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Fractionation of Paraffin Wax Mixtures

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Experimental results for the supercritical fluid extraction (SCFE) of paraffin wax using supercritical carbon dioxide are presented and compared with short path distillation (SPD). A simple simulation algorithm is presented and used to simulate SCFE cases. From these simulations it appears that supercritical extraction with reflux can be used to produce products with narrower carbon number distributions than those that can be obtained with SPD.

Paraffin waxes are used as feedstock for a large number of applications. Products manufactured include car, leather, and upholstery polish, printers ink, wood-treatment products, paper-treatment products, cosmetics, candles, glue, rubber, hot-melt adhesives, thermal-transfer wax, and thermostat wax. Some of these products require wax fractions with a low oil content or a very narrow melting point range. In the past, wax fractions were produced by means of liquid−liquid extraction and solvent crystallization. These processes suffered from a lack of sharp cuts and residual solvent in the product. Melt crystallization (sweating) is used as a way of de-oiling wax but may not be so successful because of the trapping of oil in the crystalline wax matrix. Recently, short path distillation (SPD) has been used to fractionate waxes. High operating temperatures and the fact that only one separation stage can be achieved disadvantage this process. Two preliminary studies[1,2] on the separation of paraffins with supercritical solvents have been published, but the use of supercritical solvent extraction for the fractionation of waxes is still not used in industry. The advantages of supercritical fluid extraction (SCFE) over the other fractionation methods are as follows: (1) no residual solvent in the product; (2) relatively low operating temperatures compared to those of SPD; (3) more environmentally friendly supercritical solvents than the solvents used in liquid−liquid extraction and solvent crystallization; (4) better cut sharpness; (5) low utility costs.

This work investigates the use of SCFE for the de-oiling of wax mixtures. An SPD unit is used to produce samples for characterizing the SPD process and as a reference against which the performance of the SCFE fractionations are evaluated.

SCFE Column Setup. A process flow diagram of the SCFE column is shown in Figure 1. The extraction column has an inner diameter of 29 mm, has a length of 5 m, and is packed with 4.32 m Sulzer DX packing. The column is designed to operate at a maximum pressure of 300 bar and a maximum temperature of 150 °C. The column is heated to the extraction temperature with an oil jacket and insulated with a ceramic blanket. The operating pressure is controlled with a hand-operated needle valve in the overhead extract line. Liquid from the bottom of the column is discharged to an expansion vessel via a pneumatic valve controlled by an optical interface sensor. The gaseous solvent flow from the raffinate expansion vessel is measured with a positive displacement flowmeter.

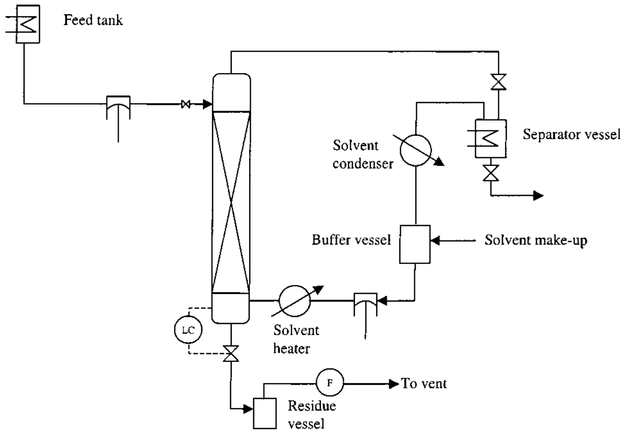

Figure 1. Process flow diagram of the supercritical extraction process.

The extract from the column is expanded through a needle valve, and the gaseous solvent and liquid extract are separated in a heated separator vessel. The gaseous solvent is condensed in a heat exchanger and collected in a buffer vessel. Liquid solvent from the buffer vessel is pumped to the column with a variable-stroke-length diaphragm pump. The liquid solvent then passes through a heat exchanger, heating the solvent to the extraction temperature, and enters the column near the bottom. The solvent flow rate is measured after the solvent condenser with a corriolis-type mass flowmeter. The feed to the column is pumped from a heated feed vessel with a variable-stroke-length diaphragm pump. All feed, raffinate, and extract lines are traced with oil-heated copper tubing to prevent blocking from congealed wax.

