R = 8.31441 \text{ J mol}^{-1} \text{ K}^{-1}$$

To precisely calculate the vapor pressures of the pure compounds, the following Soave-type[3] function, developed by Rauzy,[4] was used:

$$a(T) = 0.457236 \frac{R^2 T_c^2}{P_c} \left[1 + m \left(1 - \left(\frac{T}{T_c} \right)^{0.445075} \right) \right]^2$$

with

$$m = 6.812553$$
$$\overline{[\sqrt{1.127539 + 0.517252\omega - 0.003737\omega^2} - 1]}$$

To calculate the correct densities, the molar volume solution of the EOS must be reduced using a volume translation c, as proposed by Péneloux et al.[5]

$$v_{\text{correct}} = v_{\text{EOS}} - c \quad \text{with}$$

$$c = \frac{RT_c}{P_c} [0.1153758 - 0.440642 Z_{\text{RA}}]$$

In the previous equation, Z_{RA} is the Rackett compress-

Table 1. Physical Properties of Pure Compounds

molecule	normal boiling point T_b/K	critical temperature T_c/K	critical pressure P_c/MPa	acentric factor ω	Rackett compressibility factor Z_{RA}
CO_2	−	304.21	7.38	0.225	0.27280
limonene	178	661.0	2.76	0.330	0.26187
citral	229	694.6	2.29	0.536	0.25204

ibility factor appearing in Spencer and Danner's[6] modification of the Rackett equation.

For a mixture designated by m containing p compounds of mole fraction x_i, classical mixing rules were used

$$b_m = \sum_{i=1}^{p} b_i \qquad c_m = \sum_{i=1}^{p} x_i c_i$$

$$a_m(T) = \sum_{i=1}^{p}\sum_{j=1}^{p}[\sqrt{a_i(T)\,a_j(T)}\,x_i x_j(1 - k_{ij}(T))]$$

where k_{ij} are binary parameters that characterize the interactions of unlike molecules. Because extraction experiments were performed at different temperatures, it was decided to use a temperature-dependent function for k_{ij} in order to have a precise description of our ternary system. The following equation, developed by Abdoul et al.,[7] was used:

$$k_{ij}(T) = \frac{E_{ij}(T) - (\delta_i - \delta_j)^2}{2\delta_i\delta_j} \quad \text{with} \quad \delta_i = \frac{\sqrt{a_i(T)}}{b_i} \quad \text{and}$$

$$E_{ij}(T) = A_{ij}\left(\frac{298.15}{T}\right)^{(B_{ij}/A_{ij} - 1)} \quad (1)$$

For a given binary system, A_{ij} and B_{ij} are two parameters. Abdoul et al.[7] developed a group contribution method (GCM) that allows for the calculation of both of these parameters. Because the aldehyde function appearing in the citral molecule is not defined in this GCM, it was decided that A_{ij} and B_{ij} for each binary system (CO_2−citral, CO_2−limonene, and citral−limonene) would be obtained from a regression of the phase equilibrium experimental data. This means that each molecule is considered as a group, and thus, the GC aspect of Abdoul et al.'s method is totally lost.

Pure-Component Physical Properties. As was previously done by De Azevedo et al.[8] and Brandani et al.,[9] critical properties of limonene and citral have been calculated with the Lydersen GCM.[10] The corresponding normal boiling points (T_b) are from the 66th edition of the *Handbook of Chemistry and Physics*. Knowing the critical parameters and the normal boiling points of limonene and citral, the acentric factors (ω) were estimated by the corresponding state method developed by Lee and Kesler.[11] To verify the ω estimations, the acentric factors were also calculated using

$$\omega = \frac{3}{7}\frac{\theta}{1 - \theta}\log_{10}(P_c/\text{atm}) - 1 \quad \text{with} \quad \theta = \frac{T_b}{T_c}$$

For limonene, both values are close, but for citral, they are quite different, and so, the average value was selected. To estimate the volume correction, the Rackett compressibility factor of the terpene molecules was calculated using the experimental liquid density and the Rackett equation. The physical properties of the three molecules are summarized in Table 1.

Table 2. Parameters Allowing for the Calculation of the Binary Interaction Parameter (k_{12}) between CO_2 (1) and Limonene (2) at Any Temperature

A_{12}	345 J cm^{-3}
B_{12}	1450 J cm^{-3}

Binary Interaction Parameters. Designating CO_2, limonene, and citral as components 1, 2, and 3, respectively, it is necessary to estimate the six parameters A_{12}, A_{13}, A_{23}, B_{12}, B_{13}, and B_{23} in order to compute the three binary interaction parameters (k_{12}, k_{13}, and k_{23}) at any temperature. In this study, these six parameters were obtained from a regression of the phase equilibrium experimental data.

CO_2−Limonene System. The vapor−liquid equilibrium of limonene in supercritical carbon dioxide (SC-CO_2) was measured at 13 different temperatures ranging from 337.3 to 349.3 K by several authors.[12−15] A total of 100 experimental points including critical points are available from the literature. Both parameters A_{12} and B_{12} were calculated from all of these experimental data by minimizing the following objective function:

$$S = \sum_{i=1}^{m}(y_{\text{exp}} - y_{\text{cal}})_i^2 + \sum_{j=1}^{n}(x_{\text{exp}} - x_{\text{cal}})_j^2$$

where y_{exp} and y_{cal} are, respectively, the experimental and calculated values of the carbon dioxide mole fraction in the vapor phase and m is the number of experimental values ($m = 73$). Similarly, x_{exp} and x_{cal} are the experimental and calculated values of the CO_2 mole fraction in the liquid phase, and n is the number of experimental values ($n = 33$). The six critical compositions were considered simultaneously as liquid-phase and gas-phase compositions. The resulting parameters are given in Table 2.

Figure 2 shows the calculated isothermal phase diagrams for the CO_2−limonene system at seven different temperatures, whereas Figure 3 shows the calculated critical point locus in a pressure temperature plane. It is then possible to conclude that the PR-EOS coupled with the Abdoul et al.[7] equation to estimate the binary interaction parameter k_{12} allows for the phase behavior of the investigated system to be reproduced with a very good accuracy regardless of the temperature.

