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U.S. DEPARTMENT OF COMMERCE / National Bureau of Standards

A Review of Supercritical Fluid Extraction

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A Review of Supercritical Fluid Extraction

James F. Ely
Jolene K. Baker

Chemical Engineering Science Division
National Engineering Laboratory
National Bureau of Standards
Boulder, Colorado 80303

U.S. DEPARTMENT OF COMMERCE, Malcolm Baldrige, Secretary

NATIONAL BUREAU OF STANDARDS, Ernest Ambler, Director

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Foreword

The purpose of this report is to summarize the results obtained from a brief investigation of supercritical fluid extraction principles and applications. This study was one portion of a project funded by the U.S. Department of Energy, Office of Fossil Energy, contract number DE-AI01076PR06010, in response to a preliminary proposal submitted by the authors. This report sometimes uses company trade names to identify processes and patent holders. This usage implies no endorsement by NBS. Note also that some figures reproduced from other sources do not conform with NBS policy concerning SI units.

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A REVIEW OF SUPERCRITICAL FLUID EXTRACTION

by

James F. Ely and Jolene K. Baker

Chemical Engineering Science Division
National Engineering Laboratory
National Bureau of Standards
Boulder, Colorado 80303

During the past ten years there has been intense interest in the application of dense gas separation techniques to various chemical processing problems. An example is known as supercritical fluid extraction. The purpose of this report is to summarize various aspects of supercritical fluid extraction including a definition of the phenomena, current industrial applications, technical difficulties and, where possible, the identification of areas where further research would be of value. In addition, processing aspects which impact on the cost effectiveness of supercritical fluid extraction are considered.

Current research which bears upon the development of supercritical fluid extraction is presented and recommendations for certain high risk research activities are summarized. In addition, a brief review of supercritical fluid chromatography is presented and chemical kinetics in supercritical phases are briefly discussed.

Key words: extraction; fluids; research needs; review; supercritical.

1. Introduction

During the past ten years, there has been renewed interest in the use of dense gases in chemical engineering processes. These processes include both chemical reactions and extractive separations or a combination of the two. Most interest has been in separations and is referred to as supercritical fluid extraction (SFE) or critical solvent extraction (CSE) although the name destraction has also been proposed [1]. The term supercritical refers to the fact that the solvent is at a temperature above its vapor-liquid critical point. Thus it cannot be liquefied by increasing the system pressure as illustrated in figure 1. Under these conditions (near critical solvent), a typical solvent/solute(s) mixture exhibits "unusual" phase equilibrium and mass transfer behavior. The basic idea of the process is to exploit this unusual behavior by contacting a mixture which is either in a solid or liquid state with a supercritical fluid such as carbon dioxide, ethylene, water, etc. The density of the extract mixture is then reduced, by either pressure reduction or heating, causing the solvent and extract(s) to phase separate.

It should be emphasized that supercritical fluid extraction along with the more conventional separation processes of distillation and liquid solvent extraction, can be regarded as the same basic process, i.e., they exploit phase equilibrium behavior between different states of matter at different operating conditions. Figure 2 attempts to illustrate this point by showing p-T projections for a binary mixture fluid phase diagram. Regions where different processing techniques might be applied are indicated. Not shown are the solid-fluid regions. The point of this figure is that at different temperatures, pressures and mixture compositions, different types

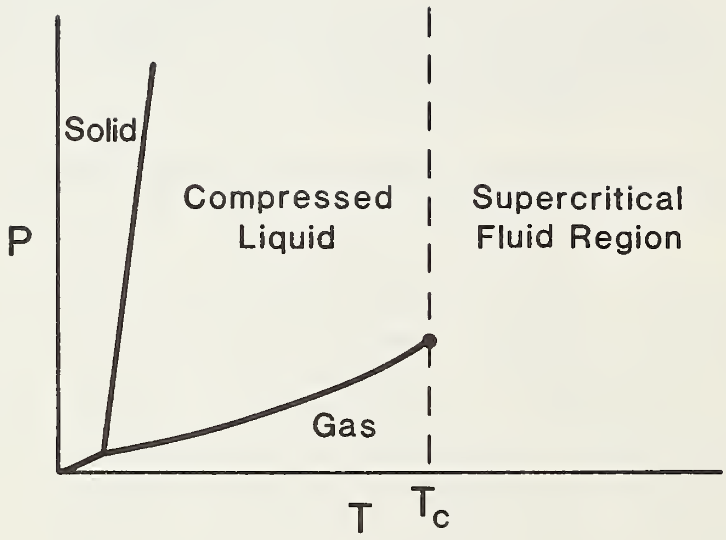

Figure 1. Schematic pT diagram showing the pure fluid supercritical region.

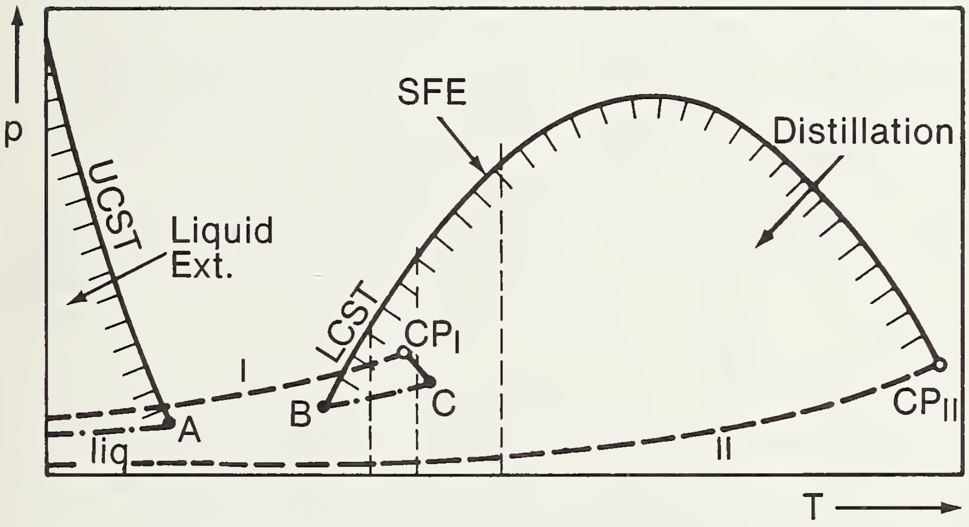

Figure 2. Mixture pT phase diagram illustrating different regions for separation techniques.

of phase equilibria may be exploited to effect a separation of mixture components. Of the three possibilities which are illustrated, distillation is by far the most common with solvent extraction being the next most prevalent method. Supercritical fluid extraction is only a viable alternative when one of the first two has a marked weakness or shortcoming. An example of this in distillation is when thermal degradation of a product occurs or when the distillation is particularly energy inefficient. For example, separation of oxygenated organic chemicals from aqueous solution is particularly energy inefficient [2,3] as are distillations (pyrolysis in the presence of hydrogen) associated with the liquefaction of coal. SFE appears to be a possible alternative to liquid solvent extraction when inexpensive, non-toxic supercritical fluids may be used to replace toxic solvents in the food and drug industry. An example in this case would be the decaffeination of coffee beans with carbon dioxide as opposed to liquid extraction using a methylene chloride solvent.

In addition to chemical processing, it should also be pointed out that the physical principles associated with supercritical extraction can be exploited as an analytical tool and for thermophysical property measurements. The primary area here is called supercritical fluid chromatography. It has also been proposed that supercritical extracts of fossil materials (coal, shale, etc.) can be used as geological markers and to provide primary coal structural information. These areas will be discussed briefly later in the report.

The overall goal of this report is to broadly analyze the status of and future prospects for supercritical fluid extraction. The specifics of this analysis may be conveniently summarized as follows:

1) Analyze and define the physical phenomena involved in SFE.
2) Survey current commercial uses and ongoing process development of this separation technique and identify key processing considerations.
3) Survey current research activity which bears on SFE and identify scientific problems.

and 4) Suggest elements of a long range research program which will be required to better utilize the supercritical fluid extraction concept.

Since most of the current industrial research in this area is considered to be proprietary, the applications reported here and resulting conclusions draw exclusively on material appearing in the open literature. Every effort has been made to provide detailed literature references to the material used in the preparation of this report.

2. Definition of the Physical Phenomenon

Early research dealing with supercritical fluid extraction has been reviewed several times during recent years [4-9]. As pointed out in these reviews, the physical phenomenon was first observed over a hundred years ago by Hannay and Hogarth [10]. Generally speaking most pre-1960 work in the field dealt more with experimental observation and exploitation of the physical behavior than with theoretical understanding. Some of these observations, however, were of an unfavorable nature. For example, in high pressure steam power generation it was found that the steam deposited silica on turbine blades as the pressure decreased [11]. In the petroleum industry it was discovered that supercritical gas mixtures exhibited retrograde phenomena such as condensation of components upon isothermal expansion. An important current day negative observation of SFE involves the high solubility of common pipeline dehydrating agents such as glycols in supercritical carbon dioxide.

The earliest patented application of supercritical extraction was for the deasphalting of oils as described in Messmore's 1943 patent application [12]. In 1945, Katz and Whaley demonstrated that supercritical natural gas mixtures could be used to separate liquid hydrocarbon mixtures [13]. Other early applications include the work of Zhuze [14-16] and more recently the work of Zosel in Germany [1,17-22]. In Zosel's most recent U.S. patent [22], approximately 84 examples of separations incorporating a wide spectrum of supercritical solvents are cited.

2.1 Qualitative Description of Phase Equilibria

The experimental approach to SFE described above is extremely difficult in that the location of the critical lines and phase boundaries must be identified for every system. A casual inspection of just binary mixture fluid phase diagrams shows that there is a great variety of behavior that one would encounter in this effort. For example, some systems have simple regions of coexisting phases (e.g., liquid-vapor), others have azeotropes and isolated regions of liquid-liquid immiscibility are common. Studies based on the van der Waals equation of state [23,24] have shown that different classes of fluid behavior may be identified by the shapes and number of critical lines, the existence or absence of three phase lines and the manner in which the critical lines connect with the pure component critical points and three phase lines. The occurrence of azeotropy gives rise to subclasses but does not change the qualitative structure of the classification scheme. A critical point is a pressure, temperature composition thermodynamic state point where a phase exhibits incipient stability.

In this classification system there are six basic types of fluid phase diagrams which are illustrated in figure 3 as p-T projections. In this figure the dashed lines are critical loci and solid lines are either pure component vapor pressure lines or three phase lines. Type I systems are the simplest of those encountered and typically have a continuous critical locus which connects the two pure fluid critical points. Usually systems of this category are composed of molecules of roughly the same size and polarity, e.g., methane/propane or benzene/toluene. Figure 4 which was taken from the recent review of Street [25] shows the three dimensional space model for this system and some isothermal and isobaric cross sections. The essential feature of these cross sections is that the two phase region extends above the critical point of the lighter component. Also note that above the critical locus the components are miscible in all proportions.

As the size and polarity difference between the mixture components increases, we find a class of systems where the critical line is still continuous between the two pure fluid critical points but the system also exhibits a region of liquid-liquid immiscibility. This is a Type II system in figure 3 and the corresponding space model and cross sections are shown in figure 5. The line DU is a line of upper critical solution temperatures (UCST) which are critical temperatures for liquid-liquid equilibria. This line terminates at the upper critical endpoint

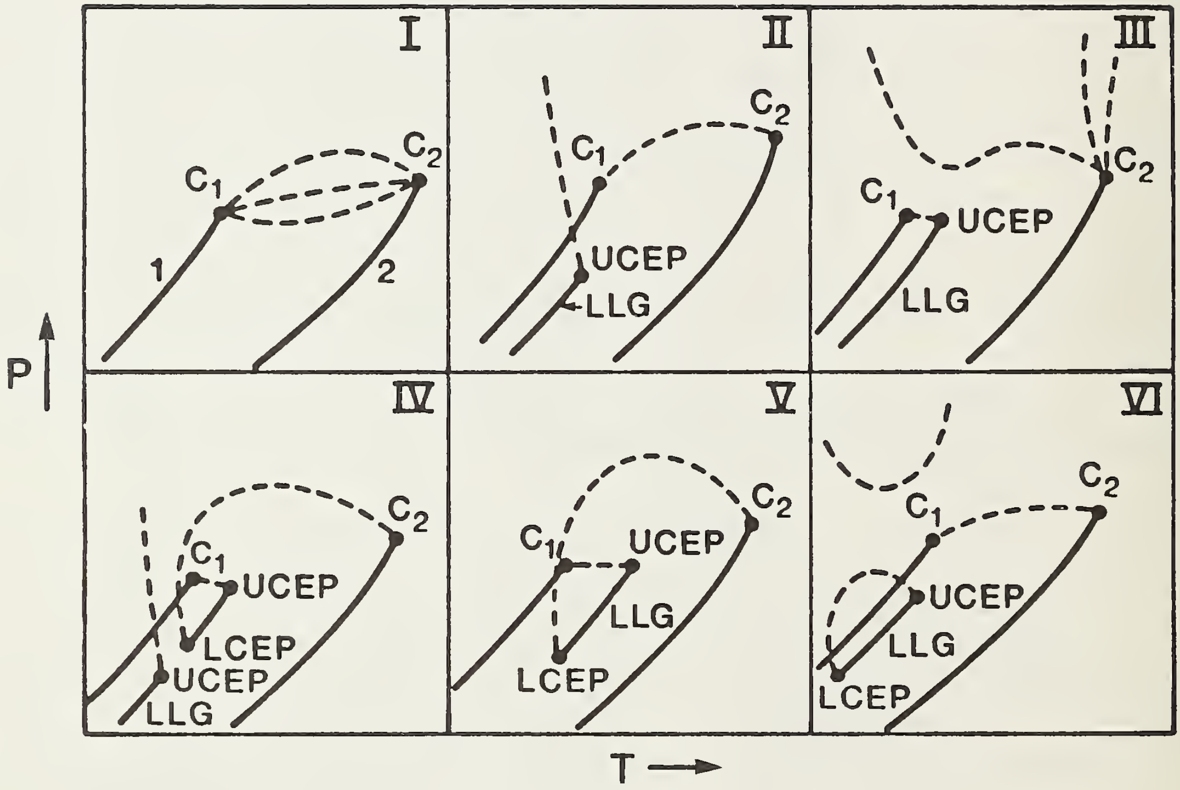

Figure 3. Classification scheme for binary mixture fluid phase diagrams.