A run is considered to be at steady state if it has been running for 3 h or more at a steady pressure and temperature. After steady state is reached, wax extract and raffinate are collected for at least 1 h. The solvent feed temperature, extract stream temperature, and column pressure are also logged. The wax samples are weighed and analyzed on a megabore GC column with a flame ionization detector. Toluene is used as a solvent for the GC analysis.

A mixture of 2-methylnaphthalene and hexadecane was used to test the separation efficiency of the column. Carbon dioxide was used as the supercritical solvent. Equilibrium data of the ternary system was obtained

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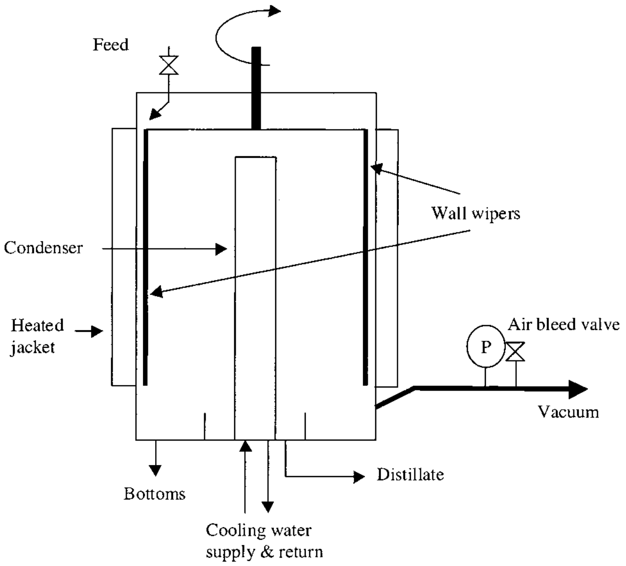


Figure 2. SPD column.

by operating the column at a low solvent-to-feed ratio (10−15) and a low percentage extraction of feed (<10%). The temperature was kept at 80 °C and the pressure at 125 bar. This equilibrium data was used to construct a Janecke diagram, which was used to calculate the number of theoretical stages graphically. An extraction run at a solvent-to-feed ratio of 48 was then done to determine the number of theoretical stages in the column. Seven theoretical stages were calculated, although it appears as if the operating line and equilibrium line pinch. Work is in progress to measure more equilibrium data for carbon dioxide/hexadecane and carbon dioxide/2-methylnaphthalene by du Rand and Nieuwoudt[3] in order to fit the phase equilibria of the system with an equation of state. This is necessary to better model the extraction process.

SPD Setup. A wiped wall unit with rotating poly(tetrafluoroethylene) bush wipers has been used for the SPD runs. See Figure 2 for a schematic of the SPD column setup. Runs were done at absolute pressures between 40 and 70 Pa. The shell temperature ranged between 120 and 170 °C. The feed rate to the column is controlled by a needle valve in the feed line. The absolute pressure inside the column is controlled by bleeding air into the column with a needle valve.

The pressure in the vacuum line to the column is measured with a pirahni-type pressure gauge. The bottoms and distillate are analyzed as described for the SCFE runs.

The results of the SPD runs were simulated as single-stage flash operations. The ideal gas law was used to calculate the *K* values used in the flash algorithm. Vapor-pressure correlations for the paraffins were taken from the ProII simulation package. When the SPD runs were simulated, the feed composition and absolute pressure were specified. The flash temperature was then adjusted until the simulated and measured distillate fractions were the same. This was done because the temperature of the film in the SPD unit could not be measured accurately.

In Figure 3, the distillate composition of a typical run is shown with the calculated composition of a flash simulation. A series of SPD runs were conducted, and it was found that this method of simulating the SPD runs predicted the product compositions very well.