CO_2−Citral System. As was previously done for the CO_2−limonene system, experimental vapor−liquid equilibrium data for the CO_2−citral system were used in order to determine the A_{13} and B_{13} parameters. For this system, a total of 75 experimental points (54 CO_2 mole fractions in the gas phase, 14 CO_2 mole fractions in the liquid phase, and 7 critical points) were found. The A_{13} and B_{13} values leading to the best agreement between experimental and calculated values are shown in Table 3.

Figures 4 and 5 show, respectively, the calculated isothermal phase diagrams for the CO_2−citral system at six different temperatures and the critical points locus in a pressure−temperature plane.

Once more, the selected thermodynamic model allows for a good correlation with the experimental data.

Limonene−Citral System. To our knowledge, the binary limonene−citral system has never been studied experimentally. To find the temperature dependence of the binary interaction parameter k_{23}, experimental data by Kalra et al.[16] of the CO_2−limonene−citral ternary
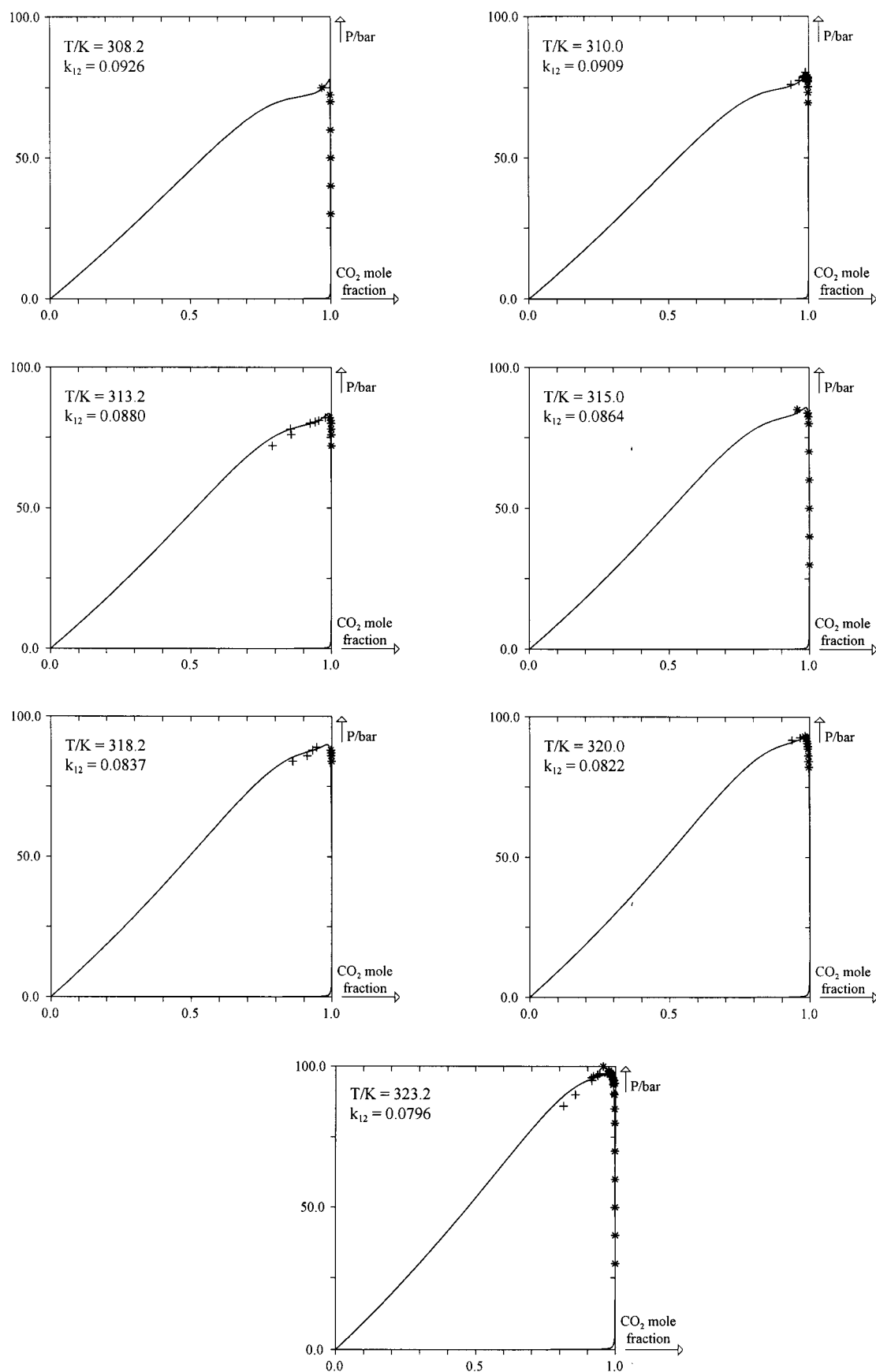
Figure 2. Phase behavior of the $CO_2(1)$−limonene(2) system at temperatures of 308.2, 310, 313.2, 315, 318.2, 320, and 323.2 K. (+) Experimental CO_2 mole fraction in the liquid phase. (*) Experimental CO_2 mole fraction in the gas phase. (−) Calculated phase envelope.

system were used. In this section, k_{12} and k_{13} were calculated by the correlations developed in the previous

sections. In a first step, it was thus decided to determine A_{23} and B_{23} in order to have the best agreement between
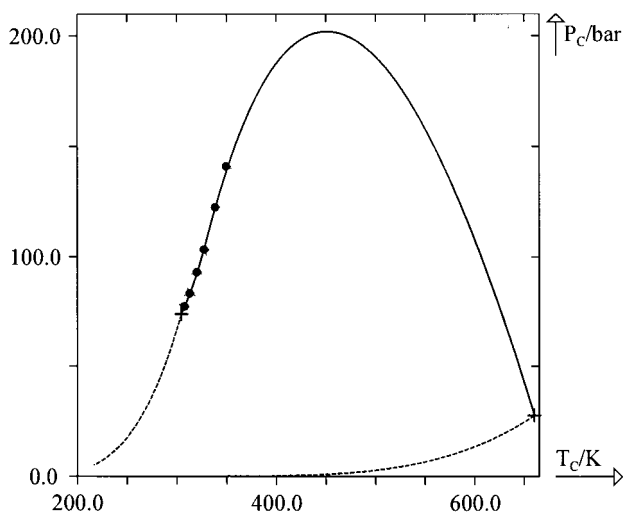
Figure 3. (—) Calculated critical points locus for the CO_2-limonene system. (---) Calculated vaporization curve of pure components. (●) Experimental critical points of the mixture. (+) Critical points of pure components.

