

Supercritical Fluid Technology:

Reviews in Modern Theory
and Applications

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**DESIGN AND CONTROL OF SUPERCRITICAL EXTRACTION
PROCESSES—A REVIEW**

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ABSTRACT

Design studies are important in assessing the feasibility of supercritical extraction (SCE) processes since they properly weigh factors such as the scale of the process, the value of the product, the need for a nontoxic solvent, etc. Once the most promising design is located, the decision to invest in the SCE process can be made with confidence. In this chapter, both experimental and simulation approaches to design are discussed. The experimental studies aim to determine the effect of the key process parameters, and where possible, to collect fundamental data to aid in the development of more rigorous models for simulation and design optimization. Examples discussed include the decaffeination of coffee beans, the extraction of edible oils, and the dehydration of alcohols. Applications of simulation and optimization methods have been less common, due primarily to the difficulty of modeling the complex systems. Good success, however, has been obtained when these techniques have been applied to the dehydration of alcohols and ketones. Several examples are discussed that indicate that SCE can be competitive for these separations on the basis of energy consumption. A more complete study, which includes the cost of the equipment, demonstrates that SCE is not competitive since the products are low-value, high-volume chemicals. Other work is described that attempts to model more competitive SCE processes, such as the extraction of lecithin from soya oil and the isolation of β -carotene from fermentation broths; however, the designs for the recovery of these high-value, low-volume chemicals are more uncertain since simplified models were used. Finally, the transient behavior and control of SCE processes is discussed. Although this challenging problem is only beginning to be addressed, initial studies indicate that maintenance of the proper phase distribution in the extractors and separators is difficult to achieve with conventional control schemes. As design models are extended to simulate the dynamics of SCE processes, new model predictive control algorithms can be expected to significantly improve the control of the phase distribution.

I. INTRODUCTION

SCE is an increasingly important technology in the food and pharmaceutical industries because it allows the substitution of nontoxic, environmentally safe solvents such as CO_2 for traditional liquid solvents such as methylene chloride and hexane. At the present time, this is most applicable in the food and pharmaceutical industries where the use of toxic solvents is regulated; however, more stringent regulations regarding toxic waste disposal may eventually broaden the significance of this technology to include many segments of the chemical process industry.

In Europe, and on a more limited scale in the U.S., SCE is used commercially to decaffeinate coffee and tea¹ and to extract hops² and spices.³ These commercial successes indicate that SCE is a viable alternative for the preparation of some food products; however, as elucidated by Krukonis,⁴ its feasibility is determined by the scale of the process, the value of the product, the need for a nontoxic solvent, etc. Design studies properly weigh these factors, and identify the most promising SCE processes for a particular application. They provide the best designs upon which to base the decision to invest in SCE processes.

II. EVOLUTION OF A PROCESS DESIGN

In designing a SCE process, consideration must be given to the properties of the feed material (i.e., solid or liquid), the solute concentration in the feed, the required production rate, and the thermodynamic and mass transfer relationships between the solute and solvent.⁵ Marentis⁶ suggests a design protocol in which these concerns are addressed through a series of experimental steps from which the process design evolves.

First, the feasibility of using SCE to affect a particular separation is assessed in “screening unit testing”. Then, larger vessels and solvent recycle are incorporated in “process development unit testing”. At this stage, the extractor and separator temperatures and pressures, solvent-to-feed ratios, and processing modes (i.e., batch, semi-batch, or continuous) are varied to establish favorable operating conditions. Experience is also gained in the control of the proposed process. Manipulated and controlled parameters are selected and a control scheme (e.g., PID) is proposed.

Finally, when a design is promising, pilot-plant testing is initiated to minimize scale-up uncertainties. Pilot plant tests verify vessel configurations and sizes, and identify mechanical design problems, such as clogging of pipes, valves, and heat exchangers due to precipitation of the solute. Materials handling and clean-up are also considered. The resiliency (i.e., controllability) of the process is studied further, as well as the sensitivity of the proposed design to changes in operation (i.e., flexibility).

At each stage, the economics are estimated at the reduced scale of the process, and unfavorable designs are modified or eliminated. When the pilot-plant studies for a particular design appear promising (i.e., have favorable economics), development of the process proceeds through the construction of the full-scale plant. A good discussion of the economic considerations in designing a SCE plant are given by Novak and Robey.⁷ They utilized proprietary data to prepare a preliminary design for a multiproduct spice and herb extraction plant. The base case design used two 973 L extractors to process 0.8 million kg of spices or herbs per year. In the design, the extractors are operated batch-wise, in staggered cycles. The sensitivities of the capital and operating costs to the size of the plant were determined. The capital costs were shown to decline 40% as the plant size is increased to four times the base case. Although the operating costs per hour increase 87% in the larger capacity plant, the operating cost per unit feed decreases 54%. Process costs per kilogram of extract are given for 12 spices and 8 herbs. The costs range from \$4.00/kg for nutmeg extract to \$113/kg for Arnica extract. No comparisons were given to the costs of conventional extraction. It should be noted that since the process parameters (i.e., pressure, temperature, solvent-to-feed ratio, etc.) were not optimized, more economical operating regimes may exist.

Additional discussions of the construction and operation of full-scale SCE plants are given by Eggers,⁸ Koerner,⁹ Herderer and Heidemeyer,¹⁰ Eggers and Sievers,¹¹ and Marentis and Vance.¹²

Because there are relatively few commercial installations of SCE, most of the design and control studies for these processes have been at the feasibility or process development stage. Consequently, this chapter concentrates on process development and design. These studies often involve experimentation to determine the effect of the key process parameters and, where possible, to develop more rigorous models for simulation and design optimization.

III. EXPERIMENTAL STUDIES FOR DESIGN

Because SCE processes typically involve complex mixtures for which fundamental phase equilibria and mass transfer data are not available, many workers study the effect of different process parameters for a particular system in small-scale pilot plant experiments.

For example, Brunner^{13,14} used this approach to study the extraction of caffeine from coffee using supercritical CO₂. The effect of extractor temperature, pressure, and bed height was considered for the semi-batch extraction of caffeine from moist, roasted coffee beans. Figure 1 shows the caffeine extracted as a function of the solvent-to-feed ratio for two different extraction times. Note that the rate of extraction is nearly twice as high after 30 min than after 240 min. Also, the rate of extraction increases more rapidly with the solvent-to-feed ratio at shorter extraction times; i.e., at 30 min, the caffeine extracted increases sharply as the solvent-to-feed ratio is increased to 90. At longer extraction times, however,

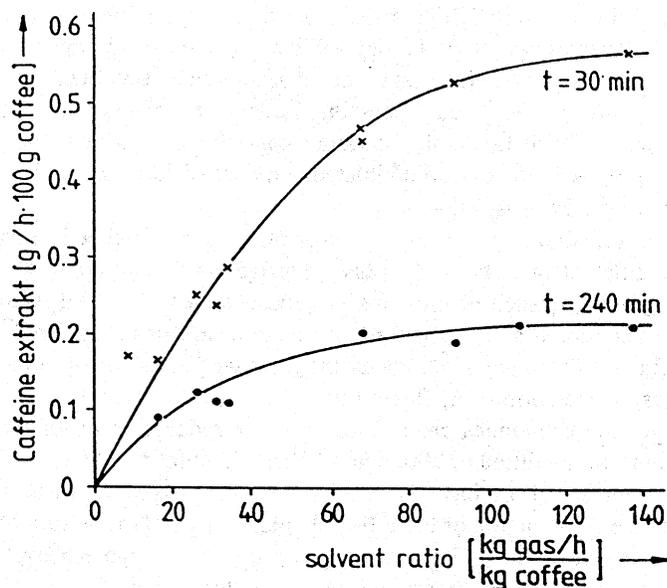


FIGURE 1. Caffeine extract as a function of solvent-to-feed ratio. (From Brunner, G., *Proc. Int. Symp. Supercritical Fluids*, Perrut, M., Ed., Société Française de Chimie, Nice, 1988. With permission.)

only small changes were recorded for solvent-to-feed ratios above 30 because the extraction efficiency is limited by intraparticle diffusion. Once the caffeine in the outer edges of the bean is depleted, it must diffuse from the center to be solubilized by the CO_2 , reducing the extraction rate. Brunner also studied the mass transfer effects for the caffeine- CO_2 system and estimated the mass transfer coefficients.