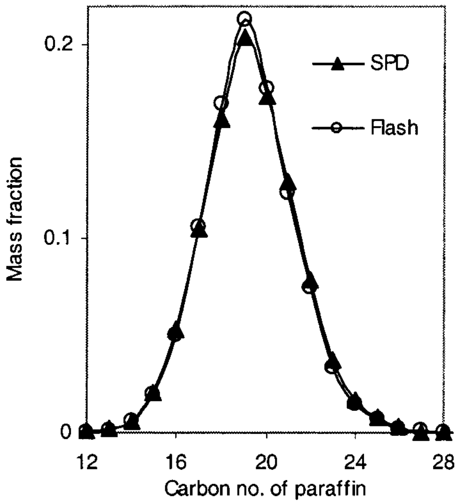


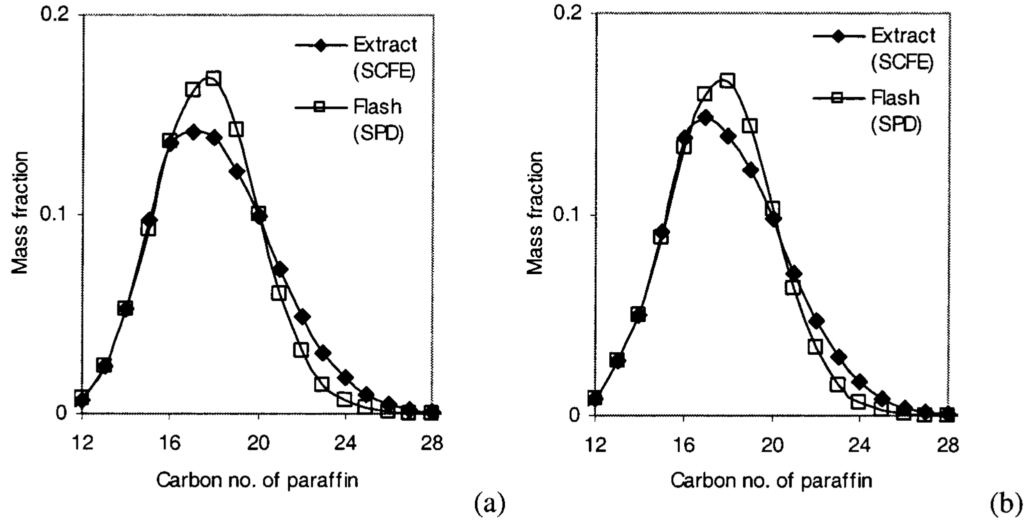
Figure 3. Simulated and analyzed distillate composition for an SPD run.

Wax Extractions Using CO_2 as the Supercritical Solvent. The results for some of the CO_2 extractions are shown in Figures 4 and 5. The extract composition of some of the SCFE runs are compared with SPD products that are calculated using the single-stage flash described above. The flash pressure was kept constant at 40 Pa, whereas the temperature was adjusted to obtain the same vapor-to-feed ratio as that in the SCFE.

In Figure 4, the extract compositions of two extraction runs at different temperatures, but at the same solvent-free extract-to-feed ratio, are shown. To compare the extracts from different runs, the extract composition of a run is plotted with the distillate composition of a SPD run, where the absolute pressure is kept at 40 Pa and the temperature is adjusted to match the extract-to-feed ratio of the extraction. This method is necessitated by the varying feed composition between different extraction runs, which made direct comparison between the extract compositions unpractical. It can be seen that there is almost no difference between the two extracts shown in Figure 4.

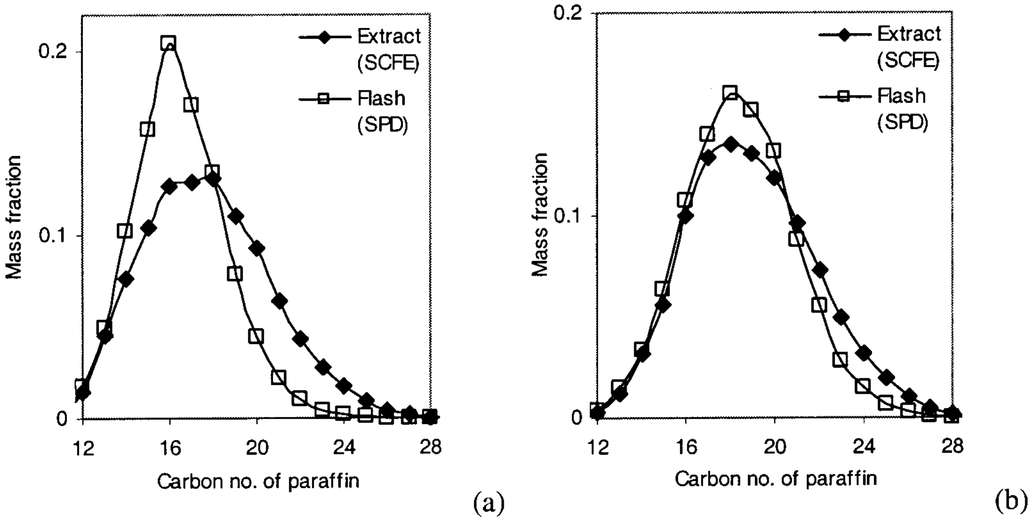
In general, one would expect the relative volatility of the paraffins to decrease with an increase in temperature, leading to worse separation at higher temperatures, and the diffusion coefficients to increase with an increase in temperature, leading to better mass transfer and more theoretical stages in the column. On the basis of Figure 4, it appears that the two phenomena cancel out, so that the separation efficiency is not greatly influenced by small changes in temperature.