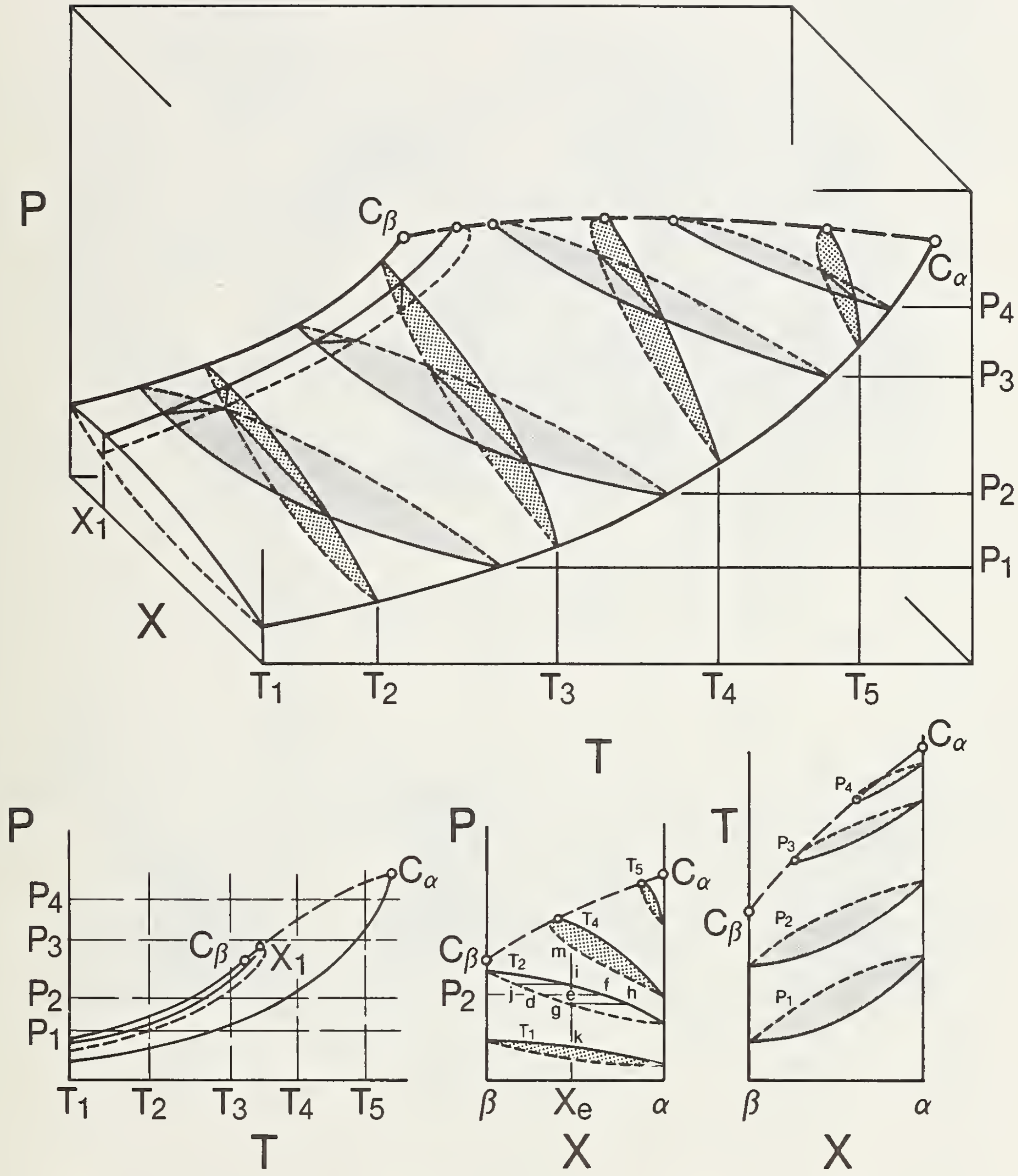

Figure 4. Three dimensional space model and cross sections for a Type I binary mixture [26].

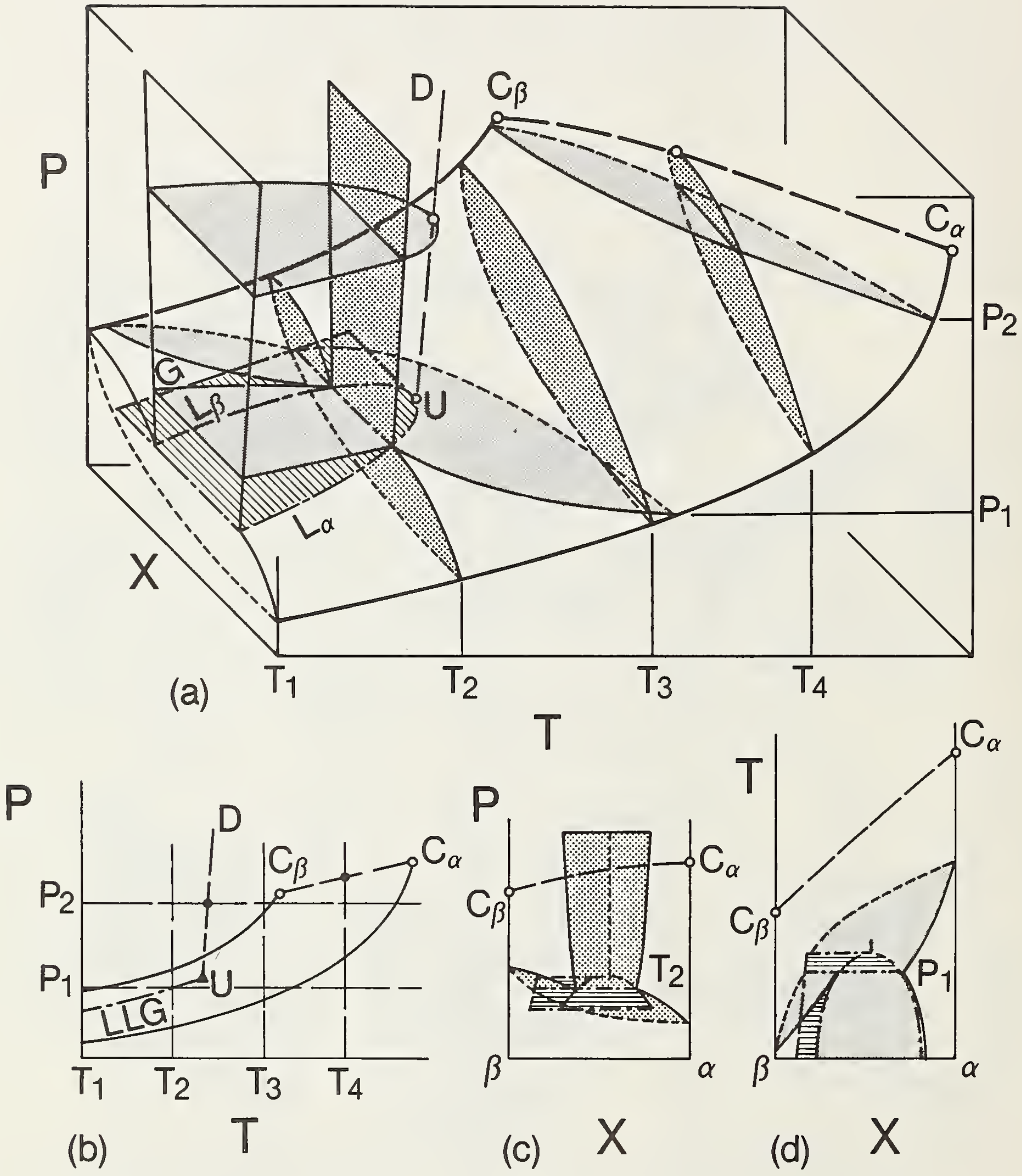

Figure 5. Three dimensional space model and cross sections for a Type II binary mixture [26].

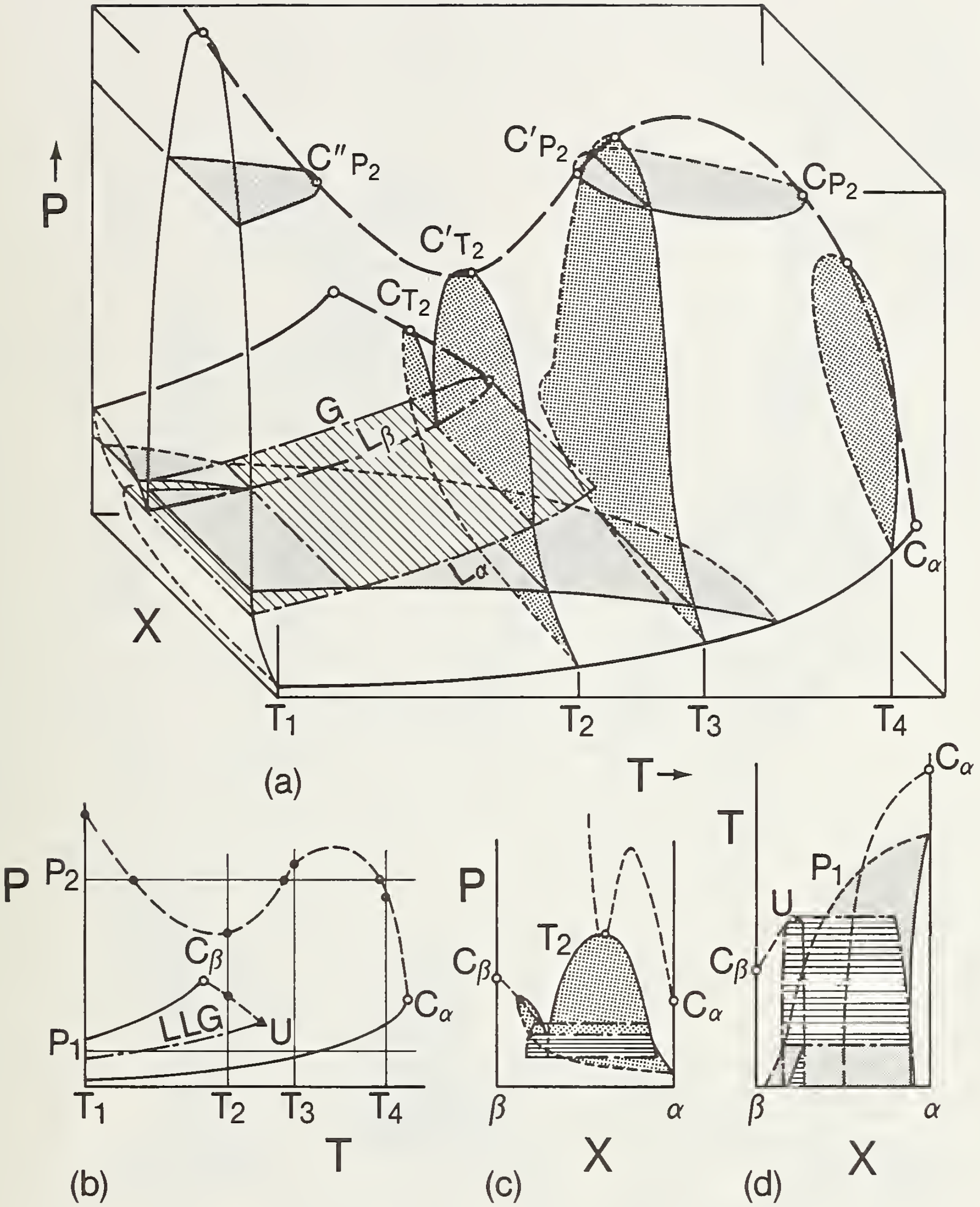

Figure 6. Three dimensional space model and cross sections for a Type III binary mixture [26].

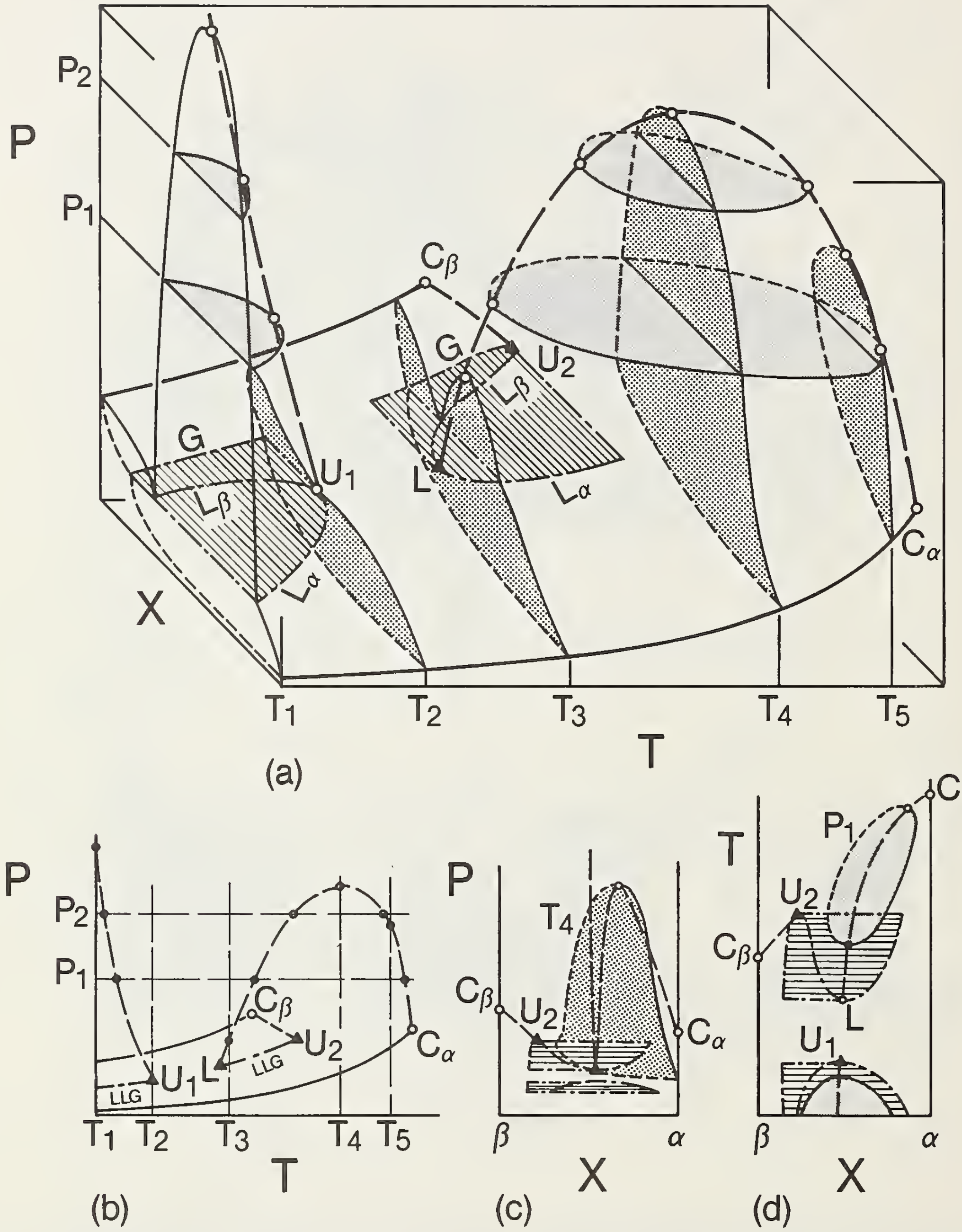

Figure 7. Three dimensional space model and cross sections for a Type V binary mixture [26].

(UCEP) which is the point U. The line running horizontially from U is a three phase line where two liquids and a vapor coexist. Examples of this type of system are carbon dioxide/octane, and ammonia/toluene. It is interesting to note that the slope of the UCST line can be either positive or negative.

A further increase in size and polarity difference gives rise to Type III systems where the liquid-vapor critical locus is no longer a continuous curve between the two pure fluid critical points. One branch runs from the critical point of the more volatile component and terminates at the UCEP where it intersects the three phase region. The other branch exhibits minimum and maximum temperatures and rises to very high pressures. The three dimensional model and cross sections are shown in figure 6. Note that the branch of the critical curve originating with the less volatile component goes continuously from liquid-vapor to liquid-liquid equilibria. This is a very difficult system to model. Examples of this type of system are methane/H_2S, carbon dioxide/hexadecane and carbon dioxide/water.

As a final example of different types of phase equilibria that can be encountered in SFE, lets consider a Type V system. In this type system there are two branches of the critical curve but the branch from the less volatile component reaches a maximum in pressure and then decreases until it intersects the three phase line at a lower critical endpoint (LCEP). The liquids are miscible in all proportions below the LCEP. The three phase line in this case is typically very short, maybe extending over just a few degrees in temperature. Figure 8 shows the space model and cross sections for this type of system. Typical examples are propane/lubricating oils, methane/hexane and hydrocarbon/polymers. For a discussion of Types IV and VI, see reference [25].