The extraction of edible oils from seed materials using supercritical CO_2 has been studied extensively by Friedrich and co-workers,¹⁵⁻¹⁸ Stahl,¹⁹ and others.^{20,21} These investigators examined the impact of the extractor and separator temperatures and pressures, the condition of the feed material (crushed, flaked, etc.) and the design of the extractor (e.g., extruder-type for continuous processing), on the quality of the product (i.e., the taste, appearance, and color). Unfortunately, SCE is probably not economically feasible. Soybean oil, for example, is produced in large quantities (approximately 2000 tons/d) and sells for a relatively low price (\$0.25/lb). Although detailed economic analyses have not been published, it seems clear that SCE is too expensive for this application, even though the SCE product is superior to that obtained using traditional extraction methods.

Supercritical solvents have also been considered for the dehydration of dilute alcohols and ketones. Moses et al.²² studied the extraction of ethanol, isopropanol, and sec-butanol from water using CO_2 at 65 atm and 40°C in a 0.16 L sieve-tray extractor. An energy-efficient configuration was proposed in which the vapor from the distillation column is compressed and subsequently condensed as it vaporizes the bottoms liquid in the reboiler. Extractor tray efficiencies were determined, and the effect of changing the solvent-to-feed ratio was explored. The most favorable solvent-to-feed ratios (beyond which little appreciable increase in the solute recovery was recorded) were 10 for ethanol, 4 for isopropanol, and 1.5 for sec-butanol. Furthermore, the mass transfer efficiency was observed to increase with the molecular weight of the solute. Tray efficiencies measured for an 8 tray (7-in. tray spacing) extractor were 12 to 20% for ethanol, 35 to 40% for isopropanol, and approximately 50% for sec-butanol. It was concluded that extraction with CO_2 may be advantageous since it can save 10 to 40% of the energy required for distillation.

Seibert and Moosberg²³ and other researchers at the University of Texas^{24,25} used the alcohol/water system to examine the rates of mass transfer in high-pressure towers. Their experimental apparatus is shown in Figure 2. The stainless-steel extractor had an inside diameter of 9.88 cm, was 215 cm high, and had 32 high-pressure sapphire windows to permit viewing of the contacting phases. The pilot plant included an extensive process control system to regulate temperatures, pressures, and liquid levels by adjusting the four valves shown. Analyses were performed by on-line gas chromatography (GC). Extraction conditions ranging from 82 atm and 297 K to 150 atm and 318 K were studied for the dehydration of isopropanol using supercritical CO₂. Assuming a linear equilibrium relationship, dilute solute concentration, a pure solvent, and a straight operating line, the number of transfer units (NTU_{oc}) was calculated from:

$$\text{NTU}_{oc} = \frac{\ln\left(\left(\frac{x_r}{x_r}\right)\left(1 - \frac{1}{\lambda}\right) + \frac{1}{\lambda}\right)}{1 - \frac{1}{\lambda}} \quad (1)$$

$$\lambda = \left(\frac{U_D}{U_C}\right)M_{dc} \quad (2)$$

and x_r is the mass fraction of isopropanol in the recycled solvent, x_r is the mass fraction of isopropanol in the raffinate, U_C is the superficial velocity of the continuous (aqueous) phase based on the column area, U_D is the superficial velocity of the dispersed (CO₂) phase, and M_{dc} is the equilibrium distribution coefficient. Since the contact height (Z) is known, the overall height of a transfer unit (based on the continuous phase, HTU_{oc}) was calculated from:

$$\text{HTU}_{oc} = \frac{Z}{\text{NTU}_{oc}} \quad (3)$$

Finally, the height equivalent of a theoretical stage (HETS) was determined from:

$$\text{HETS} = \left(\frac{\lambda \ln \lambda}{\lambda - 1}\right) \text{HTU}_{oc} \quad (4)$$

Note that the HETS varies inversely with the efficiency of the separator. Figure 3 shows the HETS for four contacting devices: a spray tower, a tower with sieve trays, and packed towers with Raschig rings (RR) and metal Intalox saddles (IMTP). Note that the sieve trays are most efficient, followed closely by the Raschig rings and Intalox saddles. The inefficiency of the spray tower is attributed to increased back-mixing in the continuous phase and a smaller residence time for the CO₂ droplets. In general, column efficiencies are higher for supercritical than liquid-liquid extractors due to higher mass transfer coefficients in the supercritical phase. These studies provide a more reliable basis for the design of full-scale extractors and separators. Although not competitive economically, alcohol/water systems continue to be studied, since they are well characterized and, unlike most food systems, do not exhibit variability from batch to batch.

Bohm et al.²⁶ discuss critical factors in the design and operation of multipurpose plants for the continuous extraction of liquids with supercritical fluids (SCFs). A design strategy was employed in which the height equivalent of a theoretical plate (HETP) was determined by stagewise computer simulation of pilot plant experiments. Care was taken to ensure flexibility in the design of the mechanical and electrical units in the plant. For example, the

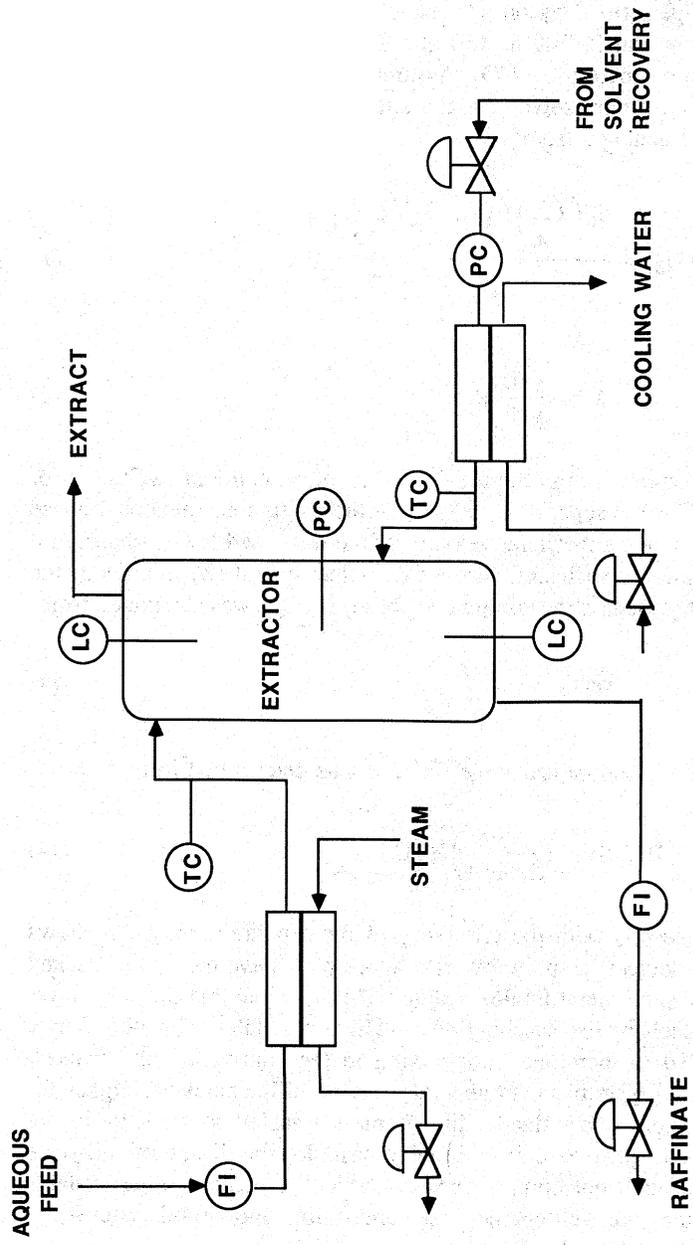


FIGURE 2. Extractor section of Seibert and Moosberg apparatus.²³ LC, TC, and PC are level, temperature and pressure controllers, respectively. FI are flow indicators.