Table 3. Parameters Allowing for the Calculation of the Binary Interaction Parameter (k_{13}) between CO_2 (1) and Citral (3) at Any Temperature

A_{13}	300 J cm^{-3}
B_{13}	1800 J cm^{-3}

the calculated and experimental mole fractions. The objective function

$$Q = \sum_{i=1}^{m}(y_2^{exp} - y_2^{cal})_i^2 + (y_3^{exp} - y_3^{cal})_i^2 +$$
$$\sum_{j=1}^{n}(x_2^{exp} - x_2^{cal})_j^2 + (x_3^{exp} - x_3^{cal})_j^2 \quad (2)$$

was minimized only for A_{23} and B_{23}. However, because of the fact that the binary interaction energies E_{23} were positive at low temperature and negative at higher temperatures, it was impossible to correlate them with eq 1. In the particular case of the binary limonene–citral system, it was decided to use the following equation:

$$E_{23}(T) = A_{23}\left(\frac{298.15}{T}\right)^{(B_{23}/A_{23}-1)} + C_{23}$$

The three parameters A_{23}, B_{23}, and C_{23} were thus determined in order to minimize eq 2. The resulting parameters are given in Table 4. Figure 6 shows the three isothermal and isobaric phase diagrams for the ternary system.

Because it was possible to define a thermodynamic model capable of reproducing with good accuracy all of the experimental data of the systems investigated in this study, it was decided to use it in order to model the extraction column.

Extraction Column Modeling. *First Step.* The first step of the extraction column modeling consists of determining the initial state of the column. The porous volume of the column, i.e., the total volume of the column minus the volume occupied by the glass beads, is perfectly known. Such a volume is denoted V and is occupied by the fluid phase(s) inside the column. As explained in the Experimental Section, a predetermined amount of terpene(s), n_T, is initially introduced into the

column thermostated at a given temperature T. Then, the top of the column is closed, and a quantity of CO_2, denoted n_{CO_2}, is introduced by the bottom of the column until the pressure reaches the desired value P.

Knowing P, V, T, and n_T, a flash calculation based on the previously described PR-EOS allows for a calculation of n_{CO_2}, the state of the column (monophasic or diphasic), and the amount of each phase. The column is then divided into N theoretical stages of equal volume V_0. In this study, we chose N = 4 in order to reduce computing times as the extraction profiles calculated with $N = 20$ were very similar to those obtained with $N = 4$.

When the column is initially monophasic, it is then possible to determine the amount of each component in each stage. On the other hand, when the column is initially diphasic, it was assumed that the liquid phase was located in the bottom of the column and that it was topped by a gas phase. To determine whether such an assumption was correct, the decantation speed of the liquid and gas phase was roughly calculated using the correlation developed by Dumoré and Hagoort.[17] The viscosity of each phase used in the correlation was estimated by the method developed by Bray and Lohney.[18] The calculations lead to a decantation speed close to 1 cm/s, meaning that, in a few seconds, the two phases are perfectly separated. The knowledge of the liquid and gas phase densities (determined by the PR-EOS) provides a knowledge of the number of stages in the liquid or gas state and which one is diphasic. Under these conditions, the global composition of each stage can be easily determined. An illustration of the two possible initial states of the column is shown in Figure 7.

Second Step. Once the initial state of the column, i.e., the amount of each component in each stage, is known, it is possible to start the extraction simulation. From the experiments, the CO_2 flow rate (in grams per minute) entering the column by the bottom is known. A time step is thus chosen so that the volume of CO_2 entering the column was about 50% of a stage volume. In other words, a known amount of CO_2 is added to stage 1. It is then assumed that perfect mixing takes place and that thermodynamic phase equilibrium is reached. This means that the conditions in the first stage can be described by a P/T flash calculation. After the CO_2 and the first-stage fluid are mixed, the total volume of the stage will be larger than the assumed initial stage volume V_0. The volume in excess is transferred from stage 1 to stage 2 (see Figure 8). If two phases are present, the gas phase is moved first. If all of the gas phase is moved but the stage volume is still larger than the initial stage volume V_0, then a part of the liquid phase is also moved (see Figure 9). In a second step, the excess volume formed in stage 2 is transferred to stage 3 and so on until production is obtained from the last stage.

When one batch calculation has been completed, time is increased (a new amount of CO_2 is injected into the first stage), and the stage-to-stage transfer calculation is resumed. Finally, the amounts of CO_2, limonene, and citral leaving the last stage of the column are recorded versus time.