In Figure 5, the effect of the extract-to-feed ratio on the separation efficiency is shown. The large difference in separation efficiencies between the two runs is most likely due to the pinching of the operating and equilibrium lines at the low extract-to-feed ratio run. From these extraction runs, it is clear that SCFE of wax using carbon dioxide as the solvent is not very efficient when compared with that of SPD. One of the problems identified is the posibility of a pinch between the equilibrium and the operating conditions in the SCFE column. This can be remedied by returning reflux to the extraction column. This would increase the separation efficiency first by increasing the separation achievable over a theoretical stage and second by removing the pinch and, in so doing, enabling the utilization of more theoretical stages for separation.



(a) (b)

Figure 4. Effect of the extraction temperature on the extract composition using carbon dioxide, compared to SPD distillate. (a) Extraction temperature 50 °C, pressure 110 bar. (b) Extraction temperature 60 °C, pressure 125 bar. Extract-to-feed ratio = 0.33.



(a) (b)

Figure 5. Effect of the split ratio on the extract composition using carbon dioxide, compared to the SPD distillate. (a) Extract-to-feed ratio = 0.16, pressure 125 bar. (b) Extract-to-feed ratio = 0.55, pressure = 145 bar. Extraction temperature 65 °C.

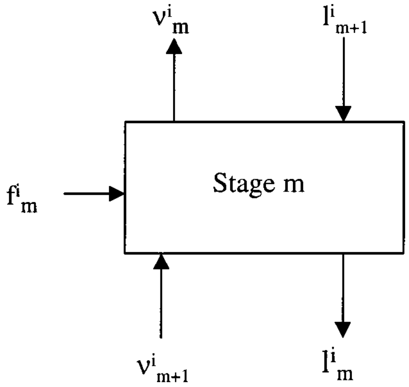


Figure 6. Equilibrium stage model.

Modeling of the SCFE Process. The equilibrium stage modeling of SCFE can be done in a very simple way if the energy balance requirements can be removed from the overall mathematical description of a stage. Because SCFE is sensitive to temperature and pressure variations (with regard to the extraction-to-feed ratio), SCFE columns should have tight control on these variables. It seems reasonable to assume that an SCFE column would operate isothermally rather than adiabatically. If it can then be assumed that the temperature profile in the column is known, only the mass balance and equilibrium conditions need to be calculated for a stage. This approach leads to a tridiagonal matrix formulation of the problem, which can be solved in a straightforward manner (see, e.g., Kister[4] and Seader and Henley[5]) using the Thomas algorithm.

A mass balance for component i over stage m (see Figure 6) gives

$$A^i_{m-1} v^i_{m-1} - (1 + A^i_m) v^i_m + v^i_{m+1} = -f^i_m \tag{1}$$

where A is defined as

$$A^i_m = \frac{L_m}{K^i_m V_m} \tag{2}$$

The dense-phase flow rate of i (l^i) is related to the light-phase flow rate of i (v^i) as follows:

$$A^i_m v^i_m = l^i_m \tag{3}$$

Table 1. Symbols Used in Eqs 1−7

symbol	description
A	defined by eq 2
f	molar feed rate
K	equilibrium distribution ratio ($K = y/x$)
L	total molar flow rate of dense (liquid) phase
l	component molar flow rate in dense (liquid) phase
p	defined by eq 5
q	defined by eq 6
V	total molar flow rate of light (vapor) phase
v	component molar flow rate in light (vapor) phase

Using the Thomas algorithm, eq 1 can be written as

$$v^i_m + p^i_m\, v^i_{m+1} = q^i_m \tag{4}$$

with p and q defined as

$$p^i_m = \frac{-1}{1 + A^i_m + A^i_{m-1}\, p^i_{m-1}} \tag{5}$$

$$q^i_m = \frac{f^i_m + A^i_{m-1}\, q^i_{m-1}}{1 + A^i_m + A^i_{m-1}\, p^i_{m-1}} \tag{6}$$

The matrix of equations formed by eq 4 over an extraction column can be solved with back substitution by noting that for the last stage in the column (solvent feed stage, s)

$$q_s{}^i = v_s{}^i \tag{7}$$

A description of the symbols used in these equations can be found in Table 1.