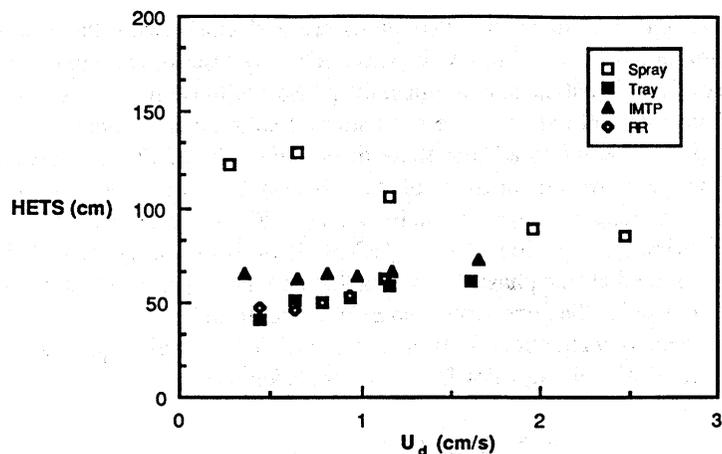


FIGURE 3. Efficiency of contacting devices for carbon dioxide/isopropanol/water at 313K and 102 atm. Dispersed phase is carbon dioxide and $U_c = 0.048$ cm/s. (Reprinted from Ref. 23, p. 2049 by courtesy of Marcel Dekker, Inc.)

extractor consisted of six modules, each with length of 1 m, linked together with connecting elements. Each connecting element has six ports that can be used for feed input, temperature and pressure measurement, reflux, or sampling. The modular nature of this design allows for relatively easy changes in the column height or feed position.

In summary, experimentation has been very important in the development of SCE processes. This is because the solubilities, vapor pressures, rates of mass transfer, etc., are very difficult to estimate for large organic molecules in carbon dioxide with various cosolvents. Yet, thermodynamic models (using pseudocomponents to represent complex mixtures), when coupled with experimental data, can be adapted to apply over limited ranges of T and P. Similarly, mass and momentum balances for complex hydrodynamic systems can be approximated, for example, with equilibrium-stage models. The benefits of utilizing these models for design optimization are discussed in the next section.

IV. SIMULATION AND OPTIMIZATION FOR THE DESIGN OF SUPERCRITICAL EXTRACTION PROCESSES

Process simulation and optimization are widely used in the chemical industry to reduce the number of pilot plant studies needed to develop the final design. Process simulation allows a broad range of operating conditions and process configurations to be explored quickly and easily, and optimization systematically determines the most favorable operating conditions for various economic objectives. These techniques are advantageous for the design of SCE processes, since there are many process parameters and because the costs associated with pilot plant construction and operation are high. In addition, dynamic simulation allows the controllability of the process to be explored in the design stage, where designs with control problems can be rejected easily.

Reliable process simulations of complex SCE systems require more accurate models, and their development presents several challenges. First, the solutes and the natural substrates from which they are extracted are difficult to characterize. The solute is often a large, organic compound for which vapor pressures and critical properties are not known, and are difficult (or impossible) to measure, and the substrate is often a "natural" solid or liquid that may contain several hundred species. Furthermore, more reliable thermodynamic models are needed that can accurately predict the complex interactions between the small, nonpolar solvents and the large, organic, often-polar solutes. These models should not be overly

complex, since phase equilibrium calculations are performed many thousands of times in an optimization or simulation. Finally, because SCE processes operate in the critical region, in the vicinity of mathematical singularities, the phase equilibrium calculations are inherently difficult to converge and require more sophisticated solution techniques.

Research is proceeding to address these difficulties. Thermodynamicists are working to develop simple, yet powerful equations of state (EOSs) that utilize density-dependent, local-composition mixing rules to bridge the gap between the EOS and activity coefficient models.^{27,28} The group contribution equation of state (GC-EOS) of Skjold-Jorgensen^{29,30} is particularly attractive since it predicts the phase behavior given only the chemical structure of the species. Another useful model is the Peng-Robinson EOS as modified by Panagiotopoulos and Reid,³¹ who added a second interaction coefficient for each binary pair, k_{ji} , and a composition-dependent term. Their mixing rules for the a coefficient are

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad (5)$$

$$a_{ij} = \sqrt{a_i a_j} [1 - k_{ij} + (k_{ij} - k_{ji})x_i] \quad (6)$$

Note that when $k_{ji} = k_{ij}$, Equations 5 and 6 are the mixing rules for the Peng-Robinson equation. This relatively minor modification significantly improves the predictions of the liquid phase compositions for mixtures such as acetone/ CO_2 and water/ CO_2 .³²

In the computation of high-pressure phase equilibria, Michelsen³³⁻³⁶ has made substantial progress toward developing efficient and reliable algorithms. For example, his implementation of the tangent-plane method for stability analysis not only indicates whether a phase is stable, but also gives excellent initial guesses for the new phase. This is especially important for phase equilibrium calculations in the critical region where the phase distribution is uncertain. In addition, his continuation algorithm for tracing phase envelopes and computing critical points is useful in bounding the feasible regions for extraction and solute recovery.

Finally, researchers are continuing to measure solubilities in SCFs, and an increasing number of experimental phase equilibria studies are being published. Vapor-liquid, vapor-solid, and vapor-liquid-liquid equilibrium data are being collected for many solutes of interest in the food and pharmaceutical industries. A few studies are demonstrating that the solubility of large, organic species in SCFs is often increased significantly with the addition of small amounts of cosolvents.³⁷⁻³⁹ For example, Wong and Johnston³⁸ measured the solubilities of cholesterol, stigmaterol, and ergosterol in supercritical CO_2 and computed an enhancement factor, E , given by:

$$E = \frac{Y_{\text{ternary}}}{Y_{\text{binary}}} \quad (7)$$

where Y_{ternary} is the mole fraction of solute in the CO_2 /cosolvent mixture, and Y_{binary} is the mole fraction of solute in CO_2 . The enhancement factor for cholesterol was shown to range from 2.4 for a mixture containing 3.5% ethanol to 7.2 for a mixture with 3.5% methanol. Although much work is needed to describe the mechanism of solubility enhancement, the increased solubility may render SCE processes more competitive.