Results and Discussion

To determine whether the proposed column modeling and the proposed thermodynamic model are able to
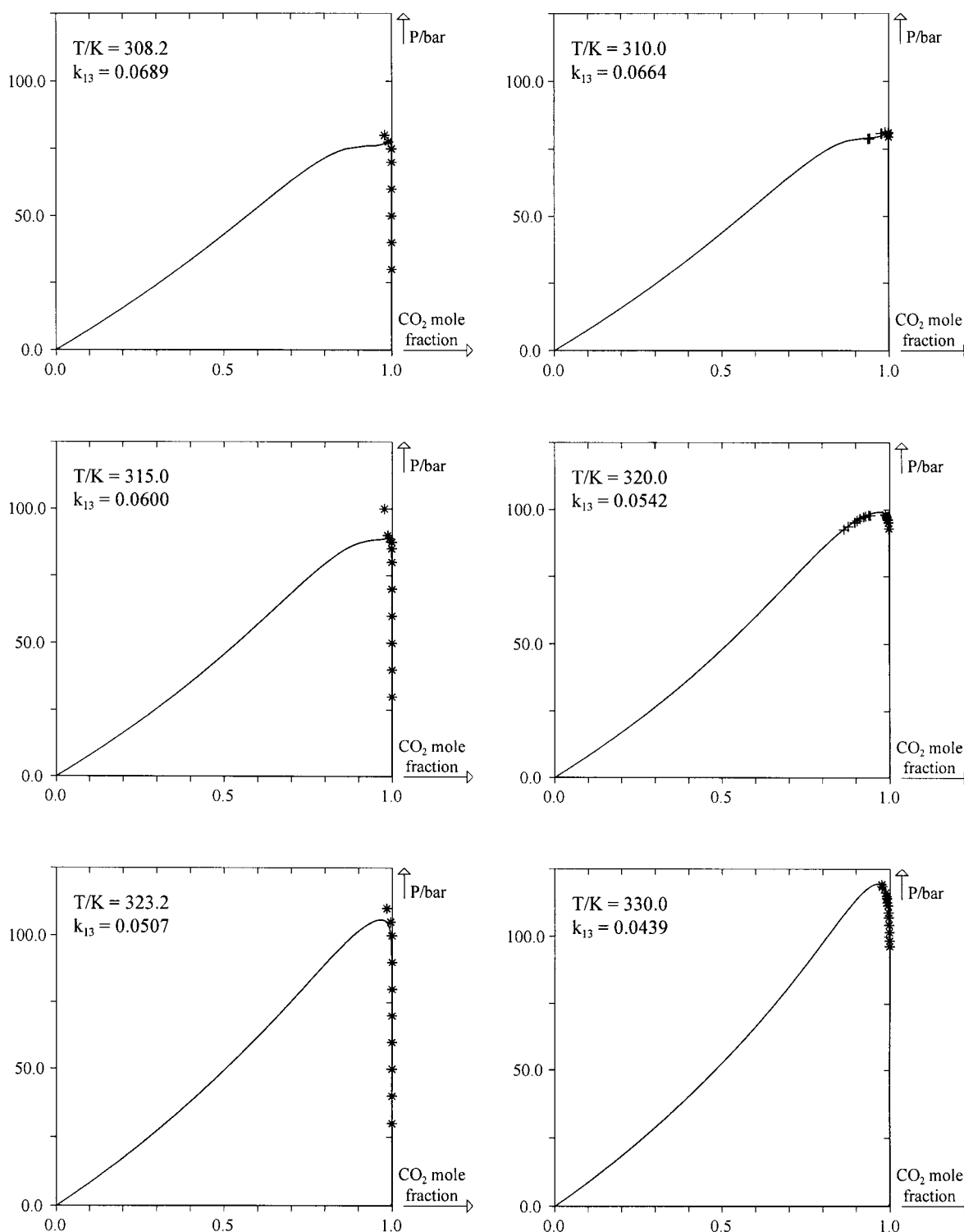
Figure 4. Phase behavior of the $CO_2(1)$–citral(3) system at temperatures of 308.2, 310, 315, 320, 323.2, and 330.0 K. (+) Experimental CO_2 mole fraction in the liquid phase. (*) Experimental CO_2 mole fraction in the gas phase. (−) Calculated phase envelope.

accurately predict the extraction profiles, it was decided to work first on binary systems and second on ternary systems.

Binary Systems. In this section, a given amount of pure limonene or pure citral is introduced into the extraction column thermostated at a selected temperature. Later, CO_2 is introduced into the column in order to reach the desired pressure. Five experiments were performed. The temperature, pressure, and amount of terpene were selected in order that the initial state of the column (before the extraction starts) was either

monophasic liquid, diphasic, monophasic gas, or supercritical. Each experiment corresponds to a dynamic extraction of about 2 h. For each experiment, the composition of the mixture exiting the column was recorded versus time. To do so, the valves located at the bottom of the cyclones were regularly opened. Each sample was weighed and analyzed by gas chromatography. Moreover, the time and thus the amount of CO_2 were recorded.

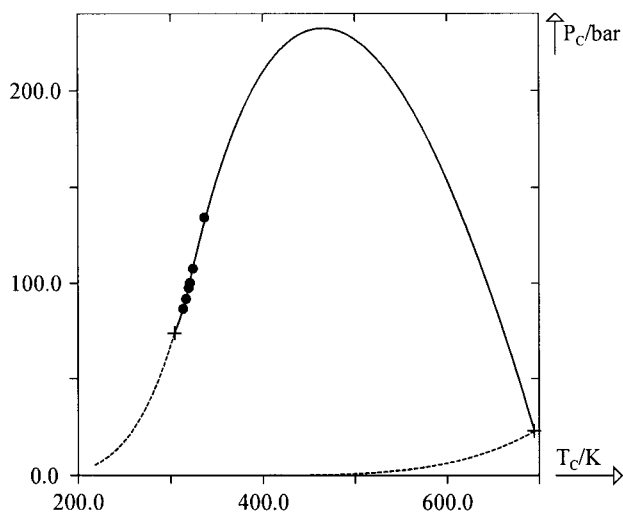To visualize our results, it was decided to plot, for each experiment, the extraction profile that is the ratio

Figure 5. (—) Calculated critical points locus for the CO_2–citral system. (---) Calculated vaporization curve of pure components. (●) Experimental critical points of the mixture. (+) Critical points of pure components.

Table 4. Parameters Allowing for the Calculation of the Binary Interaction Parameter k_{23} between Limonene (2) and Citral (3) at Any Temperature

A_{23}	2609 J cm^{-3}
B_{23}	5442 J cm^{-3}
C_{23}	−2374 J cm^{-3}

of the mass of terpene exiting the column to the mass of CO_2 versus time. Such experimental profiles were then compared to the calculated profiles.

Table 5 gives, for each experiment, the amount of terpene introduced in the column, the temperature, the pressure of the experiment, and the CO_2 flow rate. For each experiment, the pressure and temperature in the cyclones were kept as follows: first cyclone at 5.5 MPa and 302 K, second cyclone at 3.6 MPa and 289 K, third cyclone at 2.0 MPa and 289 K. In Figure 10 are compared the experimental and calculated extraction profiles. Such a figure clearly shows that the extraction profiles are seriously impacted by the initial physical state of the column. However, the shape of such profiles can be explained by thermodynamic arguments. Indeed, all of the profiles are, in fact, similar to the schematic profile shown in Figure 11a in which it is possible to distinguish five periods. In Figure 11b, a schematic isothermal phase diagram in which the five periods can be seen has also been plotted. The straight dashed line drawn in Figure 11b indicates how the composition of the mixture exiting the column changes versus time.