Obviously, the range of possible critical behavior is extensive and complex. Classical thermodynamics provides, however, a set of macroscopic criteria which must be met for phase equilibrium including critical phenomena and azeotropy. These criteria are briefly discussed in the next section. Unfortunately, as pointed out in Section 5.1.2, classical thermodynamics does not provide the link between molecular material constants and phase behavior.

2.2 Thermodynamic Description of SFE

Although a substantial amount of process oriented experimental work is still being performed, recent emphasis has been on systematic experimental studies of model systems (as opposed to complex, ill-defined mixtures) and better theoretical understanding of high pressure phase equilibria. In this section we shall consider the theoretical aspects of SFE with the goal of obtaining a macroscopic understanding of the phenomena.

2.2.1 Pure Solvent Properties

As was mentioned in the introduction, the success of SFE hinges on the unique physical properties of the near critical solvent/solute(s) mixture. From a separations point of view one must consider both the physical properties of the pure solvent and the solvent/extract mixture. In particular, the density and thermal properties of the solvent determine the loading capacity and solvent regeneration characteristics while the chemical potential in the mixture and transport properties provide the driving force and regulate the mass transfer rates. In addition, the chemical nature of the solvent greatly affects the selectivity in the separation process.

In the case of a pure supercritical solvent, the density is comparable to normal liquid densities (typically 200-900 kg/m^3) and the diffusivities are close to those of a gas (typically 10^{-5} dm^2/s). These features are illustrated in figures 8 and 10. Figure 8 shows the density of carbon dioxide as a function of temperature and pressure [26]. To illustrate the solvent loading possible in the supercritical density range, figure 9 shows the solubility of naphthalene [27,139,144] as a function of the carbon dioxide density along lines of constant pressure. The relation between the solvent density and solubility is clear. One can also make two general observations from this type of figure, namely that at constant temperature the loading capacity increases with density and at constant density it increases with temperature [30].

Figure 10 shows typical diffusivities that can be expected with a supercritical solvent [2]. Shown in this figure are diffusivities in the supercritical region and those typical of a liquid solvent. This type of behavior is to be expected on the basis of the Stokes-Einstein equation $D_{AB} = RT/6\ \eta_B r_A$ where η_B is the viscosity of the solvent. Since the viscosity of a supercritical fluid solvent is typical of a dense gas (100-300 μP) as opposed to a dense liquid (1000-100,000 μP), the diffusivities are more typical of a gas.

2.2.2 SFE Phase Equilibria

In any separation process one is by definition concerned with the phase behavior of mixtures. The fundamental macroscopic equations governing phase equilibria are well known from thermodynamics [31,152,153]. They state that the temperature, pressure and chemical potential of each component must be identical to the corresponding variable in every coexisting phase. Since the temperature and pressure are normally fixed operating variables, the essential requirement is the equality of the component chemical potentials or equivalently, fugacities.

For the gas phase extraction of liquid mixtures it is convenient to consider the liquid phase activity coefficient formulation of solution thermodynamics [31]. In this formulation, the equilibrium distribution coefficient or K value is given by

$$\begin{aligned} K_\alpha &= \gamma_\alpha(T,p^*,\{x_j\})p_\alpha^s/\theta_\alpha(T,p,\{y_i\})p = \phi_\alpha^\ell/\phi_\alpha^v \\ &= y_\alpha/x_\alpha \end{aligned} \tag{1}$$

where γ is the activity coefficient at the reference pressure p_α^s is the vapor pressure of the solute, p is the system pressure, y_α and x_α are the concentrations of α in the solvent and extract phase and θ_α is called the vapor imperfection coefficient [33]. The supercripts ℓ and v denote liquid and vapor and ϕ indicates a fugacity coefficient. At the pressures commonly encountered in distillation θ_α is close to unity and this equation reduces to the common engineering textbook expression $k_\alpha = \gamma_\alpha p_\alpha^s/p$. Obviously, the effectiveness of SFE is due to a volatility enhancement, i.e., a marked decrease in θ_α as the pressure increases. The rigorous thermodynamic expression for this quantity is given by

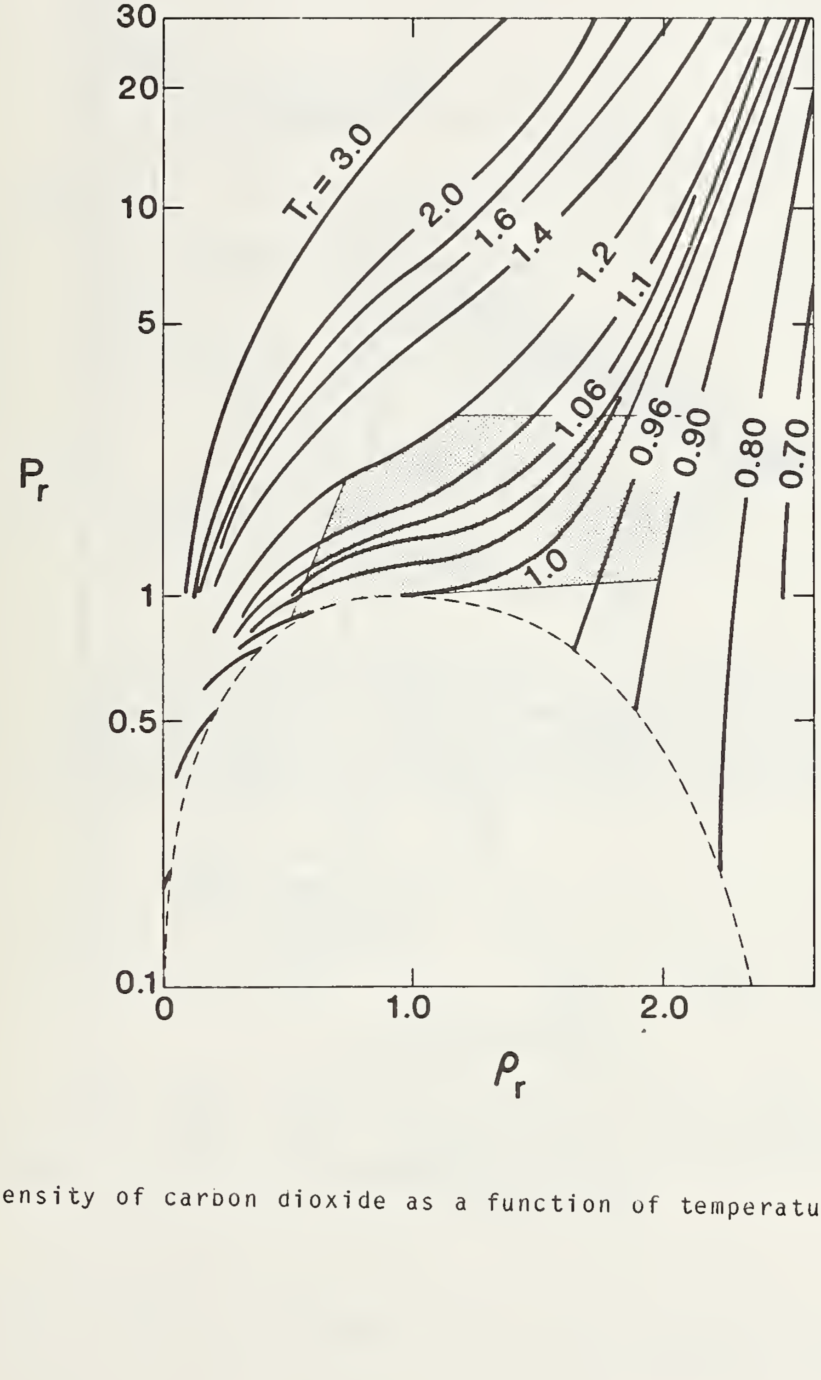

Figure 8. Density of carbon dioxide as a function of temperature and pressure.

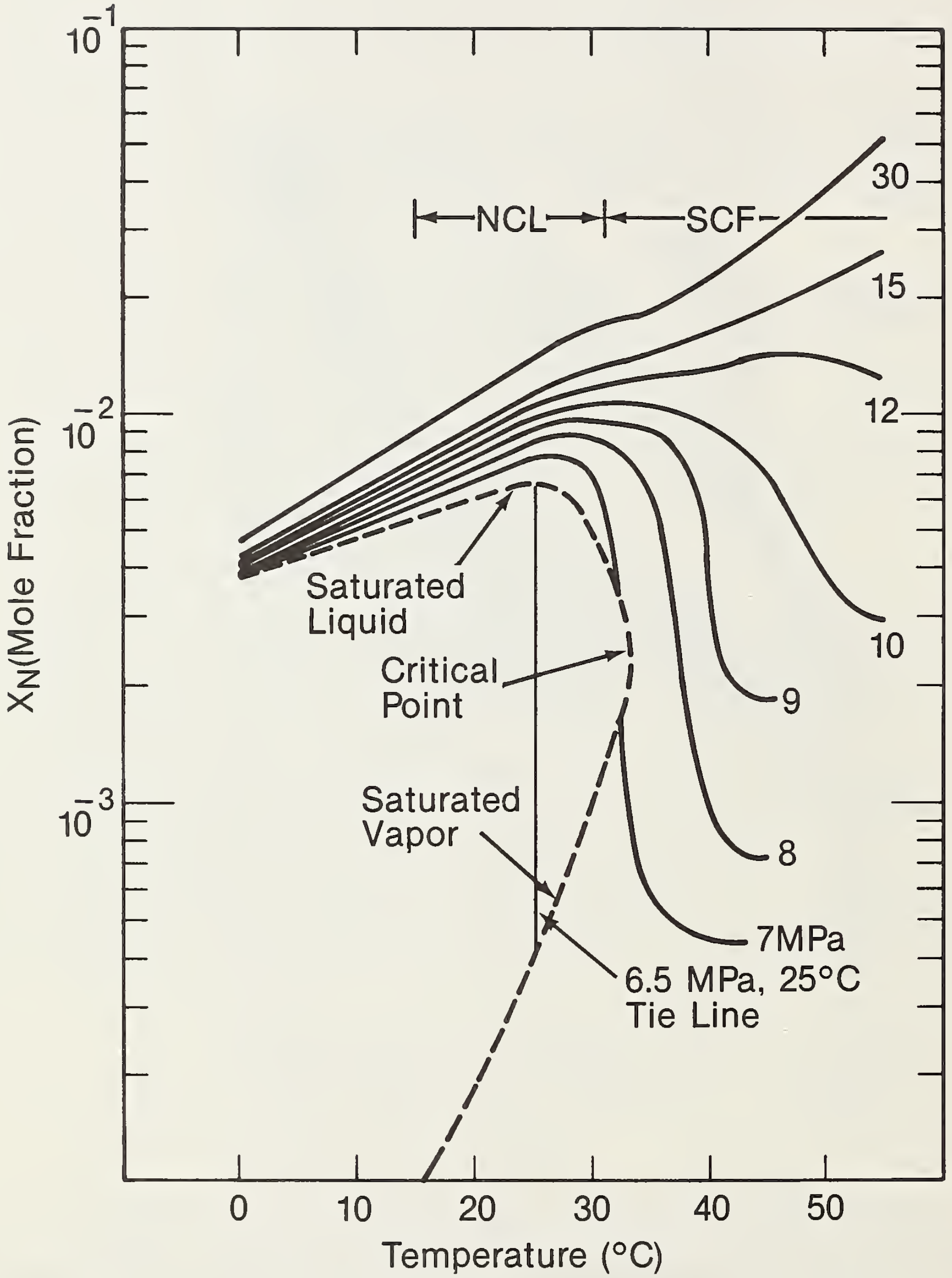

Figure 9. Solubility of naphthalene in carbon dioxide as a function of the pure carbon dioxide pressure [2].

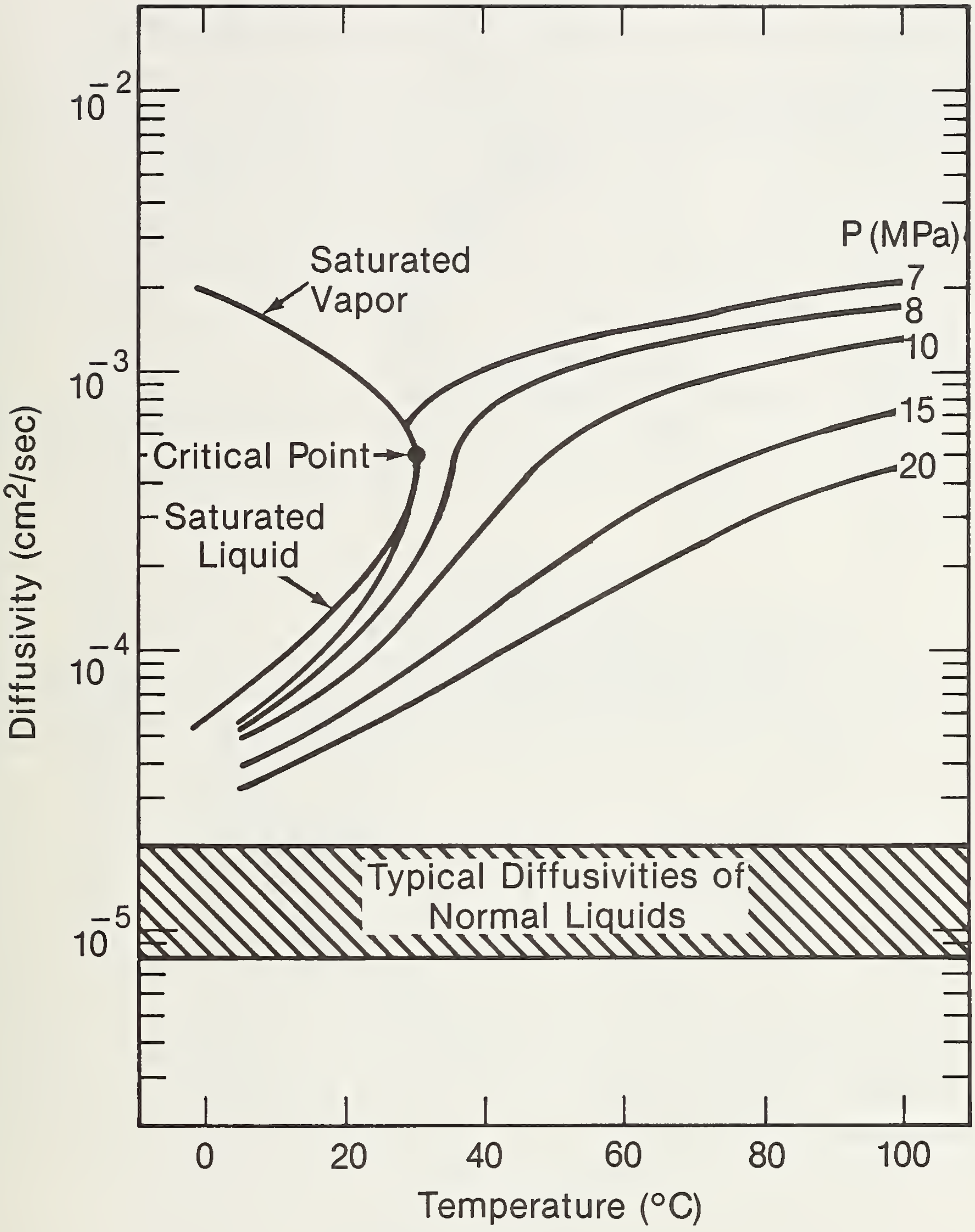

Figure 10. Diffusivity of a solute in carbon dioxide as predicted by the Stokes-Einstein equation [2].

$$\theta_\alpha = \frac{\hat{\phi}_\alpha(T,P,\{y\})}{\phi_\alpha(T,p_\alpha^s)} \exp\left[- \int_{p^*}^{P} \frac{\bar{V}_\alpha^\ell - V_\alpha}{RT}\, dp - \int_{p_\alpha^s}^{P} \frac{V_\alpha}{RT}\, dp \right] \tag{2}$$

where $\hat{\phi}_\alpha$ is a vapor phase fugacity coefficient at the specified conditions, $\bar{V}_\alpha^\ell$ is the partial molar volume of the solute in the liquid phase, and V_α is the pure solute molar volume. Since the fugacity coefficient $\phi_\alpha(T,p_\alpha^s)$ is fixed at constant temperature and the pure liquid solute is essentially incompressible, the enhanced volatility observed in SFE must come from a marked decrease in the vapor phase fugacity coefficient $\hat{\phi}_\alpha(T,p,\{y\})$ when the pressure is increased at a near critical temperature or to a drastic increase in the solute liquid phase parital molar volume or both. It is most likely that both effects are occurring but that the former is dominant.