At the present time, the most successful design and optimization studies have been accomplished for the well-characterized alcohol/water and acetone/water systems. For example, Brignole et al.⁴⁰ used the GC-EOS and the SEPSIM⁴¹ flow sheet program to investigate the dehydration of ethanol and 2-propanol. Several supercritical solvents were considered, with propane selected for ethanol recovery, and isobutane for 2-propanol recovery. Three process configurations were proposed, including cycles with vapor recompression and feed preconcentration. A flow sheet for the former cycle is shown in Figure 4. In this design,

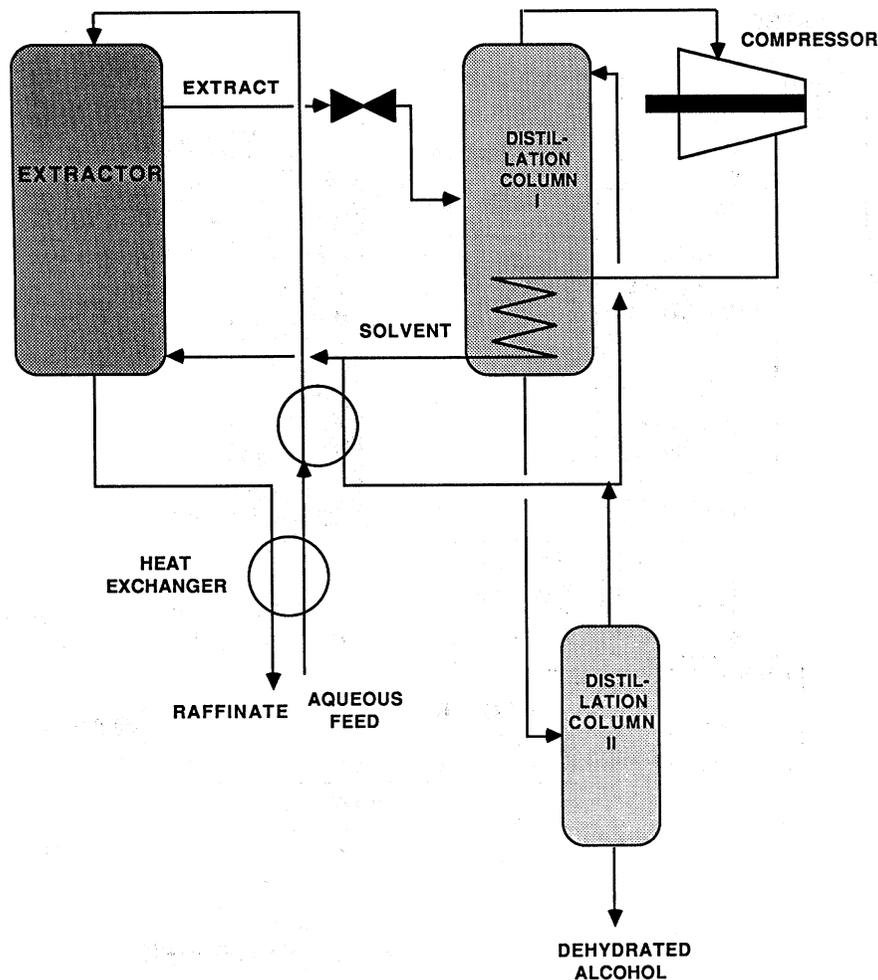


FIGURE 4. Vapor recompression cycle for alcohol dehydration. (Based upon Brignole et al.⁴⁰)

the aqueous feed is preheated by exchange with the raffinate and solvent recycle streams, and fed to the extractor. The extract is fed to a distillation column, where the overhead (nearly pure solvent) is compressed and condensed to satisfy the reboiler duty. The bottoms product is sent to a secondary distillation column for recovery of absolute alcohol as the liquid product. Brignole et al. concluded that this and similar SCE processes significantly reduce the energy consumption as compared to azeotropic distillation. It should be noted, however, that although attempts were made to optimize the important parameters such as the solvent-to-feed ratio and the extractor temperature and pressure, formal optimization strategies were not utilized, and thus the interdependence of these parameters was not properly considered. Furthermore, only the consumption of utilities was minimized; i.e., the installed cost of the equipment was not included.

Recently, Cygnarowicz and Seider⁴² formulated a strategy for designing cost-efficient SCE processes. The approach involves the development of a model for the process flow sheet (using SEPSIM) and the creation of a nonlinear program to generate designs that minimize either the annualized or utility costs. The strategy was applied to design a process to dehydrate acetone using supercritical CO₂. A flow sheet for the dehydration of acetone, with operating conditions at the global minimum in utility cost, is shown in Figure 5. As

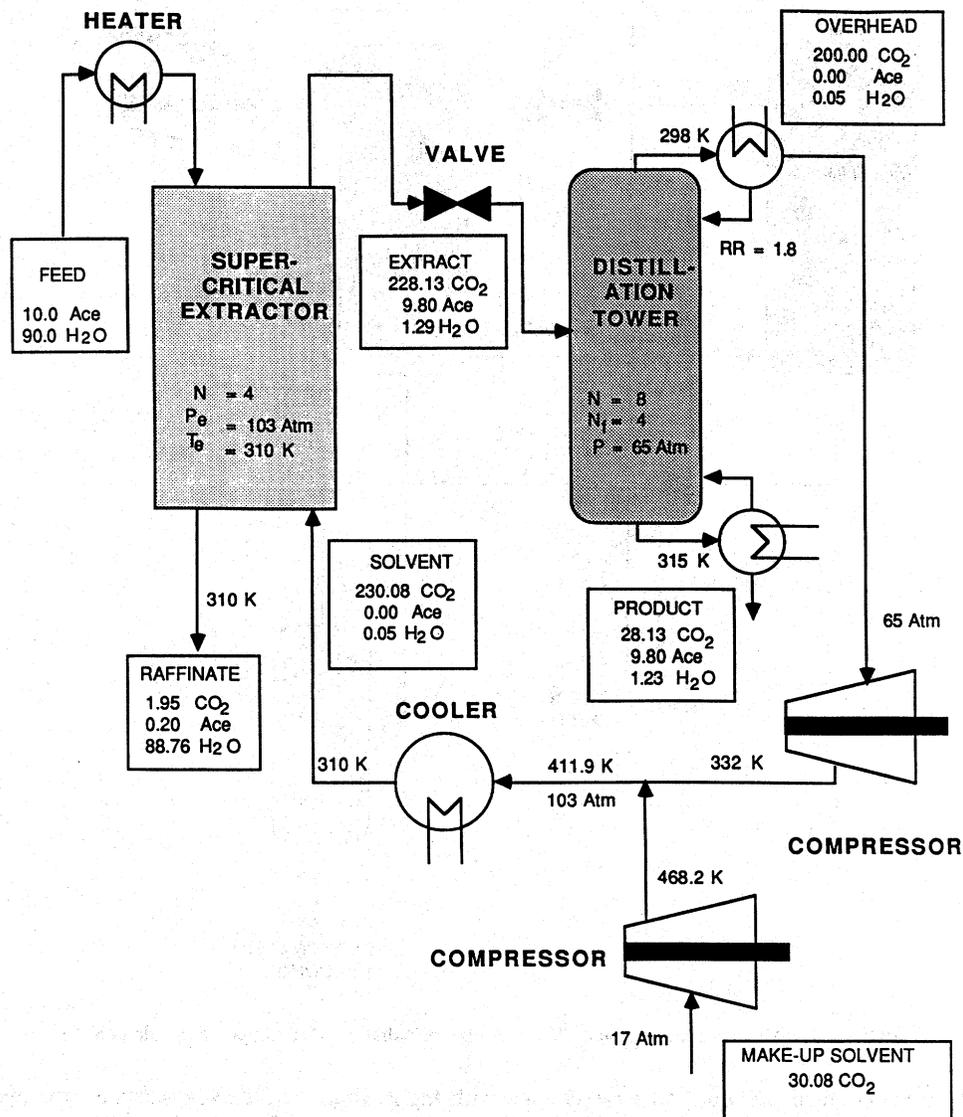


FIGURE 5. Dehydration of acetone with supercritical carbon dioxide. Stream flow rates are in mol/min. (Reprinted with permission from Cygnarowicz, M. L. and Seider, W. D., *Ind. Eng. Chem. Res.*, 28(10), 1497, 1989. © 1989 American Chemical Society.)

the supercritical CO₂ flows through the extractor, which is modeled using equilibrium stages, it preferentially dissolves the acetone, leaving the bulk of the water in the raffinate. The extract is expanded across a valve and fed to a distillation column where the acetone is concentrated at the bottom with nearly pure CO₂ in the distillate. The CO₂ stream is recompressed, mixed with make-up solvent, and recycled to the extractor.