The difference between the experimentally determined extraction profiles comes from some periods that do not always exist. When the column is initially monophasic liquid (experiment 1), the five periods

exist, and the shape of the profile can be explained as follows:

For period 1, the mixture exiting the column is a liquid. By increasing the time, this liquid phase becomes more concentrated in CO_2 because the total amount of terpene decreases in the column. For this reason, this first period is a decreasing function of time.

Period 2 starts as soon as the column becomes diphasic gas–liquid. Indeed, adding CO_2 at the bottom of the column makes a gas phase appear. Period 2 is generally very short (no more than a few minutes) and corresponds to the case where the matter exiting the column is a two phase system. The amount of gas in the column is thus very small. During this period, the matter exiting the column crosses the isothermal phase diagram at the given operating pressure condition shown in Figure 11b.

During period 3, the column is still diphasic, but the amount of gas has increased. This means that only a gas phase in equilibrium with a liquid phase exits the column. Because for a binary system at constant temperature and pressure the gas- and the liquid-phase composition are always the same, a plateau appears in the extraction profile. In Figure 11b, period 3 is represented by a single point on the dew curve.

During period 4, because a large amount of CO_2 has been added in the column since the beginning of the experiment, the column is monophasic. It is filled by a gas phase. With increasing time, the amount of terpene in the column decreases, meaning that the extraction profile becomes a decreasing function of time, as it was during periods 1 and 2.

For period 5, by the end of the extraction, the column is filled with pure CO_2, and the terpene content in the extract will be equal to zero.

The previous explanations make possible a discussion of our experimental results. In experiment 1, the column is initially liquid because a large amount of limonene has been introduced. The five periods exist. In experiment 2, periods 1 and 2 do not exist because the column is initially diphasic (a smaller amount of solute was introduced in the column). Experiment 3 is similar to experiment 2, but this experiment was stopped before periods 4 and 5 could be reached. This means that only period 3 is observed. In experiment 4, periods 1–3 do not exist because the column was initially in a gaseous state. Indeed, a very small amount of limonene was introduced in the column. This means that only periods 4 and 5 exist. In experiment 5, the selected pressure is higher than the corresponding critical pressure at the experimental temperature. This means that, during the experiment, the column is always in a supercritical state. The shape of the extraction profile is thus similar to that corresponding to the fourth experiment.

From this section, it is possible to conclude that the proposed simple column modeling allows us, for differ-

Table 5. Experimental Operating Conditions and Initial State of the Extraction Column for Binary Systems

experiment	terpene introduced into the column	mass of terpene introduced (g)	column temperature (K)	column pressure (MPa)	CO_2 mass flow rate (g/min)	initial state of the extraction column[a]
1	limonene	3.60	313.15	8.3	1.08	liquid
2	limonene	1.85	313.15	8.1	3.06	diphasic
3	citral	10.3	313.15	8.1	0.93	diphasic
4	limonene	0.28	313.15	8.2	2.39	gas
5	limonene	3.85	313.15	8.5	2.96	supercritical

[a] Calculated by the model and in perfect agreement with experimental observations.
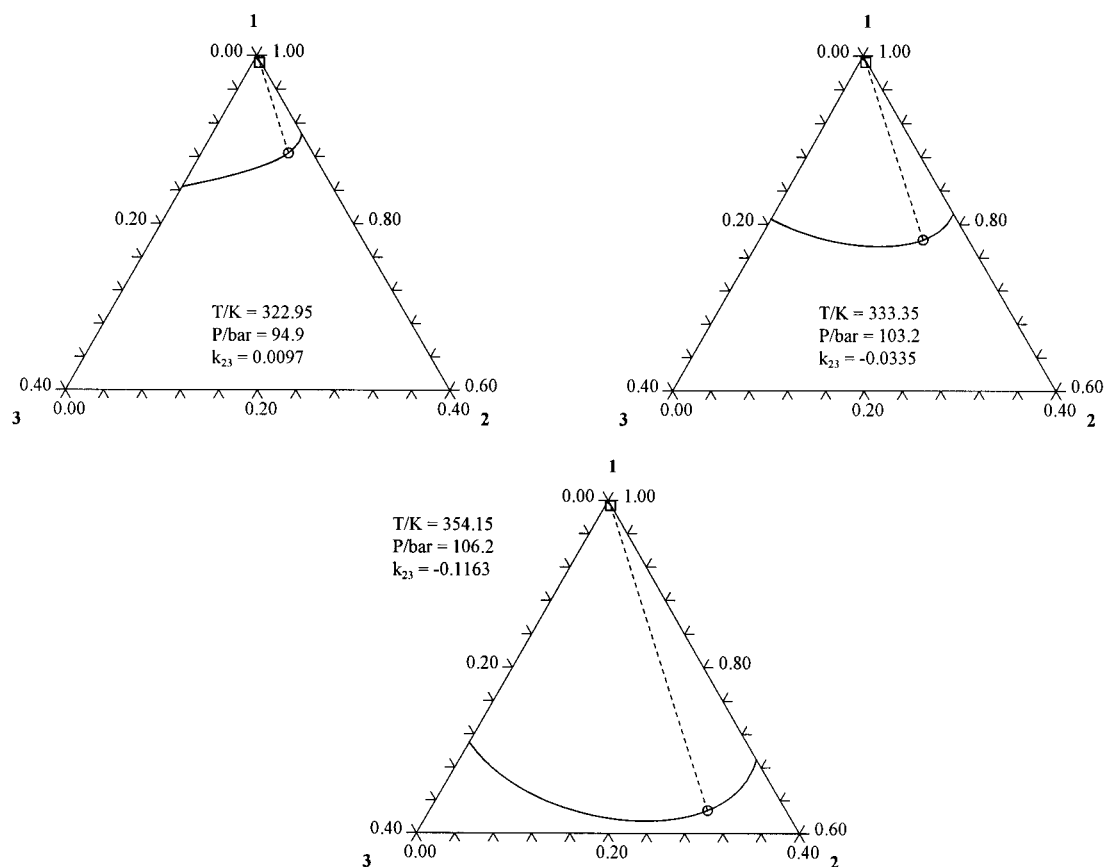
Figure 6. Phase behavior of the $CO_2(1)$−limonene(2)−citral(3) system under various conditions. (□) Experimental dew points. (○) Experimental bubble points. (---) Experimental tie line. (—) Calculated isothermal and isobaric phase diagram.