This fact is easier to demonstrate when the condensed phase is a solid mixture. The thermodynamic relations remain the same, but there are some simplifications in the imperfection coefficient. Rewriting eq (1) in terms of the vapor phase concentration we find

$$y_\alpha = \frac{x_\alpha p_\alpha^s}{P} \left[\frac{\gamma_\alpha}{\theta_\alpha} \right] \tag{3}$$

where p_α^s is the sublimation pressure of the solid at T. The bracketed quantity is called the enhancement factor [168] in solid-vapor equilibria and the term $x_\alpha p_\alpha^s/p$ is the so-called ideal solubility. The imperfection coefficient becomes

$$\theta_\alpha = \frac{\hat{\phi}_\alpha(T,p,\{y\})}{\phi_\alpha(T,p_\alpha^s)} \exp\left[- \int_{p_\alpha^s}^{P} \frac{\bar{V}_\alpha^s}{RT}\, dp \right] \tag{4}$$

where V_α^s is the molar volume of component α in the solid phase. Figure 11 shows the ideal and actual solubility of naphthalene in ethylene at 15 degrees above the critical temperature [28,29,33]. The large difference between these two is due to the imperfection coefficient since γ_α is only a function of temperature (low solubility of ethylene in naphthalene). In particular it is due to a marked decrease in the vapor phase fugacity coefficient $\hat{\phi}_\alpha(T,p,\{y_j\})$ which thermodynamically is

$$RT \ln \hat{\phi}_\alpha = \int_0^P \left(\bar{V}_\alpha^v - \frac{RT}{P}\right) dp \tag{5}$$

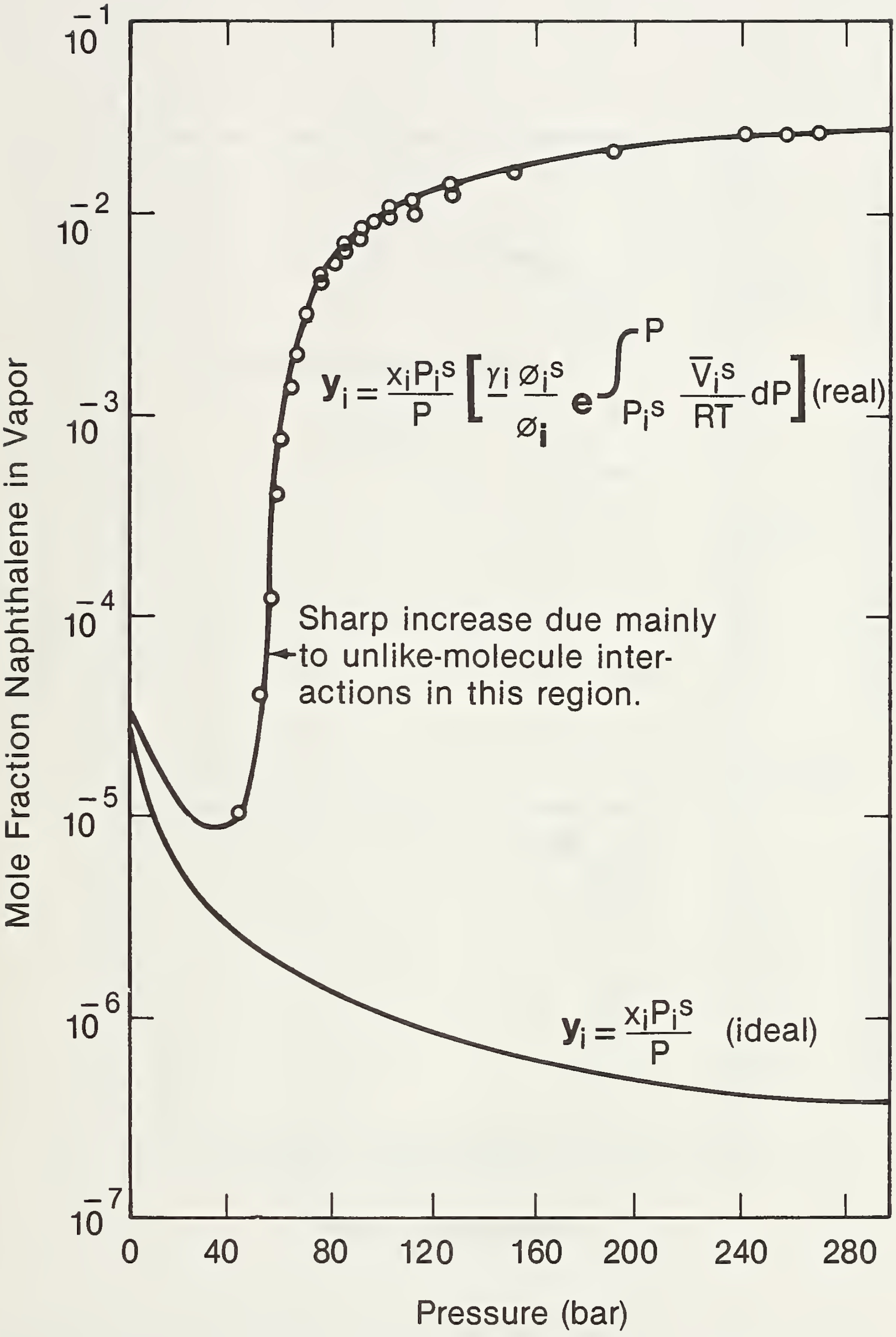

Figure 11. Actual and ideal solubility of naphthalene in ethylene [33].

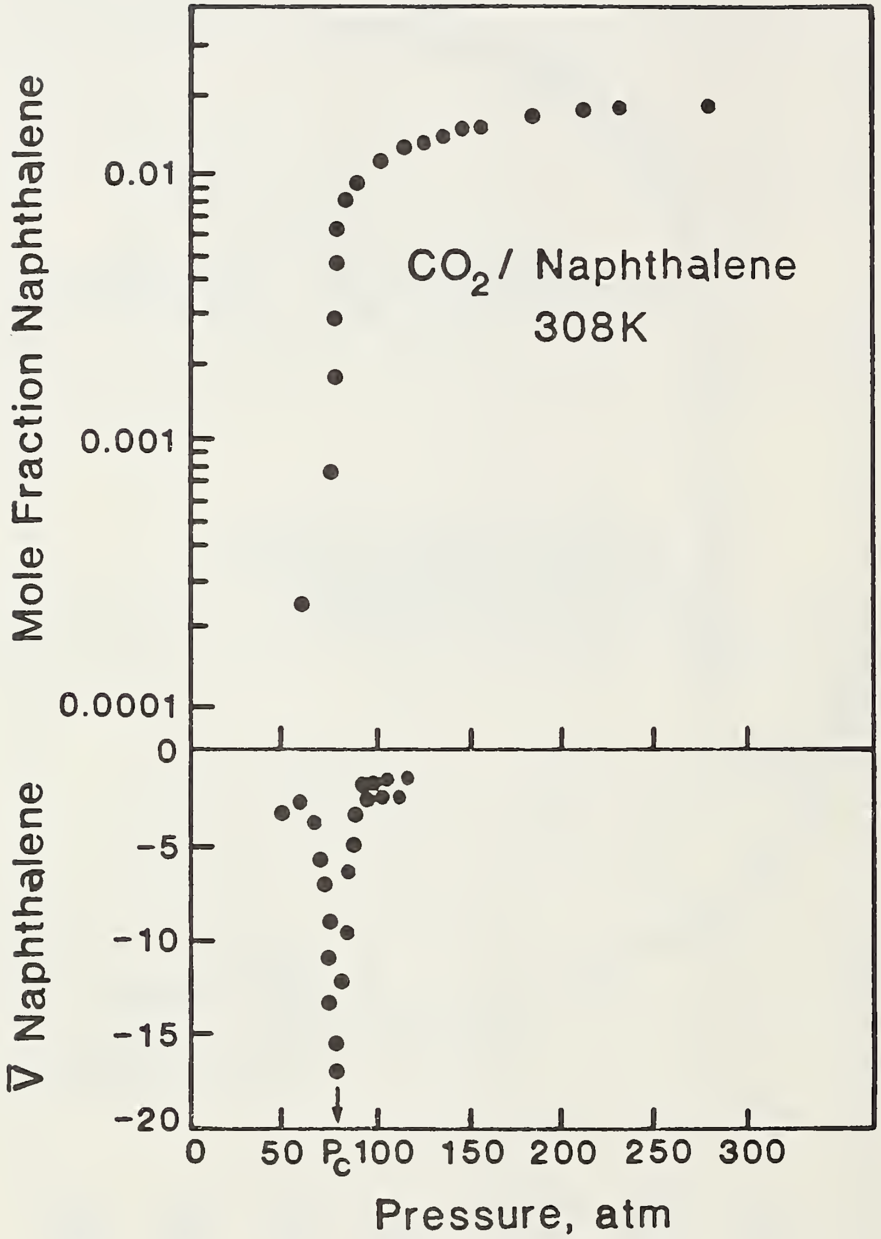

Figure 12. Solubility of naphthalene in carbon dioxide and corresponding partial molar volume of naphthalene in the vapor phase [34].

where $\bar{V}_\alpha^v$ is the partial molar volume of the solute in the vapor phase. If $\hat{\phi}_\alpha(T,p,\{y\})$ becomes small, at some point, there will be a marked increase in solubility. Figure 12 shows the solubility and partial molar volume of naphthalene in the CO_2 phase as a function of pressure near the critical temperature of CO_2 for the CO_2-Naphthalene system. As one can see, there is a pronounced effect near the critical point. Since the partial molar volume assumes a large negative value at this point, $\phi_\alpha(T,p,\{y\})$ becomes small and θ_α becomes small. Thus the concentration of naphthalene in the carbon dioxide phase increases dramatically.

The thermodynamic equations given above are not unique to supercritical extraction and apply equally to distillation. We have seen, however, that the key to supercritical extraction is the strong pressure dependence in the partial molar volumes of the solutes in the critical solvent. This dependence causes a decrease in the vapor phase fugacity coefficient and solubility enhancement.

2.3 Process Considerations

The general criteria for the design of a large scale supercritical extraction process have been discussed by Eggers [35,36]. In any separation process these considerations are the same--output capacity, operational mode, chemical nature and physical state of the solvent and material to be extracted, and residence time, e.g., efficiency. In the case of a supercritical process the key considerations are the chemical nature and physical state. These dictate the solvent and resulting selectivity, loading capacity, necessary volume flows and solvent/solute separation characteristics.

The most important consideration is most certainly selection of the solvent. Table 1 lists various potential solvents and their critical temperatures and pressures. As was discussed in the previous section, just above the critical point, more solute is dissolved by the dense gas due to the high density and strong intermolecular forces which give rise to a strongly pressure dependent partial molar volume of the solutes. As the temperature is increased at constant pressure, the density of the gas decreases so its solvent power is lessened. If both the temperature and pressure increase, however, the solute concentration in the dense gas may increase due to solvent interaction and increased solute vapor pressure. Therefore, the effect of temperature on the solubility of a substance in a supercritical gas changes with pressure and must be known. As a rule of thumb an increase in the extraction pressure will increase the solubility and for a given extraction temperature, gases of high critical temperatures are better solvents than those of low critical temperatures.

One can infer from figure 4 and subsequent discussion that chemical differences such as aromaticity or unsaturation are of secondary importance in comparison to differences in size or polarity in determining miscibility. Supercritical fluid extraction is particularly effective for the isolation of substances of medium molecular weight and relatively low polarity. It has been found that in an SFE process, separation according to the class of compound is controlled by the selective affinity to the supercritical gas (i.e., caffeine in wet CO_2) but substances

Table 1. Summary of Potential Supercritical Fluid Extraction Solvents and Their Critical Parameters

Fluid Type	Name	T_c, K	P_c, MPa
Inorganic	Carbon Dioxide *	304.2	7.38
	Nitrogen	126.2	3.39
	Argon	150.8	4.87
	Nitrous Oxide	309.6	7.24
	Ammonia	405.6	11.28
	Sulfur Hexafluoride	318.7	3.76
	Freon 13	302.1	3.92
	Freon 23	299.1	4.84
	Water *	647.1	22.05
Hydrocarbons	Methane	190.5	4.60
	Ethane *	305.4	4.88
	Ethylene *	282.3	5.04
	Propane *	369.8	4.25
	Butane	425.2	3.80
	Isobutane	408.2	3.65
	Pentane *	469.7	3.37
	Methylcyclohexane	572.2	3.47
	Tetralin	716.4	3.40
	Benzene*	562.2	4.90
	Toluene *	591.8	4.10
Oxygenated Compounds	Methanol *	512.6	8.09
	Ethanol	513.9	6.14
	Propanol	536.8	5.17
	Isopropanol	508.3	4.76
	Butanol	563.0	4.42
	Isobutanol	547.8	4.30
	p-Cresol	704.6	5.15
	Tetrahydrofuran	540.1	5.19
	Acetone	508.1	4.70
	Ethyl Acetate	523.2	3.83
	Ethyl Ether	466.7	3.64
Nitrogen Compounds	Pyridine	620.0	5.63
	Methylamine	430.0	7.46
	Ethylamine	456.0	5.62
	Dimethylamine	437.6	5.31

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* Used in mixed solvents also.

belonging to the same chemical class are taken up into the supercritical phase in the order of their increasing boiling points (i.e., olefins extracted into supercritical ethylene) [1].

The second key process consideration is the unit operation selected to separate the solvent and solute. If a supercritical solution is isothermally decompressed, the solvent power of the gas is then very small and the dissolved material can be precipitated as a separate phase. Reprecipitation of the solute may possibly be brought about by a temperature increase, by a large temperature decrease, by a pressure decrease, or exceptionally by a pronounced pressure increase causing the separation into two liquid phases or two gaseous phases. These separation processes, however, are limited to suitable behavioral regions in the critical curve phase diagrams. In most cases, material can be recovered by decreasing the density of the supercritical phase, either by reducing the pressure at constant temperature or by raising the temperature at constant pressure. In addition, it is often possible to fractionate components upon separation.

One final important aspect of supercritical fluid extraction is that of an entrainer. An entrainer is a substance added to the supercritical solvent which has a volatility intermediate between the substances to be separated and the supercritical gas. An additional or mixed solvent may be used in the sense of an entrainer in order to increase the solubility of the substrate in the supercritical phase and enable product separation to be achieved without reducing the pressure. The use of entrainers is discussed more in Section 4.1.2. Several supercritical extraction systems are outlined with diagrams in figures 13-16.

The above mentioned points and other important characteristic features of the supercritical fluid extraction which bear on the process design are summarized below.