The variables that have the greatest impact on the process cost and performance were determined by Cygnarowicz and Seider to be the extractor pressure (P_e) and temperature (T_e), the flow rate of the recirculated solvent ($F_{CO_2}^{rec}$), the distillation tower pressure (P_d), the reflux ratio in the distillation column, and the number of stages in the extractor and distillation column. In their approach, several of these variables are fixed to make the optimization more tractable. For example, the number of stages in the extractor and distillation column

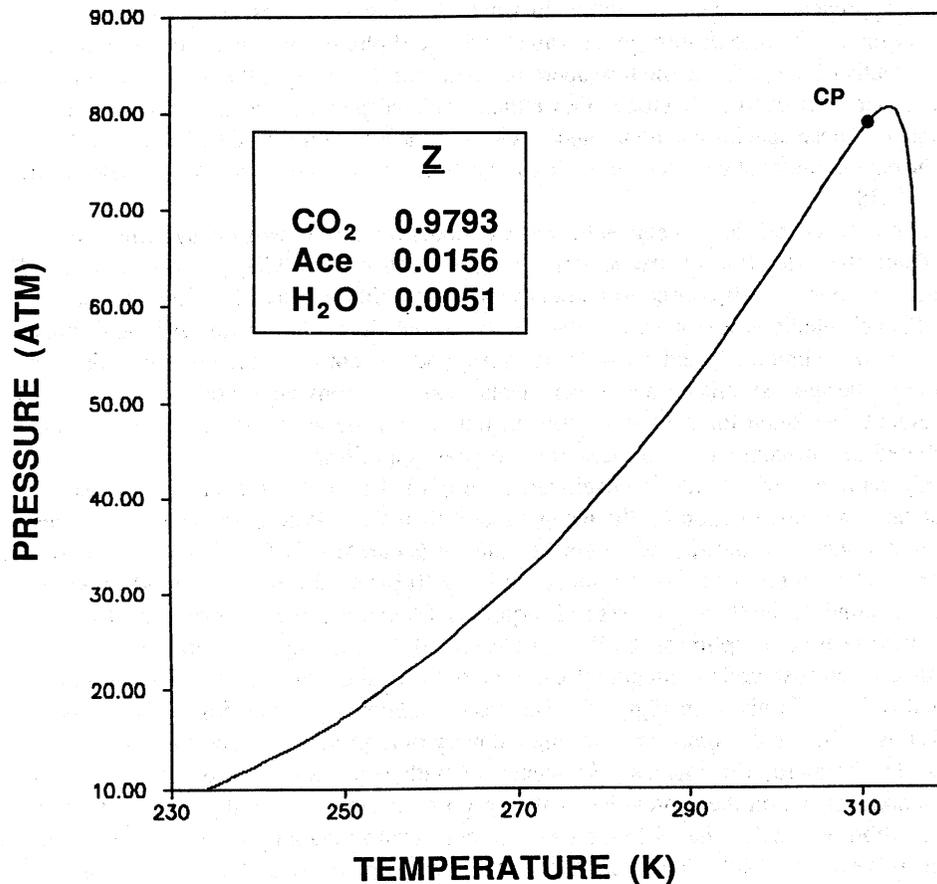


FIGURE 6. Phase envelope of typical feed to distillation column. (Reprinted with permission from Cygnarowicz, M. L. and Seider, W. D., *Ind. Eng. Chem. Res.*, 28(10), 1497, 1989. © 1989 American Chemical Society.)

are specified because their inclusion as design variables would require the solution of a mixed-integer, nonlinear program (with the number of stages as integer variables), which would significantly increase the computational complexity of the problem. Although the reflux ratio is a continuous design variable, in their experience, it is normally reduced to its lower bound and need not be varied continuously in the optimization. The distillation tower pressure is an important variable in two respects. First, P_d determines whether expensive refrigeration is needed in the condenser. In addition, the range of feasible values for P_d is tightly constrained. Figure 6 is a phase envelope calculated using the GC-EOS for a mixture with composition typical of the feed to the tower. Note that at such compositions, the two-phase region exists only at high pressures (close to the critical point) over a narrow range. The unavoidable proximity to the critical point makes the simulation of the distillation tower difficult. The Newton-based method that solves the equations is extremely sensitive to the initialization, and convergence failures are common. For this reason, P_d is fixed, and the optimal design is located at discrete values of this variable.

When minimizing the cost of utilities only, SCE was shown to be competitive with conventional separation techniques when the process was operated with low compression ratios and the distillation column pressure was close to the critical point in order to allow cooling water to be used in the condenser. This favorable result is in agreement with those of Brignole and Moses; however, at such pressures, the densities of the two contacting

phases approach each other, resulting in small flooding velocities. This sharply increases the volume required to disengage the vapor and liquid phases and raises the equipment cost significantly. Thus, despite the low operating costs for this design, the minimum annualized cost is not competitive. Acetone, like ethanol and propanol, is a high-volume, low-cost chemical. These species are poor candidates for concentration by SCE, but are well suited for the development of design methodologies since their phase equilibria are modeled reliably by an EOS.

Some successes have been achieved in modeling more realistic systems. Moricet⁴³ simulated the extraction of raw lecithin from soya oil using a CO₂/propane mixture. The Redlich-Kwong EOS was used to model the phase equilibria, and a hybrid of the sum-rates and Tomich methods was used to solve the equations for the extractor. Although only the extractor was simulated, and no attempts were made to optimize the process, this work is important because simulated and experimental concentrations were compared. Reasonable agreement was found for the liquid product, but not for the vapor product, the errors being attributed to "inaccuracies" in modeling the phase equilibria.

Cygnarowicz and Seider⁴⁴ developed a simplified model for a process to isolate β -carotene from fermentation broths using supercritical CO₂. Pure component properties for β -carotene were estimated, and solubility data for β -carotene in CO₂⁴⁵ were fit to estimate the interaction coefficients for the modified Peng-Robinson EOS. Then, models were prepared to simulate the three-phase (solid, liquid, SCF) extraction and separation steps. These models were used to optimize the SCE process. A design strategy was utilized to minimize the annualized cost while producing β -carotene of the desired quality. A design for minimum annualized cost is given in Figure 7. The results demonstrate that despite high operating pressures, SCE can be competitive for the recovery of high-value products at low production rates. Furthermore, the increases in solubility with small amounts of cosolvent have a substantial impact on the economics of the proposed design. An example is given in which the addition of 1 wt% ethanol to the CO₂ solvent transformed an unfavorable design into a competitive design. Note, however, that these results were obtained with a highly simplified model (i.e., the liquid in the fermentation broth was assumed to be pure water, and mass transfer effects were ignored). Extractions from fermentation broth are needed to quantify the modeling errors. Yet, this analysis is useful because it shows that SCE can be competitive for the recovery of high-value products at low production rates.

In summary, models for simulation and design optimization are beginning to bear fruit. Advances in thermodynamic modeling and algorithms for computing high-pressure phase equilibrium, coupled with new phase equilibrium data, are leading to improved models and more reliable designs.

V. SPECIAL TOPICS IN THE DESIGN OF SUPERCRITICAL EXTRACTION PROCESSES

While most advances in the design of SCE processes have focused on process development and parameter optimization, a few other approaches and observations are worthy of consideration.

Chimowitz and co-workers^{46,47} have based an approach to process synthesis on the "retrograde phenomenon" associated with SCFs. The retrograde phenomenon or "temperature inversion effect" is a manifestation of the complex relationship between the solubility and the solvent temperature and density. At a fixed pressure, the solubility decreases with increasing temperature close to the critical point due to a decrease in the density of the solvent, but increases with increasing temperature far from the critical point due to the increased vapor pressure of the solute.