Table 6. Experimental Operating Conditions and Initial State of the Extraction Column for Ternary Systems

experiment	mass of terpenes introduced into the column (g)	column temperature (K)	column pressure (MPa)	CO_2 mass flow rate (g/min)	initial state of the extraction column[a]
6	$m_{limonene} = 4.44$ $m_{citral} = 1.48$	319.15	9.5	1.44	diphasic
7	$m_{limonene} = 4.11$ $m_{citral} = 1.37$	323.15	9.1	2.92	diphasic
8	$m_{limonene} = 4.08$ $m_{citral} = 1.36$	323.15	9.5	2.79	diphasic
9	$m_{limonene} = 4.59$ $m_{citral} = 1.53$	326.65	9.5	2.59	diphasic

[a] Calculated by the model and in perfect agreement with experimental observations.
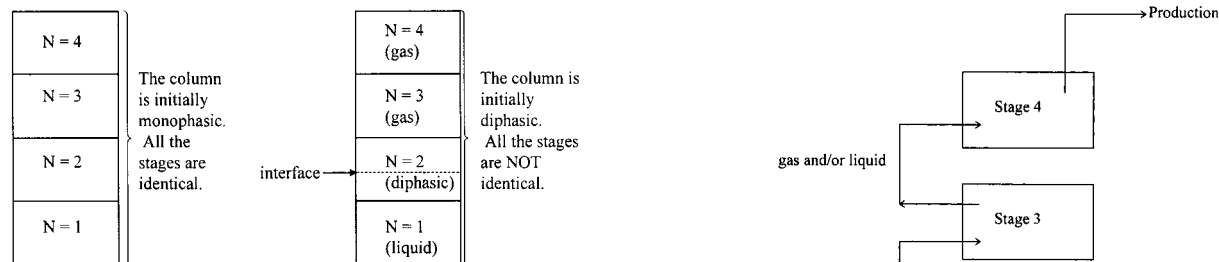
Figure 7. Illustration of the two possible initial states of the extraction column.

ent operating conditions, to reproduce with good accuracy the shape of the experimentally determined extraction profiles.

Ternary Systems. In this study, four extractions of the ternary system CO_2−limonene−citral were performed under different temperatures and pressures in order to determine the influence of these parameters on the separation quality. Each time, the terpene
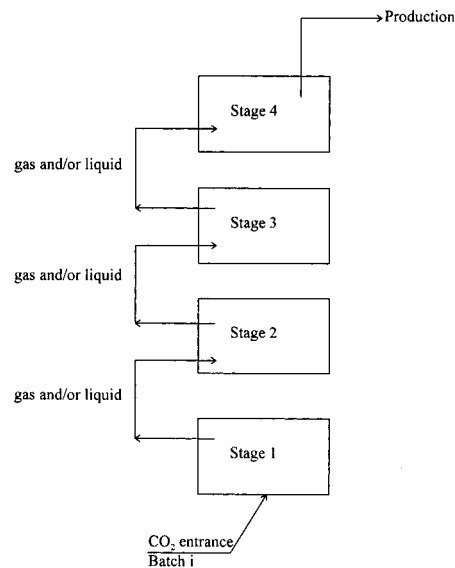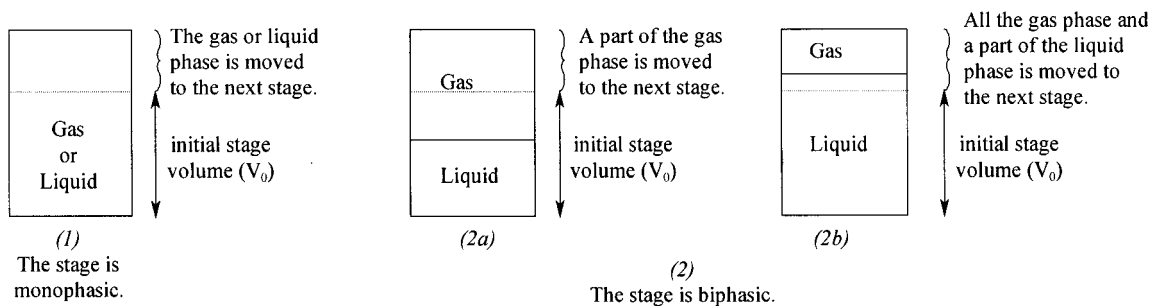
Figure 8. Logic of the stage-to-stage simulation.