1. Operating temperatures are close to the solvent critical temperature. Therefore, high-boiling, heat-sensitive components may be extracted at relatively low temperatures (similar to liquid extraction). Mild conditions are particularly suitable to the isolation of thermally labile substances as low temperature separation avoids thermal decomposition.
2. The selectivity and capacity of the solvent may be changed by varying the density and temperature (operating conditions) as well as the composition (choice of solvent and/or entrainer). These three parameters vary the properties of the solvent over a wide range.
3. The recovery of solute is straightforward since relatively small changes in the conditions can result in considerable solubility changes. This behavior is a distinct advantage over liquid extraction. Solvent/solute separation usually may be accomplished by simple unit operations (isothermal decompression or isobaric heating).
4. Solute fractionation is often possible during the solvent/solute separation.
5. Solvents vary considerably in size and polarity and introduce a wide range of extraction temperatures. The solvent range is greater than in normal liquid extraction. Solvents such as CO_2 are cheap, abundant, non-toxic, non-corrosive, non-flammable, and avoid environmental problems.

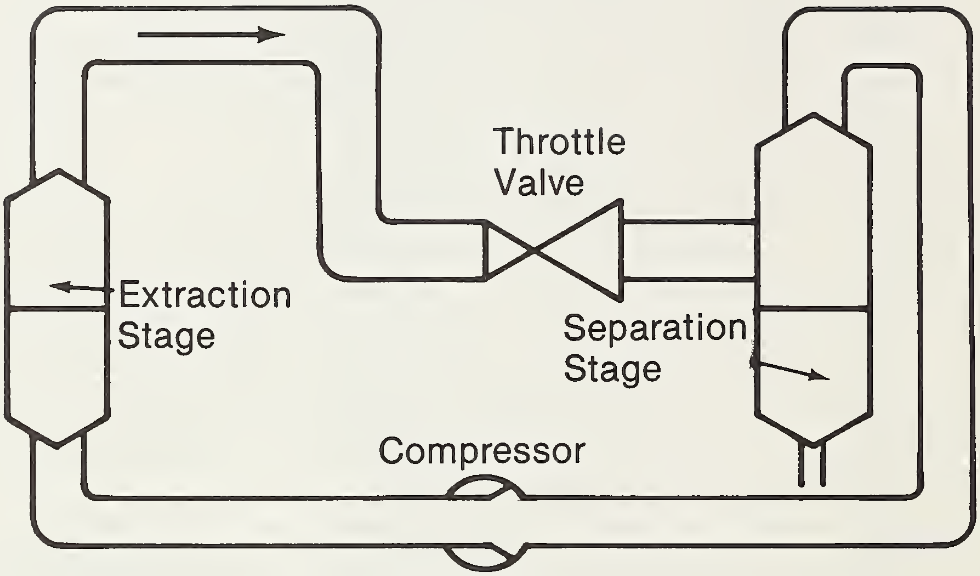

Figure 13. Process schematic for supercritical extraction utilizing pressure separation of solvent and solutes.

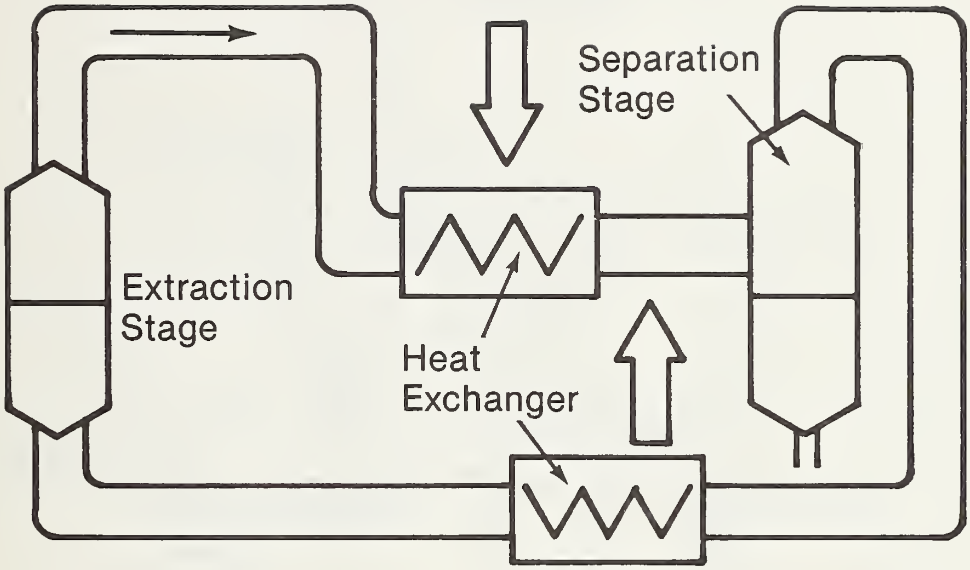

Figure 14. Process schematic for supercritical extraction utilizing temperature swing solvent/solute separation.

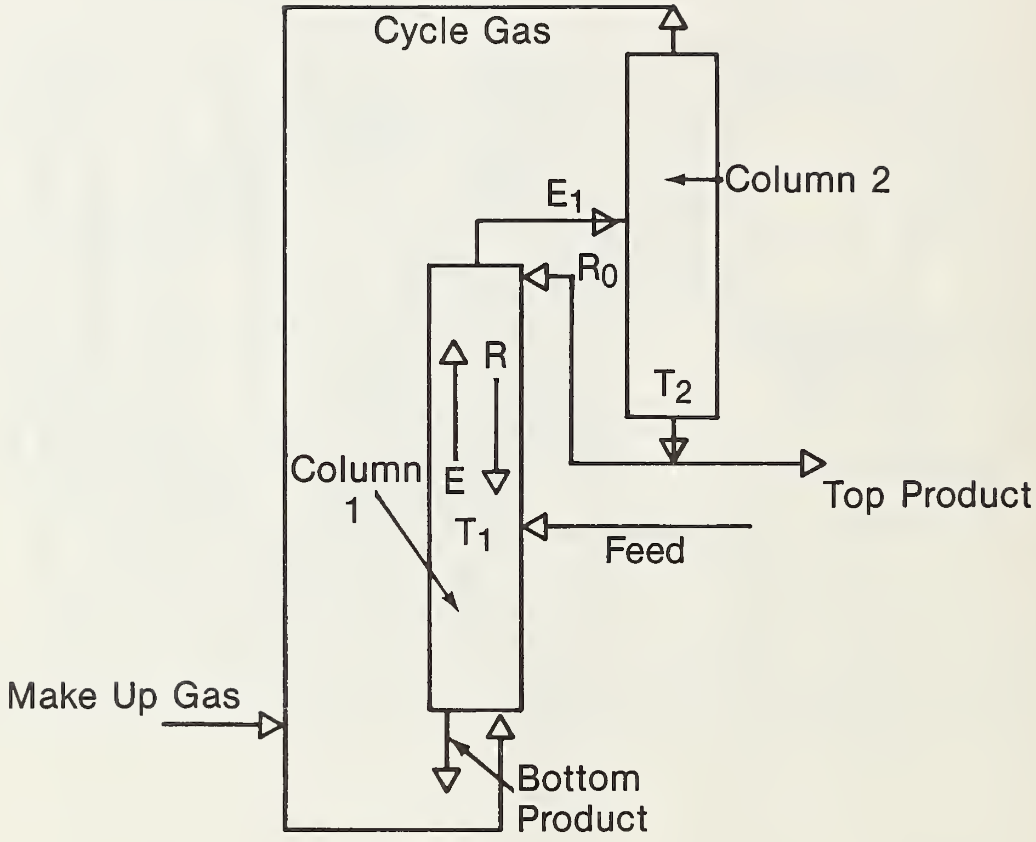

Figure 15. Process schematic illustrating use of entrainer in supercritical fluid extraction.

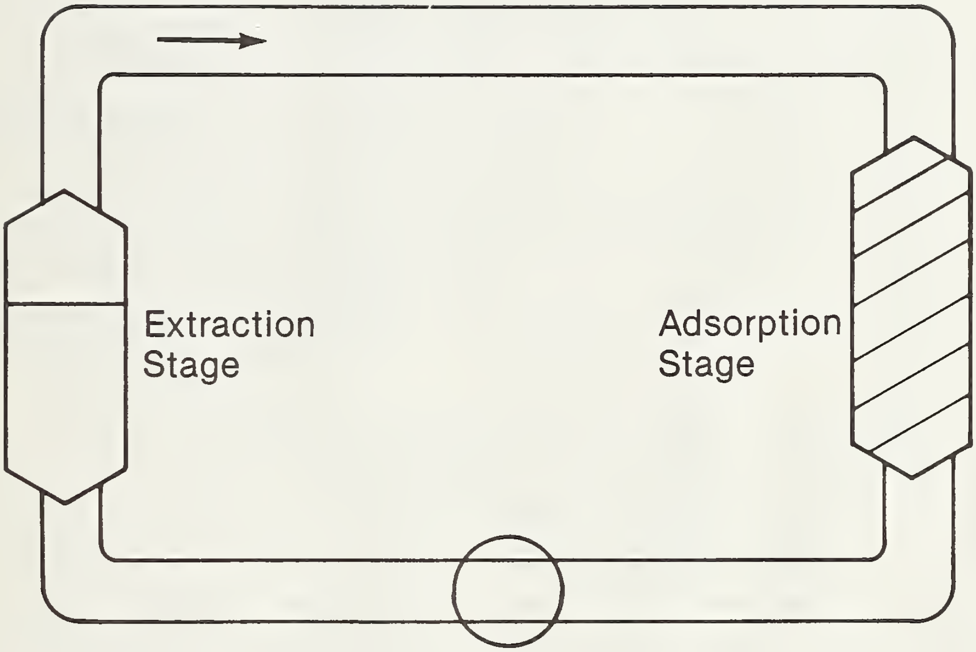

Figure 16. Process schematic illustrating supercritical fluid extraction adsorption separation.

6. The low viscosity of supercritical gases allows excellent powers of penetration into a solid structure.
7. Supercritical fluid extraction is particularly suitable for the processing of easily-oxidized materials, as pressure operation insures that no oxygen enters the system.

3. SFE Industry Process Design and Development

Within the last ten years and particularly recently there has been intense interest in supercritical fluid extraction processes. Much of this attention has been focused on the food industry (specialized food processing) and the fuel industry (fossil materials). As of yet there are few commercial processes although there have been many patents issued during the last five years. Most industrial work, however, is concentrated on process development. This section summarizes the reported work in this area.

3.1 Application of SFE in the Energy Industry

The energy crisis of the early 1970's emphasized the need to explore alternate sources of energy other than natural gas and crude oil and the need to better utilize our current fuel resources. Much of the fluid fossil fuel demand is for transportation fuels and petrochemical feedstocks, which eventually are manufactured into synthetic rubber, plastics, and other commodities. Liquid fuel products are required on such a large scale that continuous operation is essential, unlike the batchwise production of specialty chemicals. Supercritical gas phase extraction has considerable potential in energy-related areas in which solvent losses have to be minimized and processing is required of heat-labile substances which undergo decomposition during distillation. These areas include coal processing, deasphalting of heavy petroleum, tar sand and oil shale extraction and enhanced oil recovery.

3.1.1 Supercritical Extraction of Coal

Applications in the area of coal processing may be separated into direct liquefaction using supercritical gases and process stream treating, e.g., deashing. The basic problem with the direct conversion of coal to liquid or gaseous fuels and feedstocks lies in its hydrogen deficiency and the simple fact that it is a solid. Figure 17 compares the overall hydrogen content (mass percent) of coal with other hydrocarbons [37,38]. In order to increase the hydrogen (and energy) content a number of direct coal liquefaction processes have been proposed.

There are five which can be considered to be technically feasible:

1) SRC-I and SRC-II
2) Exxon Donor Solvent
3) H-Coal
4) Conoco $ZnC\ell_2$

and 5) Dow Liquefaction Process

Generally speaking the desired products from these processes are low sulfur solids and fluids. Ultimately, all direct liquefaction processes being considered can be reduced to the simplified schematic shown in figure 18 [39]. The coal is dissolved in a solvent in the presence of hydrogen at high temperature, the products are then

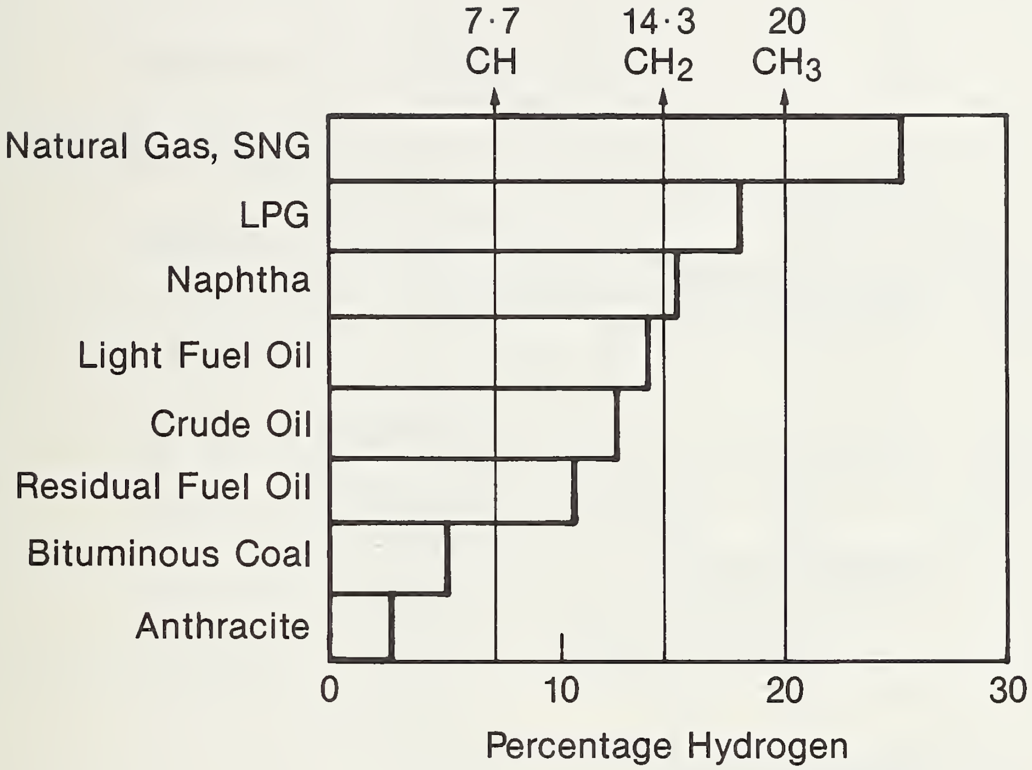

Figure 17. Comparison of hydrogen content of several fossil fuels.