For the separation of mixtures of isomeric solids into pure species, Chimowitz and co-workers show that when the solubilities of solids in supercritical solvents at several tem-

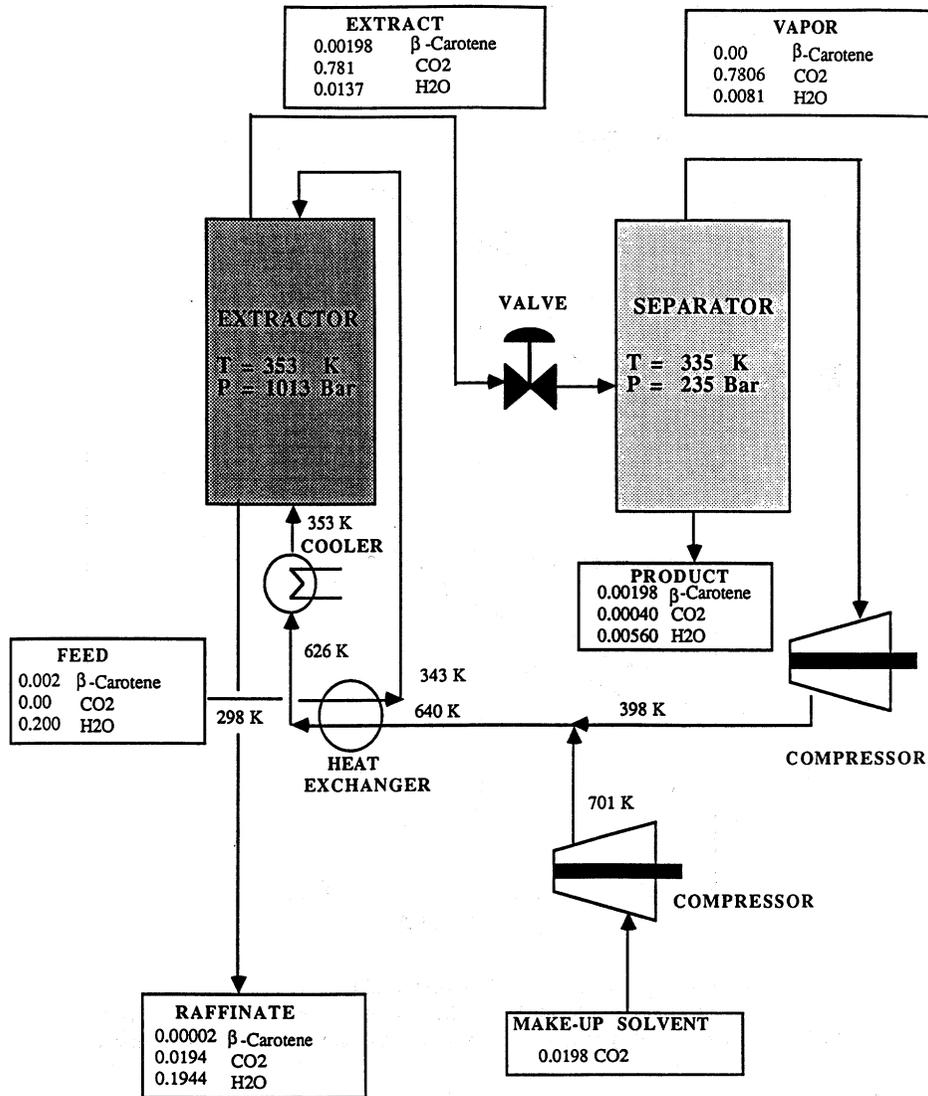


FIGURE 7. Dehydration of β -carotene with supercritical CO_2 . Minimum annualized cost = \$19.48/kg. Flow rates are in kmol/h.

peratures are plotted as a function of the pressure, the isotherms intersect at “crossover points”, as illustrated in Figures 8 and 9. Consequently, separation processes for solid mixtures can be designed in which the extractor and separator conditions lie between the crossover points of the two species. For example, consider a gas phase at a pressure P_o , intermediate to crossover points P_1^* and P_2^* , which is cooled from temperature T_H to T_L ; i.e., the process from A to B in Figure 9. Note that the solubility of component 2 increases, while the solubility of component 1 decreases. Hence, a process can be synthesized in which a mixture of components 1 and 2 is extracted at P_o and T_H , and separated by a simple temperature decrease to T_L . This approach can be extended to multicomponent mixtures. Figure 10 shows a flow sheet for a process to isolate A, B, and C, and Figure 11 shows the accompanying isotherms. The process has two parallel isobaric cascades with temperature cycling in each one. In the first cascade, the temperature cycles between T_H and T_L to isolate component C at a fixed pressure, P_2 , and in the second cascade, the same temperature cycle

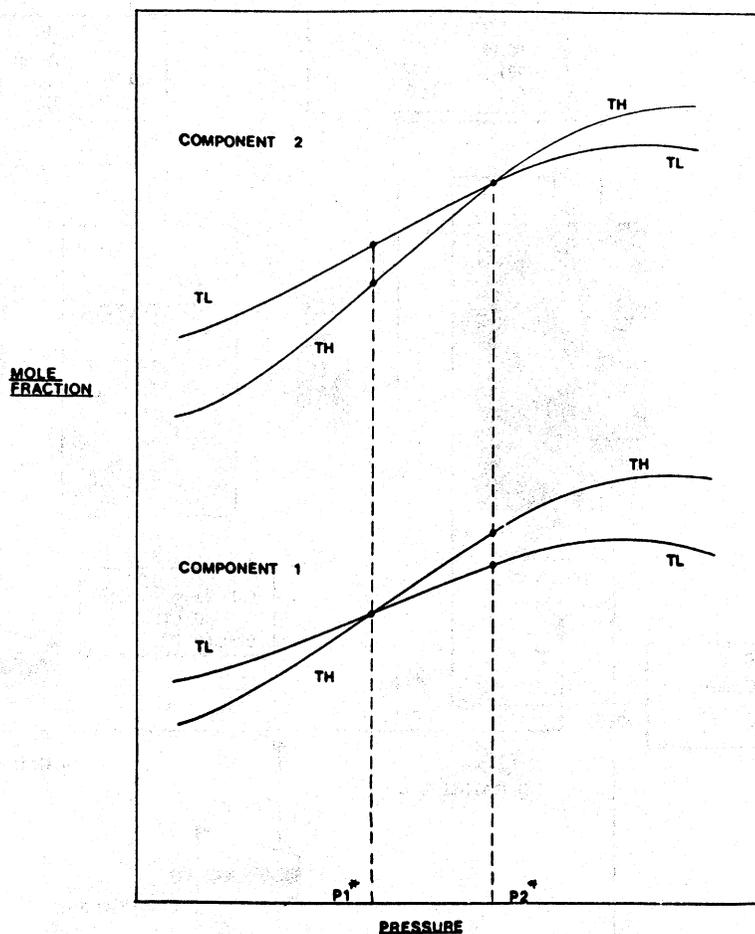


FIGURE 8. Mole fractions of solutes in supercritical CO_2 . Isotherm intersections are "crossover points". (From Chimowitz, E. H. and Pennisi, K. J., *AIChE J.*, 32(10), 1665, 1986. Reproduced by permission of the American Institute of Chemical Engineers.)

is used to isolate pure A and B at pressure P_1 . Although these studies stop short of detailed design calculations, they illustrate that solubility inversions with temperature can provide potentially useful designs.

Cygnarowicz and Seider⁴⁸ have shown the impact of the retrograde effect on the optimization of a process to dehydrate acetone using supercritical CO_2 . When minimizing the utility costs, a local minimum was found, which was related to the retrograde effect. Figure 12 shows how the moles of acetone extracted vary with the temperature and pressure for a solvent-to-feed ratio of 8, and a feed flow rate of 100 mol/min (10% acetone, 90% water). Note that nearly 100% of the acetone is recovered near the critical point of CO_2 (approximately 307 K). The recovery decreases with increasing temperature until it reaches a minimum near 316 K, beyond which it increases, in a pattern consistent with the retrograde effect. Thus, when high acetone recoveries are specified, Newton-based methods converge to either the "high-temperature" or "low-temperature" solution, depending on the initialization.