Initial estimates of the light- and dense-phase flow rates and K values are required to start solving the mass balance. In the case of SCFE, these initial estimates are extremely important to ensure convergence. The set of equations is solved in two steps: First the component flow rates are iteratively solved for a set of K values until the component flow rates converge (inside loop), and then the K values are updated using the new component flow rates (outside loop). The algorithm is terminated when the sum of the difference of the component K values between successive iterations is less than a specified tolerance. It was found that damping of the component flow rates was required when bad initial estimates were used, to prevent divergence. Initial estimates are generated by flashing the feed streams at the conditions of the top stage in the column. The flow rates and component K values on each stage are then set to the values calculated in the flash. This approach leads to the rapid convergence of simulations in most cases, without using damping.

Case Study. The above-mentioned algorithm is used to simulate the fractionation of a wax mixture using an SCFE column with carbon dioxide as the solvent. The effects of the following parameters on the mass-transfer efficiency are investigated: the solvent-to-feed ratio, the number of stages, and the reflux ratio. The reflux returned to the column is taken from the liquid stream leaving the separator, and the reflux ratio is defined as the flow rate of liquid returned to the column divided by the liquid flow rate from the separator. The following operating conditions remained constant in the simulations: the extract-to-feed ratio (0.33:1), the column, the separator temperature (50 °C), and the separator pressure (50 bar). The values of the parameters changed in the simulations are shown in Table 2. The wax feed used in the simulation contained 20 components, from n-undecane to n-triacontane. The solvent stream is pure carbon dioxide. The computer processor time used by the column algorithm for solving different column simulations is also shown in Table 2. It can be seen that the algorithm converged quickly for all cases considered.

Table 2. Conditions for Simulation Runs

case no.	solvent/feed mass ratio	pressure [bar]	no. of stages	feed stage	reflux ratio	processor time[a] [s]
base	30:1	118	10	1	0	0.6
1	30:1	118	20	1	0	1.1
2	50:1	110	10	1	0	0.6
3	30:1	130	10	6	1	2.7
4	30:1	145	10	6	2	1.4
5	30:1	200	10	6	4	1.2
6	30:1	188	15	8	4	1.9

[a] Computer: 200 MHz Pentium Pro single processor. Operating system: Windows NT. Code written in Delphi 4.

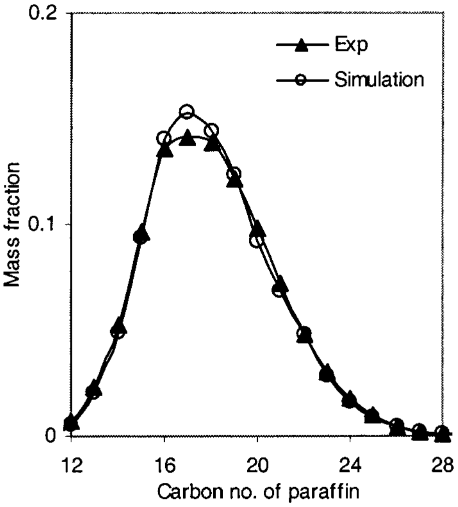


Figure 7. Comparison of the experimental counter current extract composition and simulated extract composition using the Patel−Teja equation of state with interaction parameters tuned to match the experiment.

Although some phase equilibrium data on paraffin/carbon dioxide systems are available, it is very difficult to tune interaction parameters for some cubic equations of state so that they can predict both light- and dense-phase compositions.[3] The Patel−Teja[6] equation of state was chosen to model the phase equilibrium of the carbon dioxide/paraffin wax system, because it is very flexible when two interaction parameters are used. Interaction parameters were estimated by using correlations developed by Coutinho et al.[7] and empirically modifying them until the carbon dioxide fractions in the extract and raffinate phases of an experimental SCFE run were matched. The extract composition of this run was predicted well, as is shown in Figure 7. To verify the predictive capabilities of the model, the results from two further supercritical extraction runs (with reflux) were modeled using the same set of parameters. The results of these two predictions are shown in Figure 8. It can be seen that reasonable agreement was obtained. The model can thus be used to explore the performance of a supercritical extraction unit in the case of changes in operating parameters such as the reflux ratio. It is important to note that the experimental values show a slightly sharper cut than the predicted values do. This