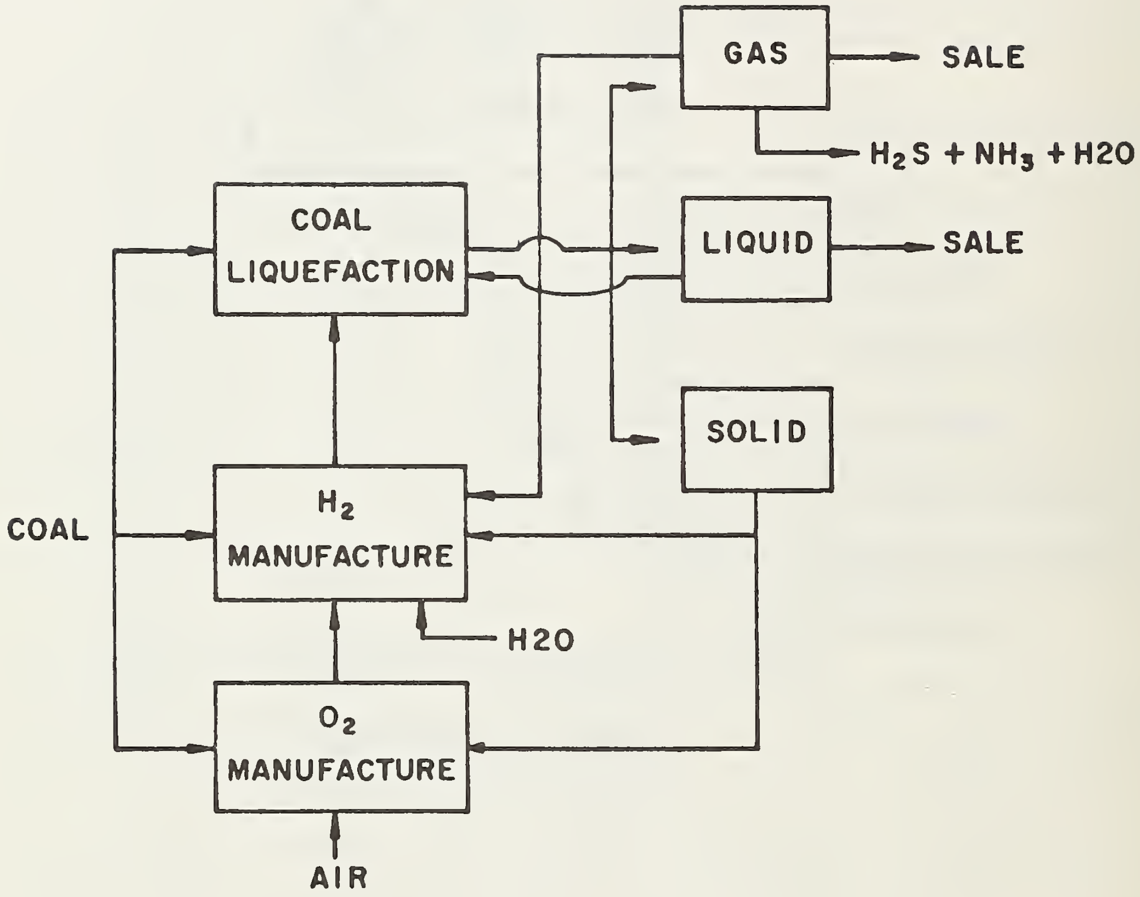

Figure 18. General schematic of direct liquefaction processes.

separated and upgraded for end use with part of the liquid product being recirculated as the liquefaction solvent. In these processes a portion of the solid product and raw coal are used for process power and hydrogen generation. Neglecting capital investment costs and operating expenses, the success of these processes hinges on the efficiency of hydrogen utilization, which is dependent upon the maximization of liquid yields and minimization of gaseous products [39]. The problem encountered, however, is that at the high operating temperatures, the heavy molecules in coal undergo pyrolysis reactions and tend to re-polymerize to form heavier and larger molecular species and gaseous products. Only a small amount of the coal "distills" as a liquid product from the decomposition reactions. Clearly, lower operating temperatures are desirable.

Supercritical fluid extraction of coal is one of the most promising processes for the production of liquid products at lower temperatures. Due to the enhanced volatility of the heavy molecules in a supercritical phase as discussed in Section 2.2.2, the liquids are effectively removed from the coal matrix as they are formed, thereby avoiding the decomposition and polymerization reactions. The solvent should be chosen so as to be critical at the decomposition temperature of the coal. This type of process has been explored by Blessing and Ross [40] of SRI International, Maddocks, et al. [41,42] but was poineered by researchers at Britain's National Coal Board Coal Research Establishment [37,38,43-50,62].

The basic SFE coal extraction process may be broken down to the following five steps [51]:

1) Penetration of the coal micropore structure by the extracting fluid.
2) Depolymerization of large molecular aggregrates and extraction of trapped molecular species and the dissolution of the resulting products in the supercritical fluid.
3) Thermal destruction of the molecular bonds between the molecular species to be extracted and the coal structure.
4) Diffusion of the extract and supercritical fluid from the coal micropore structure.

and 5) Extract recovery and supercritical fluid regeneration.

Figure 19 [49] shows a simplified integrated flow diagram for this type of process which utilizes a gasification step to produce hydrogen for use in the hydrotreating of the liquid product. It is also possible to incorporate a combustion step to provide process power. As pointed out by Thurlow [47], this type of process is an attempt to skim off a hydrogen-rich portion of coal as a liquid and to leave a carbon-rich char which can be used for other process requirements and gasification.

Typical extraction temperatures and pressures are determined by the solvent but typically range from 573-723 K with pressures to 20 MPa. Solvents which have been reported by the National Coal Board include benzene, toluene, p-cresol, p-cresol/water mixtures, dodecane and pyridine with extractions yields being between 15 and 34 percent. Materials which have been tested include most British coals (bituminous and sub-bituminous), lignites, brown coals, oil shales and tar sands.

In a recent, extensive set of laboratory tests, Kershaw and Jezko [52] have reported the results of extracting South African coals with eighteen different solvents at 723 K and 20 MPa. The results obtained are summarized in Table 2 and

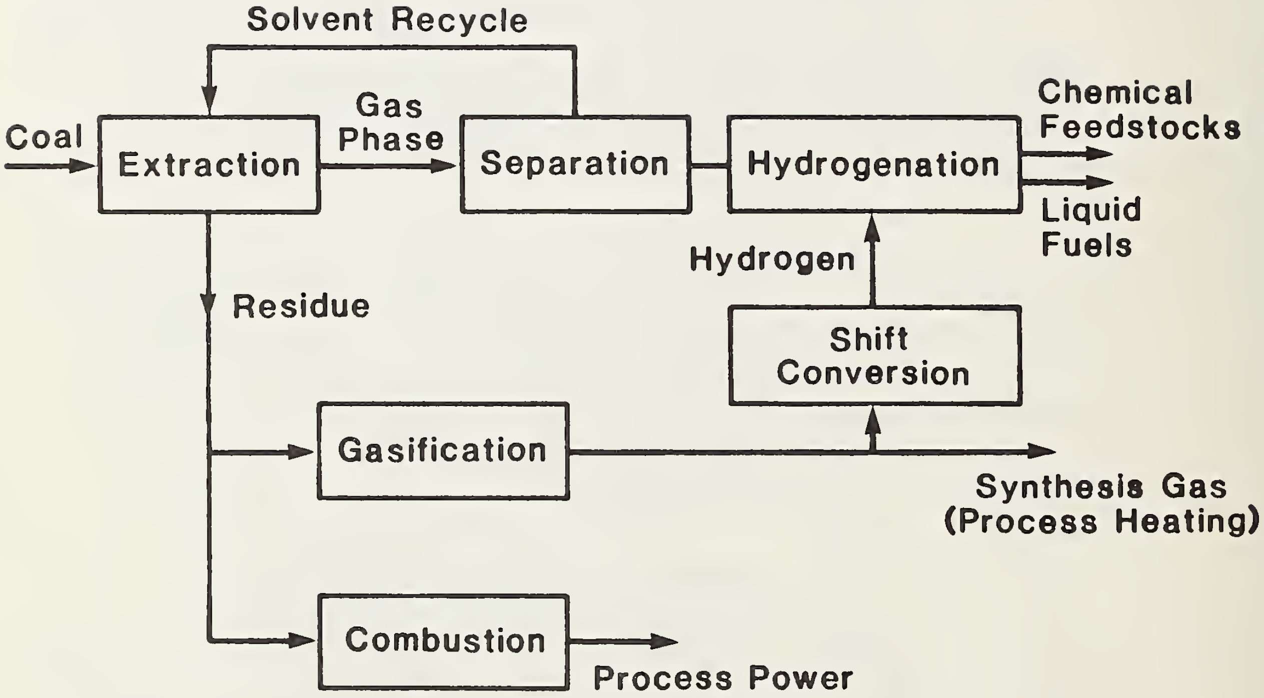

Figure 19. Schematic for supercritical gas extraction of coal [49].

plotted in figure 20. There are several interesting observations from this work, namely that the yield for non-hydrogen donor solvents can be correlated with critical temperature and that the yield for hydrogen donor solvents such as tetralin are in the 90 percent (daf basis) range. Also note that in the case of water the pressure is subcritical and the resulting yields are poor.

Table 2. Results of Extracting a South African Coal with Different Supercritical Fluids at 723 K and 20 MPa [52].

Solvent	Critical Temperature (T_c) (K)	Critical Pressure (P_c) (MPa)	Critical Density (d_c) (g/cm^3)	Density[a] (d) (g/cm^3)	Conversion (wt % daf)
Aniline	699	52.4	0.34	0.62	75.0
Benzene	562	48.3	0.302	0.38	37.9
m-Cresol	706	45.0	0.346	0.65	79.7
Cyclohexane	553	40.2	0.273	0.38	41.8
Cyclohexanol	623	37	0.293	0.48	61.8
Cyclohexanone	629	38	0.273	0.47	68.4
Decalin	664	25.8	0.254	0.51	63.2
Ethanol	516	63.0	0.276	0.19	25.5
n-Heptane	540	27.0	0.232	0.36	24.1
Isobutanol	548	42.4	0.272	0.33	45.3
Isooctane	544	25.3	0.244	0.40	21.5
Isopropanol	508	47.0	0.273	0.24	28.8
Methanol	513	79.9	0.272	0.13	18.9
Pyridine	620	55.6	0.312	0.47	50.5
Tetralin	719	34.7	0.309	0.62	95.8
Toluene	592	40.6	0.292	0.44	39.2
Water[b]	647	218.3	0.315 [a]	0.087	18.4
o-Xylene	630	35	0.284	0.48	46.7

---

[a] At experimental conditions of 450 C and 20 MPa.

[b] Water was subcritical in pressure and density.

This work also explored the effect of temperature and pressure on the extraction yields. The results are summarized in figure 21 which shows the percentage conversion with a toluene solvent as a function of temperature and pressure. This figure shows that at all temperatures there is an optimal pressure and that the effect of raising the temperature beyond 723 K is negligible.

3.1.2 Coal Structure from Supercritical Gas Extracts

A related area of process development for supercritical extraction of fossil materials has been the analytical characterization of the supercritical gas

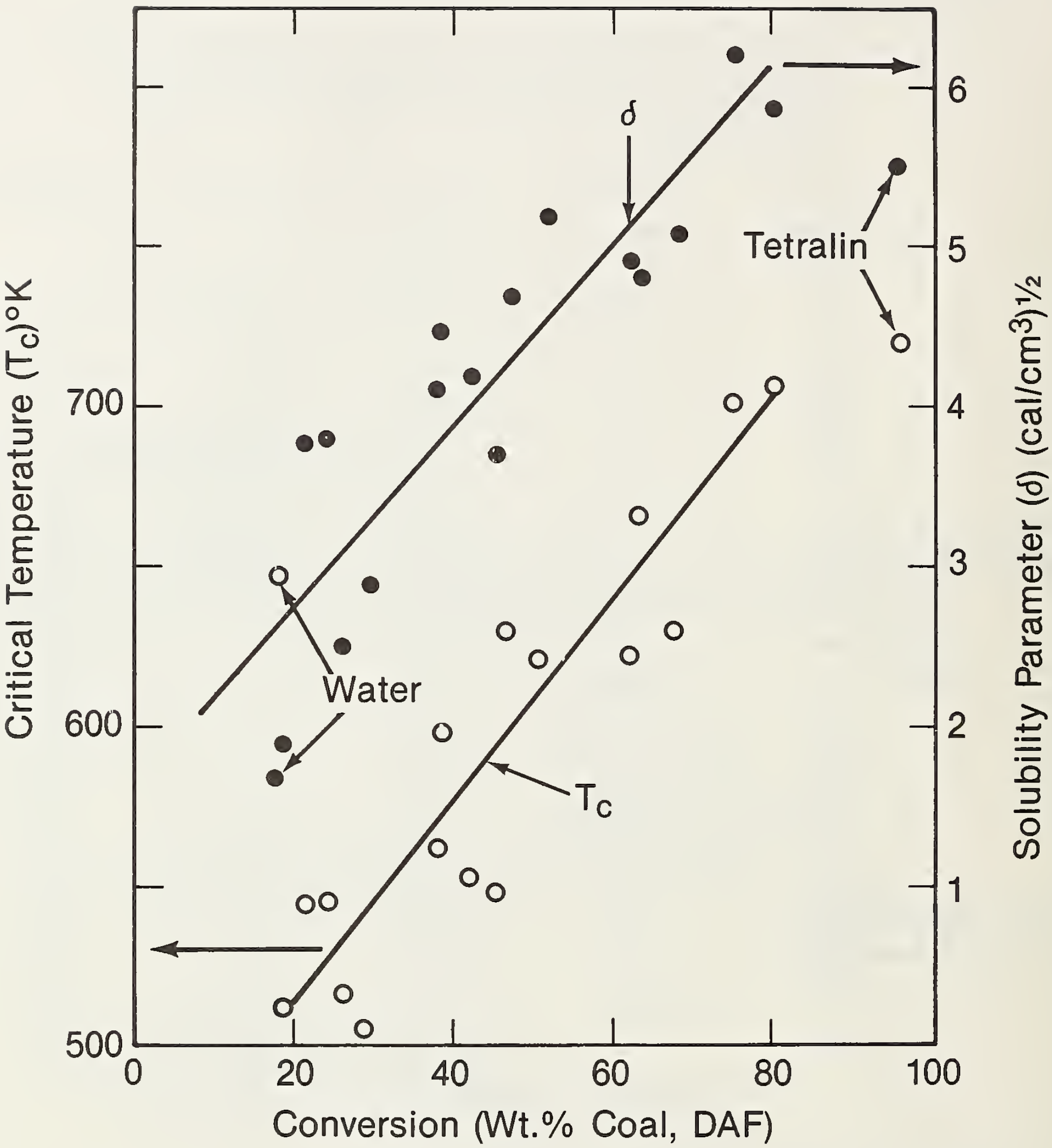

Figure 20. Plot of wt % extracted of a South African coal versus solvent critical temperature [51].