As expected, since SCE processes operate in the critical region, they are particularly sensitive to uncertainties in phase equilibria and PVT data. Enthalpy and entropy data are needed to estimate heating, cooling, and refrigeration loads, but these are derivative prop-

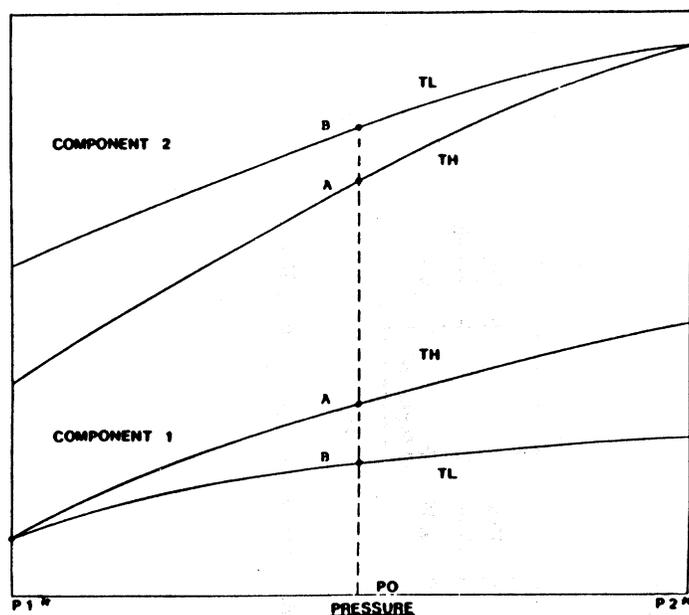


FIGURE 9. Crossover region. (From Chimowitz, E. H. and Pennisi, K. J., *AIChE J.*, 32(10), 1665, 1986. Reproduced by permission of the American Institute of Chemical Engineers.)

erties, and significant errors may be introduced when they are predicted using an EOS. To investigate this, Todd and Howat⁴⁹ considered the separation of butadiene from isoprene using supercritical trifluoromethane. This solvent has a “convenient” critical point, and volumetric data in the critical region and vapor pressure data are available. They compared two methods to estimate the heating, cooling, and compression loads for the process. The method based upon PVT data was considerably more accurate than that utilizing an EOS. It was found that the EOS predictions deviate significantly from the PVT predictions at high pressures, and these results suggest that economic analyses are sensitive to errors in the enthalpies and entropies.

VI. TRANSIENT BEHAVIOR AND CONTROL OF SUPERCRITICAL EXTRACTION PROCESSES

The previous sections have emphasized pilot plant studies, simulation, and optimization in the design of SCE processes that operate continuously and in the steady state. The design problem is complicated by modeling difficulties and the desire to operate in the critical region, where small changes in T and P can shift the extractor or separator from two to three or just one phase; however, solution of the tightly constrained design optimization does not account for the difficulties in maintaining steady operation in the face of disturbances and uncertainties. The disturbances must normally be dealt with in the short term as feed conditions, heat duties, etc., fluctuate. In addition, uncertainties can occur on a longer time frame, often over weeks and months, and arise in the fouling of heat exchangers, changes in the sources of feedstock, changes in product demand, etc. Hence, SCE processes are prime candidates for dynamic resiliency analysis,⁵⁰ to check the controllability of potential designs, and flexibility analysis,⁵⁰ to ascertain their ability to operate over a broad range of uncertain parameters.

Unfortunately, thus far little has been done to check the controllability of potential SCE

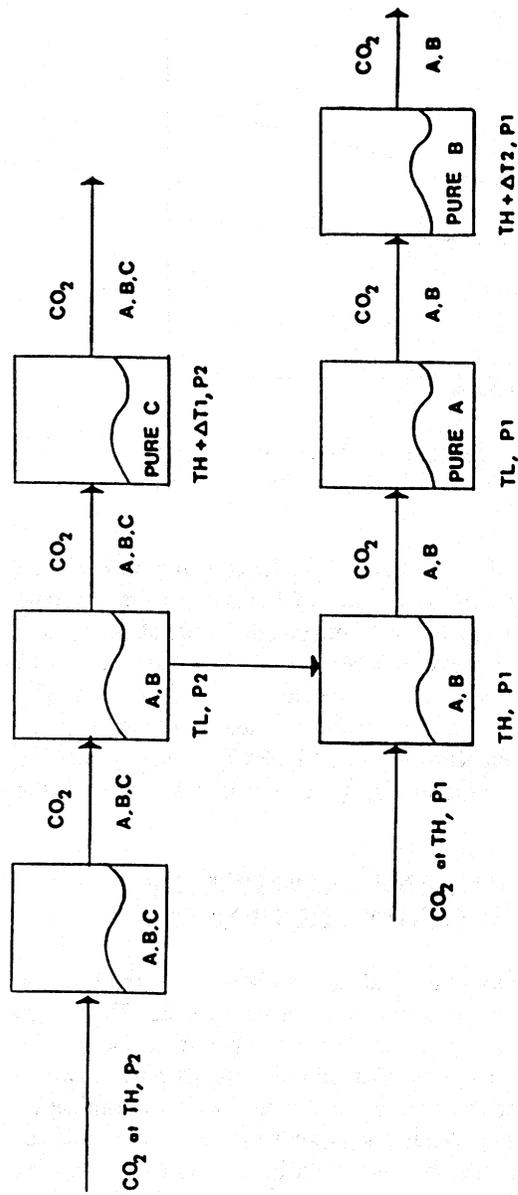


FIGURE 10. Process to isolate the species in a ternary solid mixture. (From Chimowitz, E. H. and Pennisi, K. J., *AIChE J.*, 32(10), 1665, 1986. Reproduced by permission of the American Institute of Chemical Engineers.)

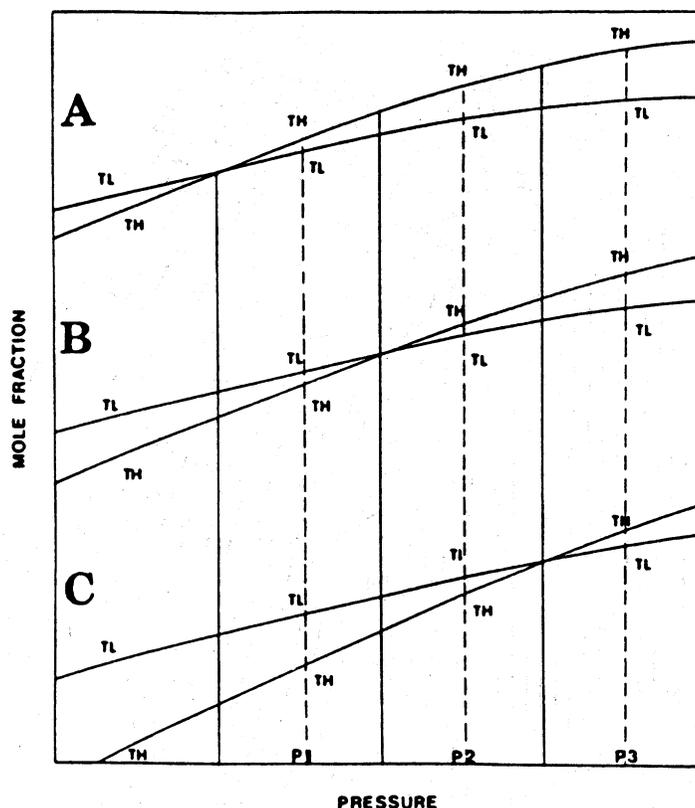


FIGURE 11. Crossover regions for a ternary solid mixture. (From Chimowitz, E. H. and Pennisi, K. J., *AIChE J.*, 32(10), 1665, 1986. Reproduced by permission of the American Institute of Chemical Engineers.)

designs. One of the first control studies was recently reported by Cesari et al.⁵¹ who studied the semi-batch extraction of ethanol from water and citral from lemon oil using supercritical CO₂. A dynamic model was prepared for the extractor, which included the mass and energy balances and the equilibrium equations, with proportional controllers used to maintain the extractor pressure and temperature by adjusting the product flow rate and the heat input to the extractor. Both the model and the physical system were sensitive to the controller actions with substantial changes causing the phases to coalesce. Such conventional controllers cannot predict the consequences of their actions, and therefore, cannot be expected to perform well in maintaining the proper phase distributions. Yet, the measurements by Cesari et al. of the vapor and liquid concentrations are in good agreement with the dynamic model, at least for the conditions considered (308 K and 17.2 MPa). Note that the extraction of citral from lemon oil was not studied experimentally.