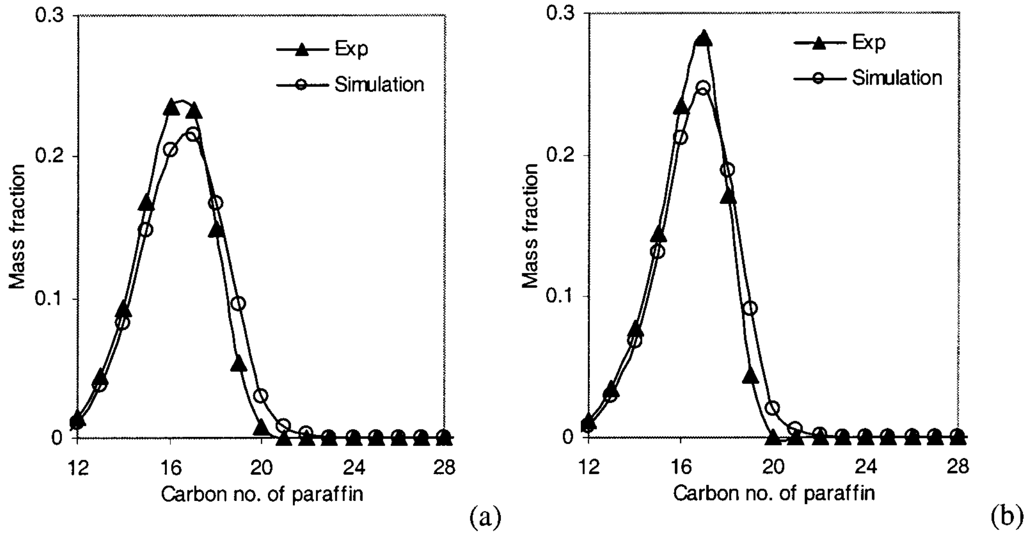


Figure 8. Comparison of the experimental extract compositions and the simulated extract compositions at different reflux ratios. (a) Reflux ratio = 3. (b) Reflux ratio = 6.