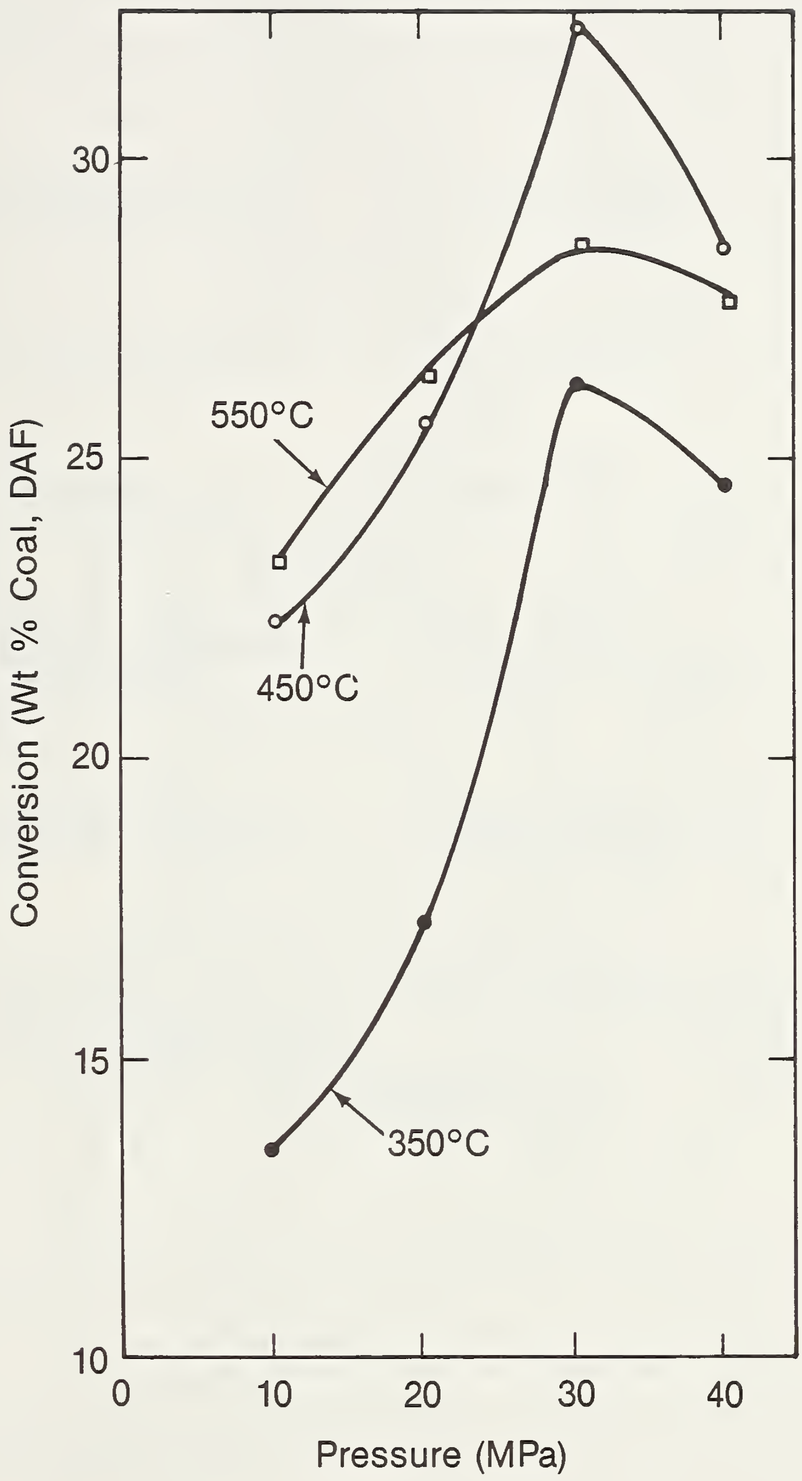

Figure 21. Coal conversion as a function of temperature and pressure using supercritical toluene [51].

extracts [53-61]. The analysis scheme used is that presented by Herod, et al. [63] which produces three primary fractions, viz., pentane solubles, asphaltenes and benzene insolubles. The analysis scheme uses ^1H NMR and ^{13}C NMR spectra. Figure 22 compares typical molecular structures for the SFE fractions with those obtained from a solvent extraction [59]. Because of the low temperatures required to obtain the supercritical extracts, the analyses of the pentane soluble fractions have been used to infer information on the primary structure of coal [53,61]. In particular, the alkane distribution of extracts at different temperatures indicates that certain size chains are liberated by bond breakage. It is conjectured that the bonds which are broken are heteroatom or alkyl bridges between the polynuclear aromatic clusters. In addition, since the reactions of alkanes in the sediment maturation process are better understood than those of the aromatic constituents, this analysis is a valuable source of geochemical information and can be used to obtain geochemical "markers" [60].

3.1.3 Critical Solvent Deashing

The only near term commercial application of SFE to coal processing appears to be Kerr-McGee's patented Critical Solvent Deashing (CSD) process. This process is designed to separate ash from liquefied coal but is basically an adaptation of the Kerr-McGee's ROSE process for extracting petroleum residua which is discussed in Section 3.1.5. The deashing step in any coal liquefaction process is essential since the dissolved coal (i.e., coal liquids) has unreacted coal and mineral matter (ash) suspended in solution. Following Knebel and Rhodes [64], the process essentially consists of two steps:

1) Ash concentrate removal where the insoluble coal and mineral matter are separated from the coal liquids which have been dissolved in a supercritical solvent.
2) A product recovery step in which the conditions are adjusted to cause the critical solvent to separate from the coal liquids, permitting the recovery of the deashed product and recycle of the extracting fluid.

The CSD process has been studied and tested at the SRC-I demonstration plant [63,65]. Figure 23 shows a simplified process flowsheet for CSD as used in the SRC-I demonstration plant [33]. Following the discussion of Brule, et al. [33], the liquids are extracted in the first stage at operating conditions which yield very high solubility. The bottoms from the first stage contains unextracted coal liquids, some solvent, and suspended coal solids which is flashed to recover the solvent and ash concentrate. The top product from the first stage is heated to separate (cf., figure 14) a heavy liquid product which is labelled the SRC product and lighter phase containing solvents and a light product (LSRC). The solvent and LSRC are then separated by reducing the pressure in the third stage (cf., figure 13). The recovered solvent streams are recompressed and recycled.

3.1.4 Extraction of Tar Sands and Oil Shale

Approximately 550 tar sand deposits are known to exist in 22 different states. Resource estimates of these reserves range between 25 and 40 billion barrels of bitumen bearing material and chances are that these estimates are low. Tar sand recovery processes can be divided into two categories--in situ and above ground,

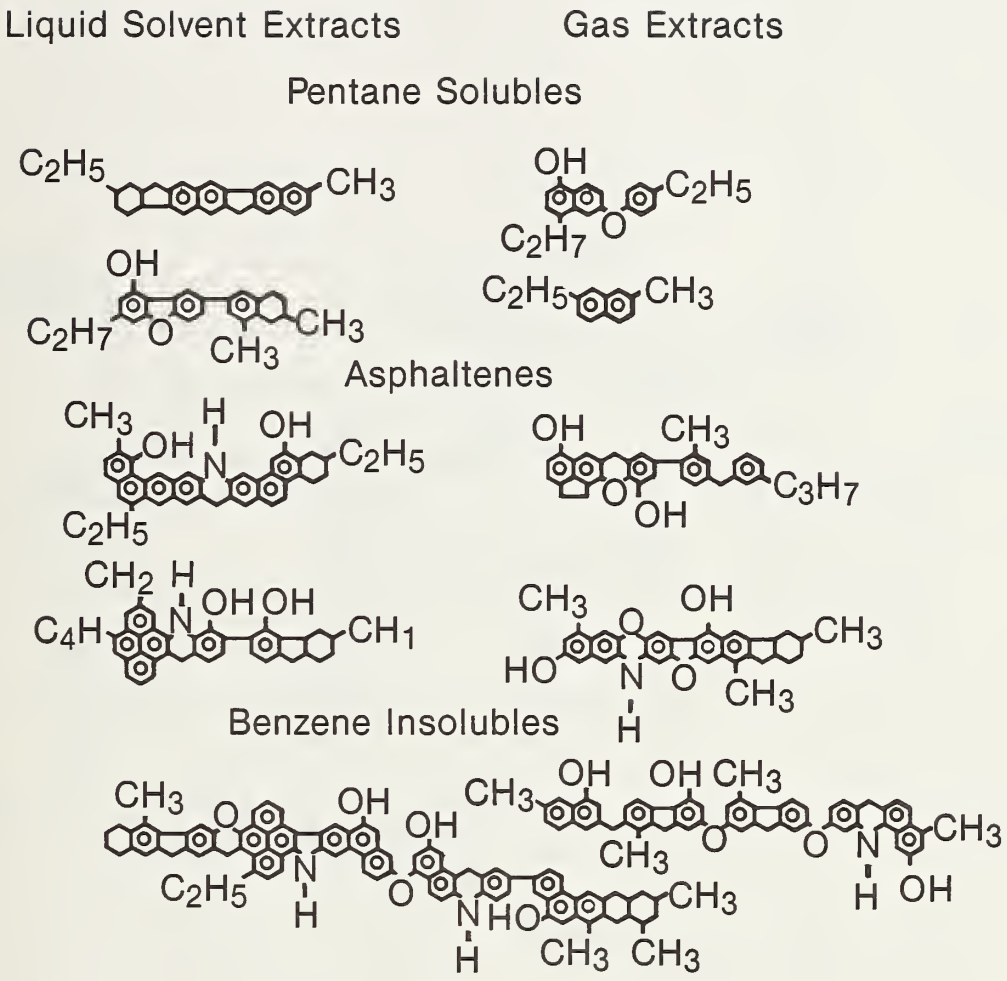

Figure 22. Typical average structures of supercritical fluid extracts of coal and liquid solvent extracts [59].

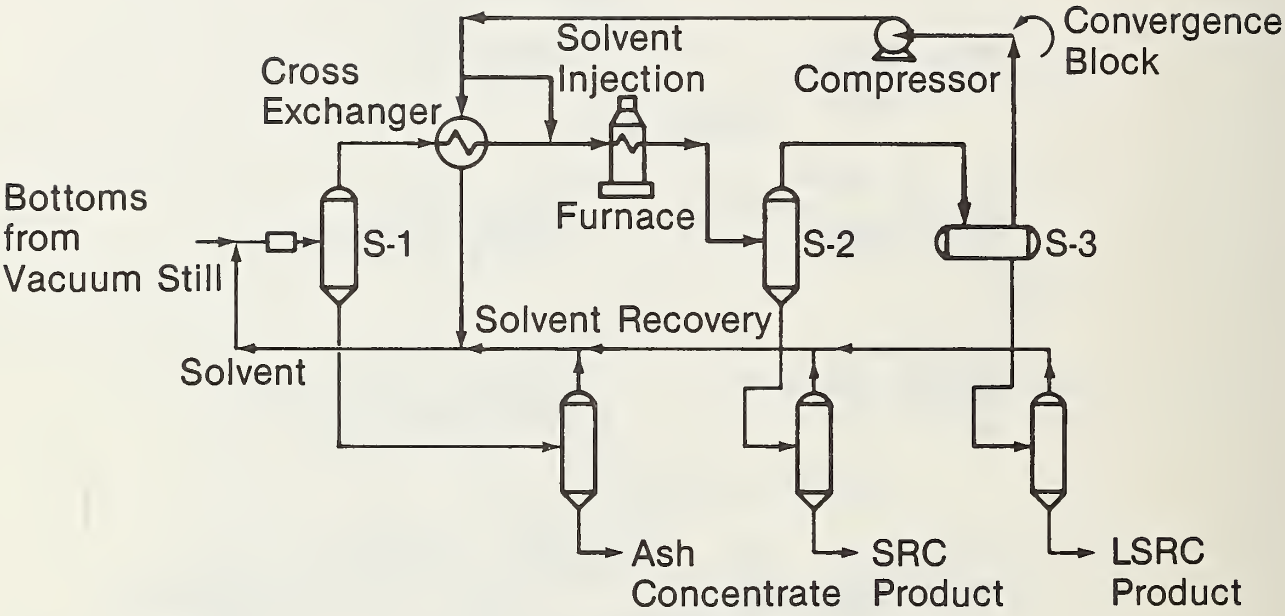

Figure 23. Process schematic flowsheet of the CSD process in the SRC-I Demonstration Plant [33].

although some processes such as leaching actually involve a combination of the two. Since 80-90 percent of the domestic tar sand is too deep to surface mine, there is great interest in the in situ recovery techniques [66,67]. Of particular interest from the point of view of SFE are the miscible displacement, solvent and steam recovery methods for the in situ processes and the area of tar sand extraction after mining.

There has been relatively little published concerning the application of SFE to tar sands. Bott [68] has, however, performed some preliminary experiments which are of interest. A block flow diagram of his batch extraction experiments is given in figure 24. The emphasis of the work was to obtain fractions of commercial interest such as a deasphalted, metal free oil fraction of tar and bitumen. It was found that it was not possible to achieve this goal by merely making an appropriate choice of solvent and extraction conditions but the process had to incorporate an adsorption step at supercritical conditions using a carbon bed. In the basic process, supercritical pentane was used as the primary solvent which, under the operating conditions, extracted the oils and resins and low molecular weight asphaltenes. After the first stage extraction the high molecular weight asphaltenes were removed from the tar sand residue with supercritical benzene. The raffinate from the first stage was then passed through the carbon bed where the low molecular weight asphaltenes were adsorbed producing a bottoms fraction containing the oils and resins. Finally the carbon bed was regenerated by elution with benzene. According to Bott, virtually all of the organic matter was removed from the sands (14.2 percent extracted as opposed to a total of 14.8 percent) with virtually all of the metals being in the asphaltene fractions.

In addition to Bott's work, Martin and Williams [69] have patented a surface treating process to extract tar sands and oil shale. In this process the material is heated with various fluids in the presence of hydrogen. The range of temperatures is 623 to 823 K with varying pressures. It was reported that the procedure extracted 75 to 95 percent of the organic material depending upon the solvents and pressures. Also, Eisenbach and Nieman have reported fractionation and extraction of tar sands using propane [83]. As in Bott's work, the extract had to be further treated to remove asphaltenes.

Methods for in situ extraction of tar sands have been proposed which essentially are adaptations of enhanced oil recovery techniques. Due to the extremely high viscosity of these materials (>10,000 cp) and low gravity (<25 API), these methods have encountered difficulties. The high viscosity means that the bitumen is essentially a plastic phase which requires very high pressures to effect displacement. Because of this, a combination of miscible drive and thermal recovery is being considered [67]. Since high temperatures and high pressures will be used, it seems logical to use a solvent with is in a supercritical state under those conditions as the miscible fluid.

3.1.5 Deasphalting of Petroleum

In the petroleum industry, high molecular weight asphaltenes containing catalytic poisons and organometallic compounds containing vanadium, nickel and iron must

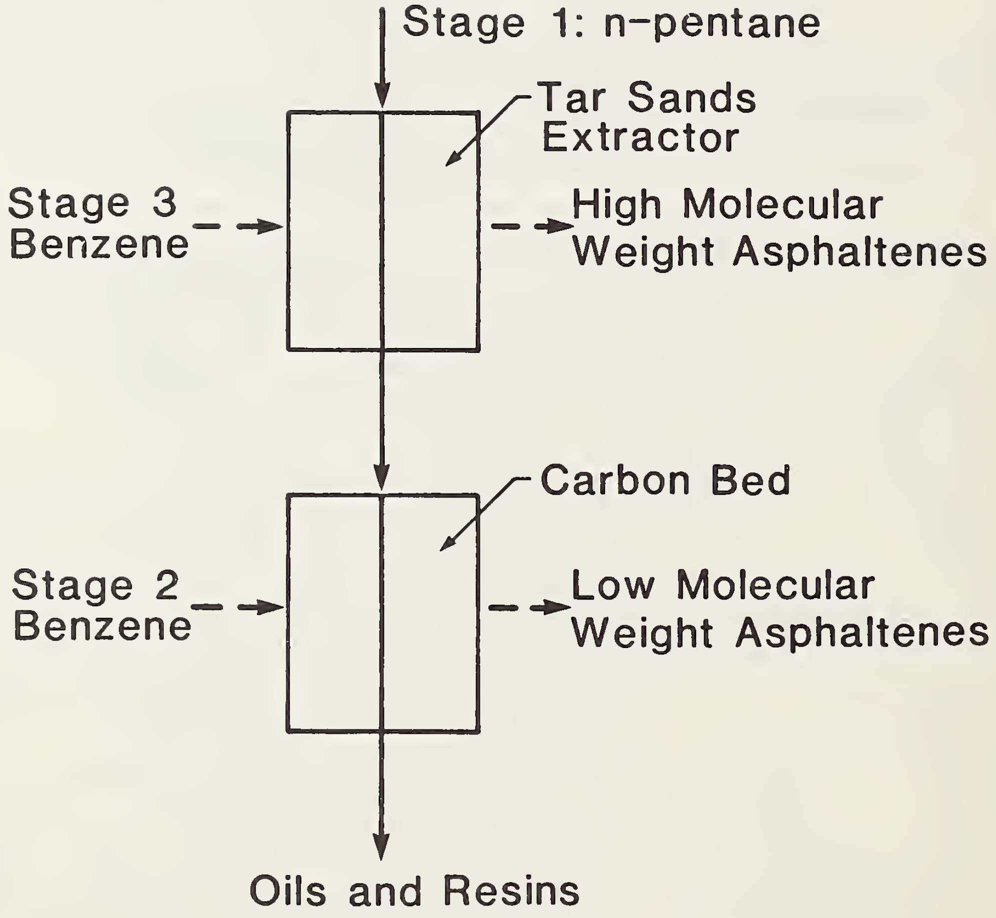

Figure 24. Schematic of laboratory scale tar sand extraction [68].

be removed from the heavy hydrocarbon fractions before catalytic hydrotreating. Subcritical liquid propane at 333 K and 3.5 MPa has been commonly used for this separation.