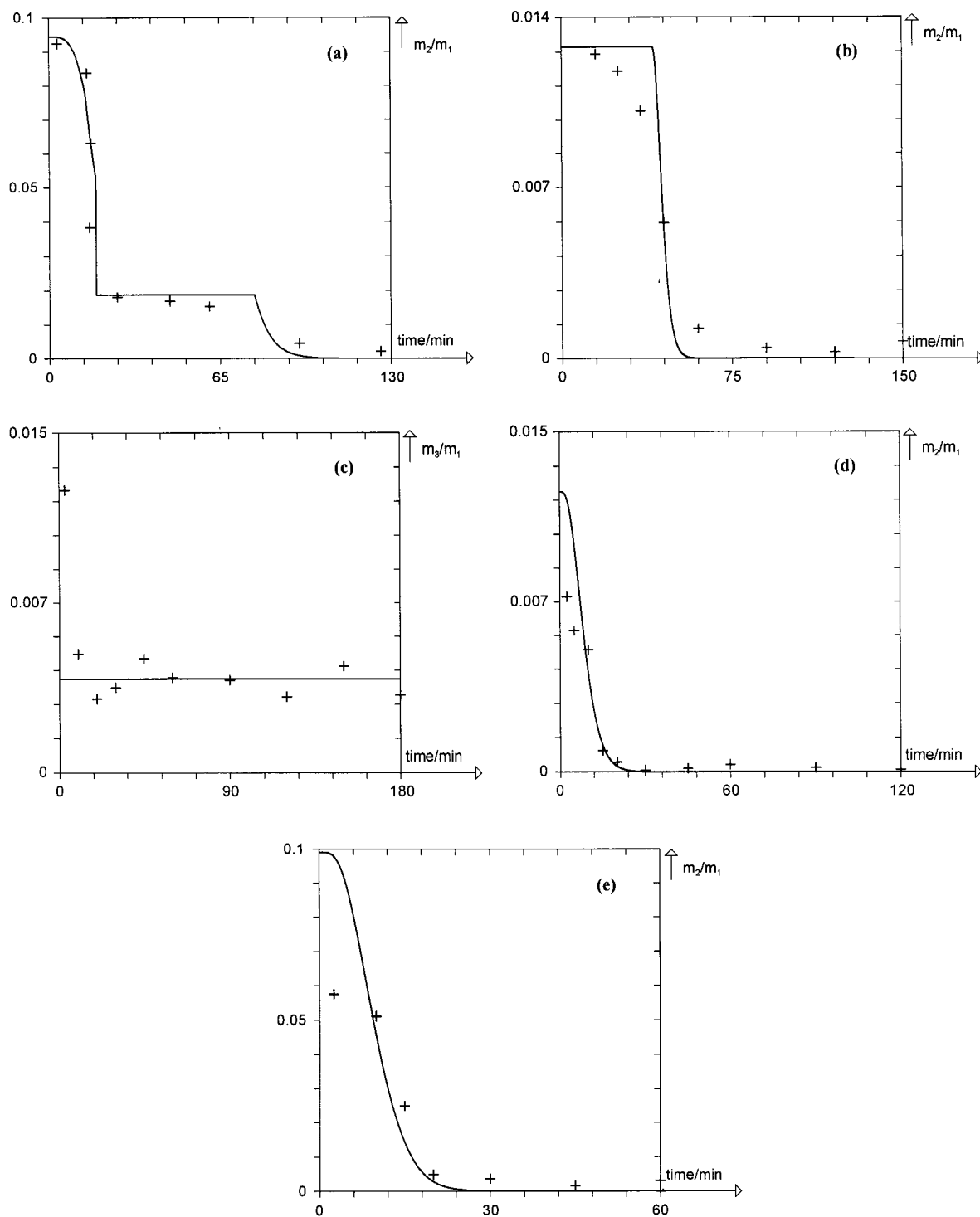**Figure 9.** Moving procedure in the stage-to-stage simulation.

Figure 10. Comparison between the experimental and calculated extraction profiles related to the binary systems. (+) Experimental points. (−) Calculated extraction profile. (a) Experiment 1. (b) Experiment 2. (c) Experiment 3. (d) Experiment 4. (e) Experiment 5.
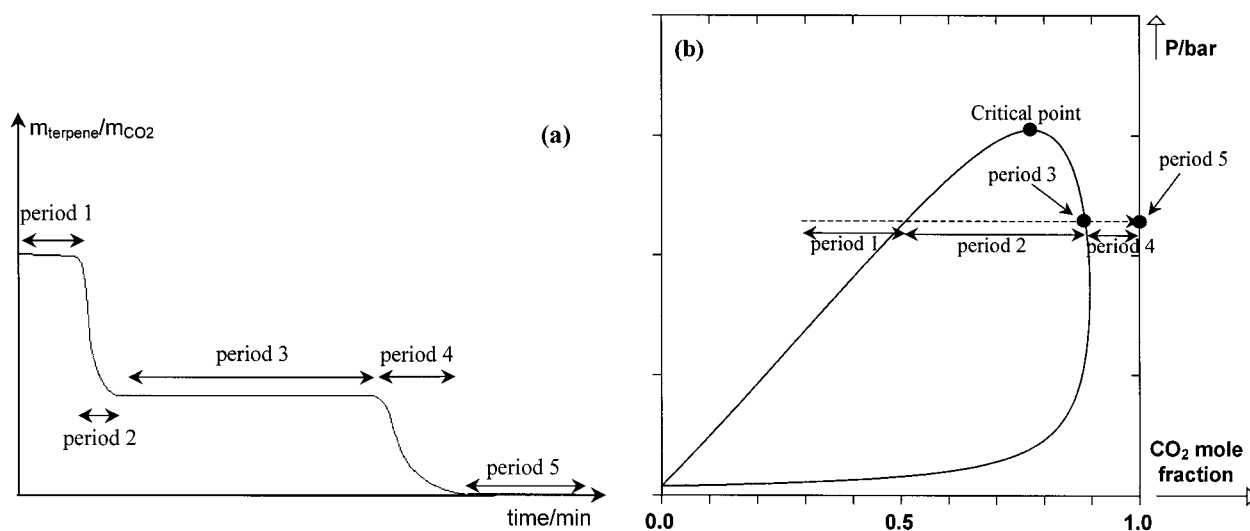
Figure 11. Case of binary systems. (a) Schematic extraction profile showing the definition of the five key periods. (b) Schematic isothermal (P,x,y) phase diagram showing how the composition of the mixture exiting the column typically varies with time (---).
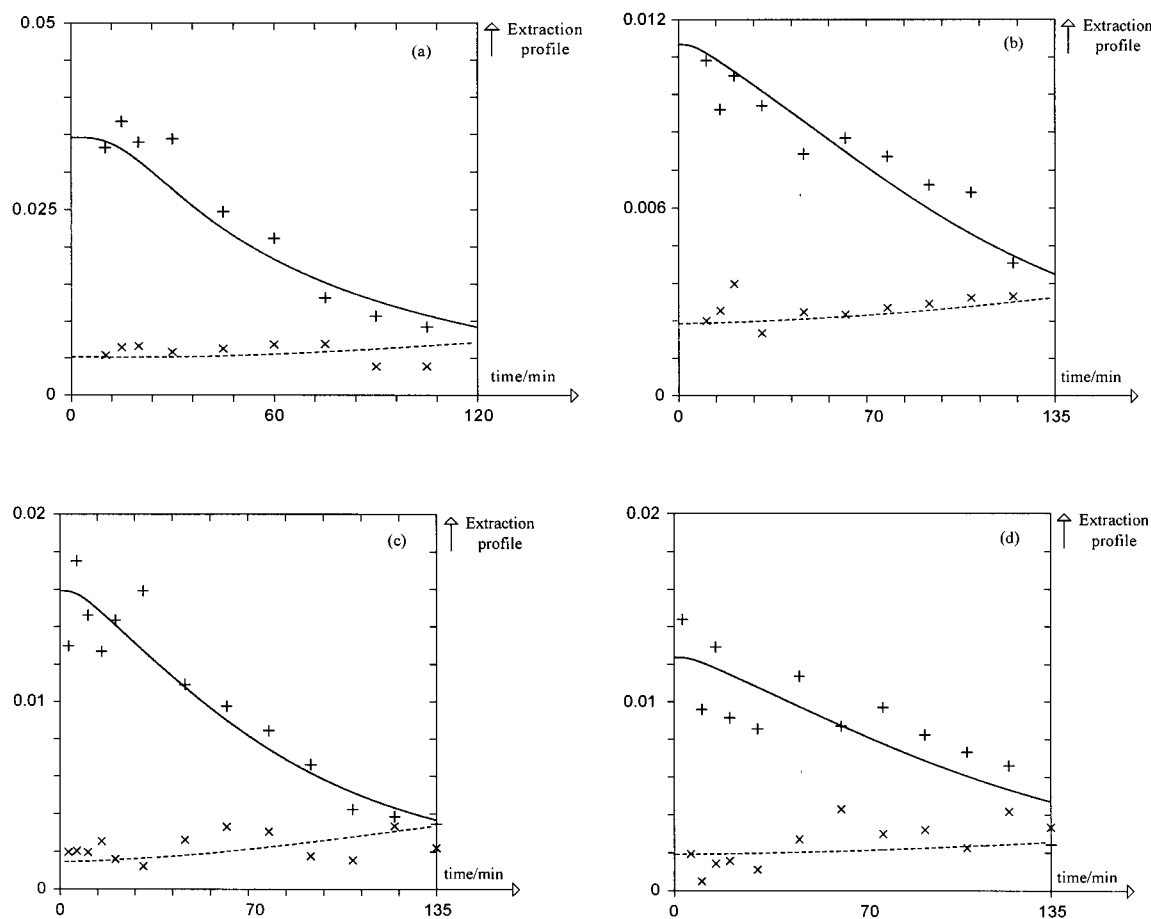