This study represents an important first step in tackling the control problems associated with SCE processes. Unfortunately, it is a poor application of proportional control because it is applied to a semi-batch process. Such processes are better regulated with optimal control strategies, in which the model plays an important role.

Cygnarowicz and Seider⁴⁴ have also performed a dynamic analysis of a process to recover β -carotene using supercritical CO₂. The analysis focused on the product separator, and addressed the question of whether conventional (i.e., proportional (P) and proportional-integral (PI)) controllers can maintain acceptable product quality. The dynamic model included a control loop in which the vapor flow rate was manipulated to maintain the desired

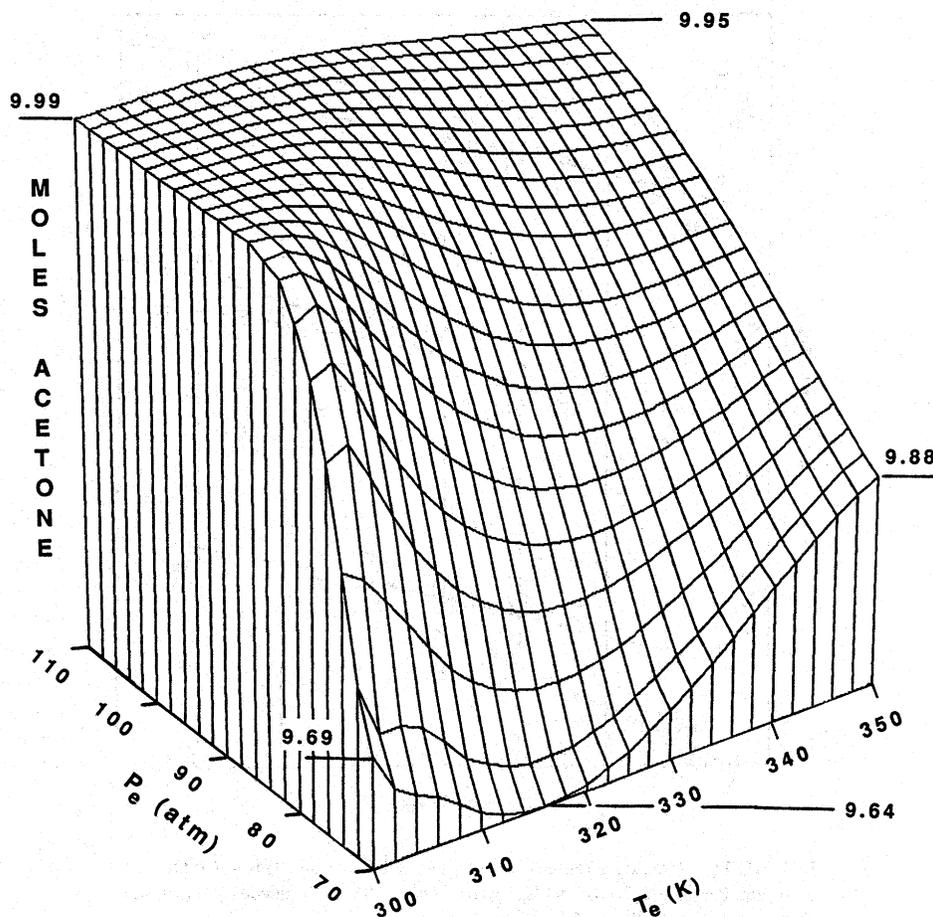


FIGURE 12. Moles of acetone extracted as a function of temperature and pressure. The solvent to feed ratio = 8. (Reprinted with permission from Cygnarowicz, M. L. and Seider, W. D., *Ind. Eng. Chem. Res.*, 28(10), 1497, 1989. © 1989 American Chemical Society.)

pressure. Although the servo response (i.e., response to a set-point change) was acceptable, the ability of the controller to reject disturbances was poor. A 10% decrease in the feed flow rate caused the product quality to drop below its design specification. The product specifications remained satisfied when the separator was oversized (i.e., when the separator pressure was increased), but the oversize increased the annualized cost. A potentially better alternative to satisfy specifications while rejecting disturbances without oversize is the implementation of advanced control strategies.

In this regard, for processes that are difficult to control, whether batch, semi-batch, or continuous, the process model is becoming an important element of more effective control strategies. New model predictive controllers (MPC),⁵² implemented in high-speed computer workstations, are providing more effective disturbance rejection and set-point response in tightly constrained operating regions. As models for the design of SCE processes improve, it can be expected that they will be incorporated in the design of model predictive controllers. This should yield designs that can be operated reliably, closer to the economic optimum in tightly constrained regions.

In yet another example, Sunol et al.⁵³ developed a process that is a hybrid of adsorption and extraction, called "supercritical exsorption", in which the solute is removed from a liquid phase by simultaneous extraction with a supercritical solvent and adsorption on a

porous solid bed. A dynamic model was developed for exsorption, consisting of four coupled, nonlinear partial differential equations with algebraic constraints, and was applied to simulate the dehydration of phenol. The model predicts that exsorption is superior to either extraction or adsorption in the efficiency and time for phenol removal, and experimental measurements are in qualitative agreement. Supercritical exsorption is more efficient since the adsorbant adds capacity for solute removal, and the high diffusivity of the supercritical solvent promotes rapid mass transfer from the solvent to the adsorbant. More experimental and theoretical work are needed to describe the mass transfer mechanism, but the preliminary results are promising.

VI. CONCLUSIONS

Most design studies have been oriented toward finding feasible SCE processes. Although experimentation has been indispensable in the development of new SCE processes, improvements in modeling and computational techniques are beginning to increase the role of simulation and optimization in SCE design studies. Furthermore, as advances in model predictive control permit more reliable operation, closer to the economic optimum, MPC can be expected to be applied and to increase the reliability and the profitability of SCE processes.

NOMENCLATURE

a	Mixture parameter in the Peng-Robinson EOS
a_i, a_j	Pure component parameters for Peng-Robinson EOS
D	Diameter
E	Enhancement factor
$F_{CO_2}^{rec}$	Flow rate of recirculated solvent
HTU_{oc}	Height of a transfer unit
k_{ij}, k_{ji}	Interaction coefficients for the modified Peng-Robinson EOS
M_{dc}	Equilibrium distribution coefficient
N	Number of equilibrium stages
NTU_{oc}	Number of transfer units
P	Pressure
P^*	Crossover pressure
P_d	Distillation tower pressure
P_e	Extractor pressure
T	Temperature
T_e	Extractor temperature
T_H	High temperature
T_L	Low temperature
U_C	Superficial velocity of the continuous phase
U_D	Superficial velocity of the dispersed phase
x_f	Mass fraction of alcohol in the solvent
x_i	Mole fraction of component i in the modified Peng-Robinson EOS
x_r	Mass fraction of alcohol in the raffinate
Y_{binary}	Mole fraction of solute in CO_2
$Y_{ternary}$	Mole fraction of solute in CO_2 -cosolvent mixtures
Z	Contact height, feed mole fraction

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