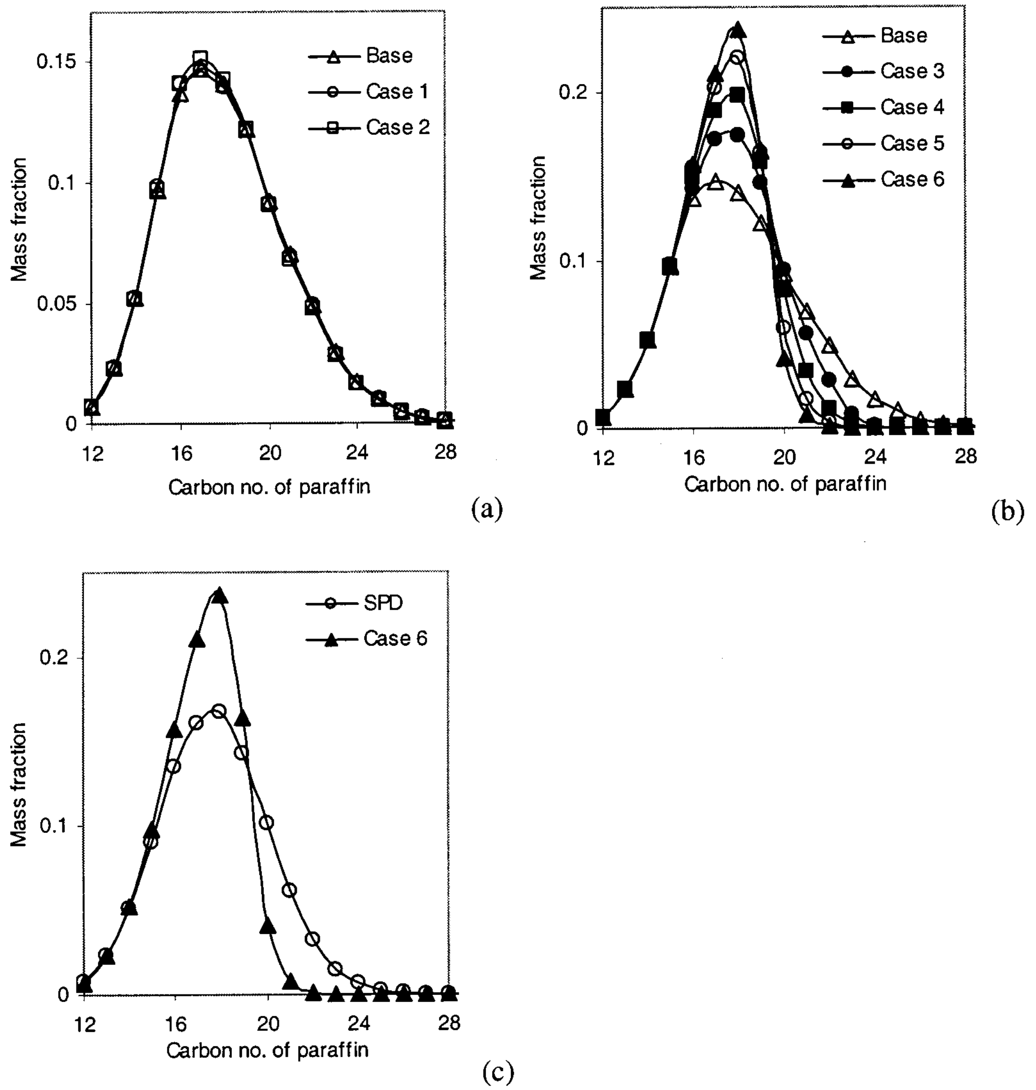


Figure 9. (a) Extract compositions of the base case and cases 1 and 2. (b) Extract compositions of the base case and cases 3−6. (c) Extract composition of case 6 and the SPD.

means that the actual products will have slightly narrower carbon-number distributions than those predicted by the model.

The results of the case study are shown in Figure 9. The extract compositions of the base case, together with cases 1 and 2, are shown in Figure 9a. From this figure, it is clear that the extract composition is not influenced by the addition of more theoretical stages or a larger solvent-to-feed ratio in a true countercurrent operation. This indicates that the extraction is operating in a pinch region. In Figure 9b, the effect of returning the reflux to the extraction is shown. It can be seen that an increase in reflux results in much improved separation (cases 3−6). From case 6, it is apparent that the addition of reflux has moved the extraction away from the pinch region, and additional stages result in a still better separation efficiency. When the extract composition of case 6 is compared with that of the simulated SPD distillate in Figure 9c, it is clear that a much sharper separation was effected. This case study highlights the importance of using reflux to enhance the separation efficiency of wax separation using SCFE and the fact that much sharper separations than those with SPD can be obtained.

These simulation results are promising and show the potential that SCFE has for wax de-oiling. Other solvents are also being investigated with the aim of finding a solvent that has either better selectivity, to improve on the separation efficiency of carbon dioxide, or a larger capacity for wax, to reduce the solvent-to-feed ratios and pressures necessary for a good separation.

Literature Cited

(1) de Haan, A. B. Supercritical Fluid Extraction of Liquid Hydrocarbon Mixtures. Ph.D. Dissertation, Delft University of Technology, CIP−Gegevens Koninklijke Bibliotheek, Den Haag, 1991.

(2) Nieuwoudt, I. The Fractionation of High Molecular Weight Alkane Mixtures with Supercritical Fluids. Ph.D. Dissertation, University of Stellenbosch, Stellenbosch, South Africa, 1994.

(3) du Rand, M.; Nieuwoudt, I. Measurement of Phase Equilibria of Supercritical Solvents and Paraffins. 5th International Symposium of Supercritical Fluids, Atlanta, GA, April 2000.

(4) Kister, H. Z. *Distillation Design*; McGraw-Hill: New York, 1992.

(5) Seader, J. D.; Henley, E. J. *Separation Process Principles*; John Wiley & Sons: New York, 1998.

(6) Patel, N. C.; Teja, A. S. A New Cubic Equation of State for Fluids and Fluid Mixtures. *Chem. Eng. Sci.* **1982**, *37*, 463−473.

(7) Coutinho, J. A.; Kontogeorgis, G. M.; Stenby, E. H. Binary Interaction Parameters for Nonpolar Systems with Cubic Equations of State: Theoretical Approach 1. CO_2/Hydrocarbons using SRK Equation of State, *Fluid Phase Equilib.* **1994**, *102*, 31−60.

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