Figure 12. Comparison between the experimental and the calculated extraction profiles related to the ternary systems. (+) Experimental limonene profile. (—) Calculated limonene profile. (×) Experimental citral profile. (---) Calculated citral profile. (a) Experiment 6. (b) Experiment 7. (c) Experiment 8. (d) Experiment 9.

mixture introduced into the column contained 25% citral and 75% limonene. Such a composition was chosen because citrus oils usually contain a large amount of terpene hydrocarbon (limonene) and a smaller amount of oxygenated terpenes (citral). Moreover, the initial state of the column was always diphasic gas−liquid in order to have a separation between the two terpenes. The operating conditions corresponding to these four new experiments are summarized in Table 6. In Figure

12 are plotted the experimentally determined extraction profiles and those calculated with the proposed model. Once again, it is possible to conclude that the proposed column modeling reproduces accurately the extraction profiles. To determine the best operating conditions, the developed thermodynamic model was used to plot the variation of the limonene content in the extract versus time (see Figure 13). From this figure, it is possible to conclude that, regardless of the operating conditions,
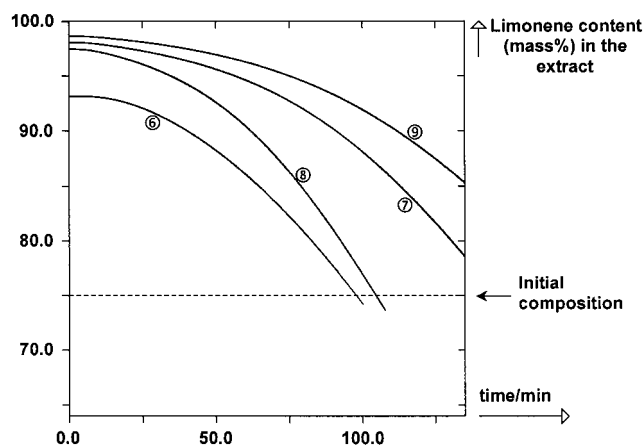
Figure 13. Calculation of the limonene content in the extract versus time. The circled numbers indicate that the operating conditions were identical to those of the experiment having the same number (see Table 6).

during the first 90 min, the mixture exiting the column is always richer in limonene than the mixture initially introduced in the column (75% limonene, 25% citral). However the calculated curves shown in Figure 13 are very different, even for small changes in the experimental operating conditions.

By comparing the curves related to experiments 6, 8, and 9, for which the pressure is the same ($P = 9.5$ MPa), it can be concluded that an increase in the temperature increases the selectivity. Indeed, by increasing temperature at constant pressure, the limonene content in the extract increases, and the duration for which the extraction composition is higher than the initial composition also increases.

Similarly, a comparison of the two isothermal curves related to experiments 7 and 8 indicates that, at constant temperature, an increase in the pressure decreases the selectivity. The influence of temperature seems dominant in comparison to the influence of pressure. Indeed, by comparing the curves related to experiments 7 and 9, for which an increase of temperature and an increase of pressure were made, it is clear that conditions of experiment 9 are better than those of experiment 7.

All of these results lead us to the conclusion that the use of low CO_2 densities improves selectivity.

Conclusion

For work with essential oils, it is usually compulsory to perform extractions under different temperatures and pressures in order to optimize the separation. Such a procedure costs a lot and is tedious.

In this paper, it is shown that a simple model of the extraction column coupled with a widely used equation of state is able to predict with good accuracy the extraction profiles of compounds present in citrus oils. For this reason, we advise that a few equilibrium measurements be performed (or found in the literature) in order to establish the temperature dependence of k_{ij} and that the theoretical model described in this paper be used to determine the optimal operating conditions. Such a procedure is precise and inexpensive.

Nomenclature

$a(T)$ = temperature-dependent function of the equation of state

A_{ij}, B_{ij} = constant parameters allowing for the calculation of the binary interaction parameters

b = covolume

c = volume correction

k_{ij} = binary interaction parameter

m = shape parameter

P = pressure

P_c = critical pressure

R = ideal gas constant

T = temperature

T_b = normal boiling point

T_c = critical temperature

v = molar volume

V_0 = initial stage volume

Z_{RA} = Rackett compressibility factor

Greek Letters

ω = acentric factor

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