The process is based on the fact that very high molecular weight materials are not soluble in propane [6]. A schematic flow diagram of a typical propane deasphalter is shown in figure 25. Zhuze and coworkers [14,16] proposed a supercritical propane/propylene solvent to replace the liquid solvent. It was claimed in this work that the advantages were a lower solvent/oil ratio (typically oil in the liquid case), easier solvent recovery and smaller equipment size [6]. Figures 26 and 27 show the solubility of deasphalted oil in propane and the vanadium concentration in the propane phase as functions of temperature [6]. Although there is no clear oil solubility advantage in the supercritical fluid case, there may be some advantage in the vanadium extraction. Zosel [1] has recently examined the advantages of this process.

A similar process, the Residual Oil Supercritical Extraction (ROSE) process was used in the 1950's for deasphalting 750 barrels/day by the Kerr-McGee Refining Corporation [70]. In this case the supercritical state was used to reduce solubility rather than for extraction. The extraction took place at subcritical conditions, yielding an asphaltene fraction. The solvent phase was then heated in a heat exchanger in order to separate a resin fraction. Finally, the solvent was heated to supercritical conditions in order to release the deasphalted oil, and was subsequently recycled.

3.1.6 Enhanced Oil Recovery

A number of processes are being tested for tertiary oil recovery from petroleum reservoirs. These processes may broadly be classified as miscible or immiscible. Of interest in the area of SFE is the miscible group. Within this group of processes are several subgroups: contact miscible drives which use solvents such as propane to form a single phase solution of solvent and oil at all concentrations; enriched gas processes which involve the injection of methane together with intermediate hydrocarbons which enrich the oil to the extent that it becomes one phase with the injected gas; and CO_2 miscible flooding.

Carbon dioxide miscible flooding involves the injection of essentially pure CO_2 into reservoirs at supercritical conditions. Even through CO_2 is only moderately miscible with reservoir fluids, it extracts via the SFE mechanism hydrocarbons of the gas-oil range (C_7-C_{30}) to form a miscible fluid [71]. Details of the displacement process have been recently summarized by Doscher and El-Arabi [74]. This fluid mixture, which has a lower viscosity than the reservoir fluid, flows more easily through the porous media in the reservoir. There are also some other benefits associated with the CO_2 injection such as the swelling of the reservoir fluid which causes some migration, but the overall phase equilibria are of prime importance.

The use of carbon dioxide to increase oil recovery is not a new idea. As pointed out by Stalkup [72], Whorton and Brownscombe patented an oil recovery process using CO_2 in 1952 [73]. It should also be pointed out that CO_2 also has

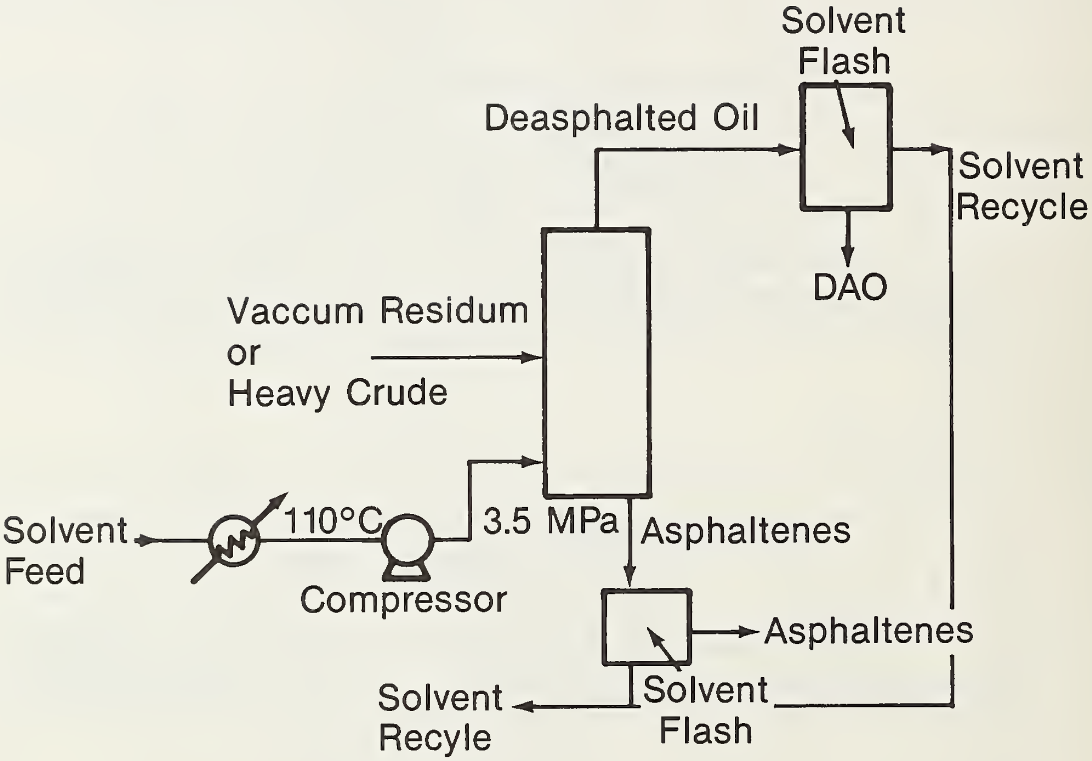

Figure 25. Schematic flow diagram of a propane deasphalter [6].

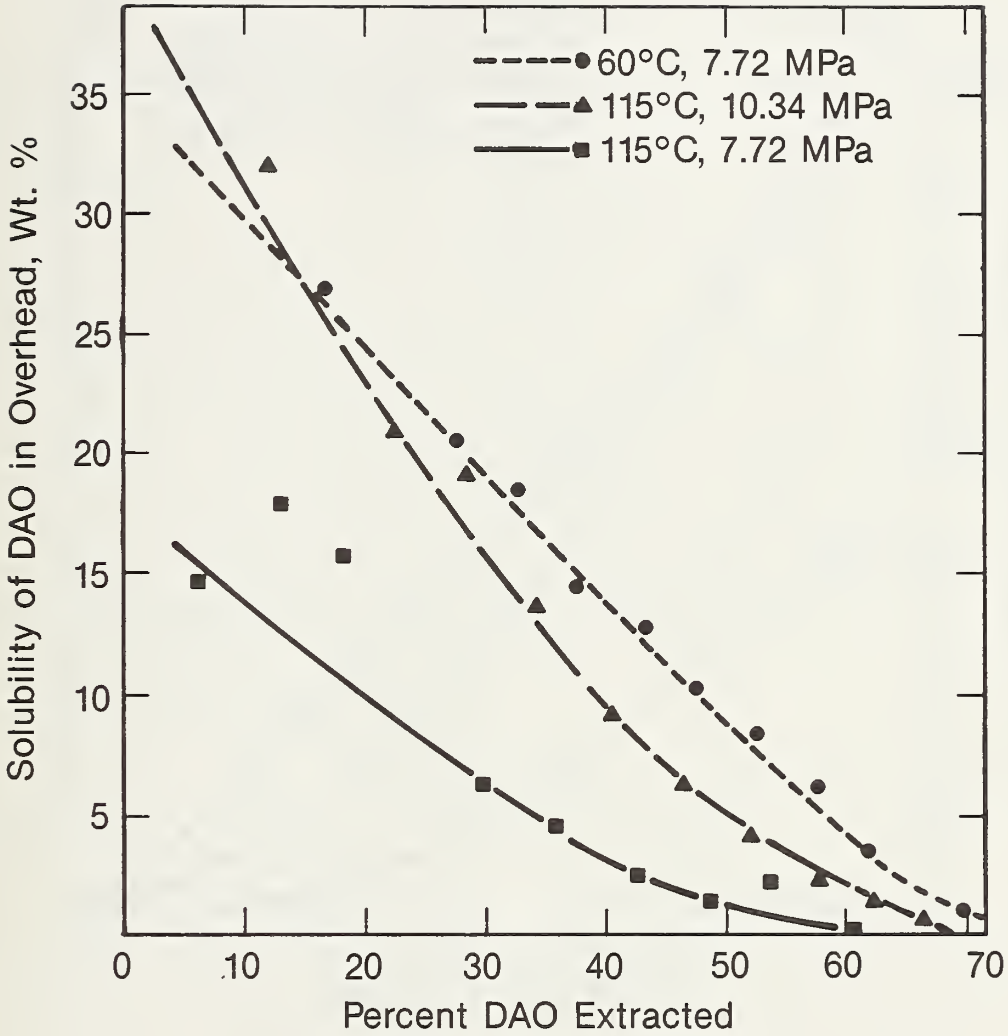

Figure 26. Solubility of deasphalted oil in propane at various temperatures [6].

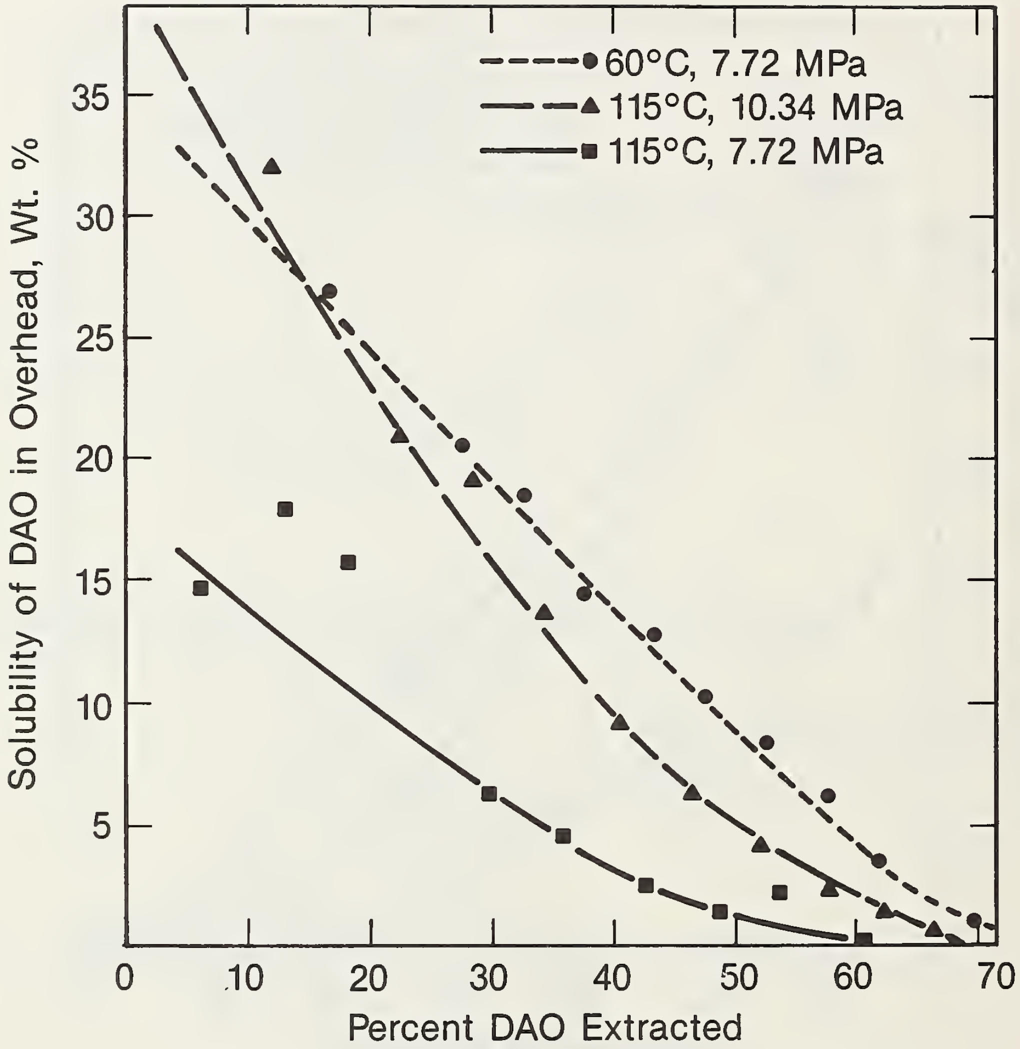

Figure 27. Solubility of vanadium in propane at various temperatures [6].

been considered for use in immiscible displacement, well stimulation and carbonated water flooding, all of which are enhanced recovery techniques. From the point of view of SFE, however, the miscible displacement process is the most interesting. Processes of this type have been successfully field tested [74-78] and large scale production is planned. Carbon dioxide pipelines from producing wells to injection sites are currently under construction to provide the necessary (large) quantities of CO_2 [79-82].

In conjunction with this effort several negative aspects of SFE have been observed. The first of these is that it is not uncommon to have multiple liquid phases and an "in situ deasphalting" situation under CO_2 miscible conditions. To this end, figure 28 [72] shows a p-x phase diagram for a crude oil and various amounts of CO_2. Note the three and four phase regions and the region of precipitation. A second problem is associated with carbon dioxide supply. The supply source locations are such that the fluid must be produced, dehydrated, perhaps recompressed and transported via pipelines to the injection site. Economics most likely will dictate that the produced CO_2/oil mixtures should be separated, perhaps in conjunction with a distillation of the light phase and the CO_2 reinjected. The possibility of utilizing the principles of SFE in the separation of the CO_2 and oil is obviously appealing since field compression costs are large. It is interesting to note that the dehydration step associated with the CO_2 supply illustrates an unfavorable aspect of SFE. Carbon dioxide is usually produced at supercritical conditions and is saturated with water. Prior to transportation in the pipeline the water must be removed to avoid the possibility of solid hydrate formation. A common method of achieving this goal is to treat the fluid with one of the ethylene glycols which have a strong affinity for water. If the CO_2 is treated in a supercritical state, it tends to extract large quantities of the glycol, thereby forcing an extra glycol recovery step which strongly affects the economics of the process.

3.1.7 Miscellaneous Energy Applications

Other than the applications discussed previously, several possible applications have been proposed which involve fractionation of fossil materials. A good example of this procedure deals with the refining of used oil [84,85]. The normal process involved acid-clay contacting which leaves large amounts of acidic resin residues. In the supercritical process the used oil is first distilled at atmospheric pressure to remove water and gas oil. The bottoms (dry-oil) is then extracted with supercritical ethane at 200 MPa and 363 K. The supercritical extract is then fractionated by stepwise pressure reduction to obtain a base oil, spindle oil and gas oil II fractions. The overall efficiency of extraction was reported to be approximately 90 percent [85].

3.2 Application of SFE in the Chemical Industry

Extraction with organic solvents is a well-established method of selective separation of specific constituents in the chemical industry. This is especially true in the food, semi-luxury chemical and drug industry because the extract provides better utilization, shelf-life, uniformity, and sterility (i.e., hops, spices) than the starting material. The main advantage offered by the use of supercritical gases is that a selective extraction can be effected of substances of

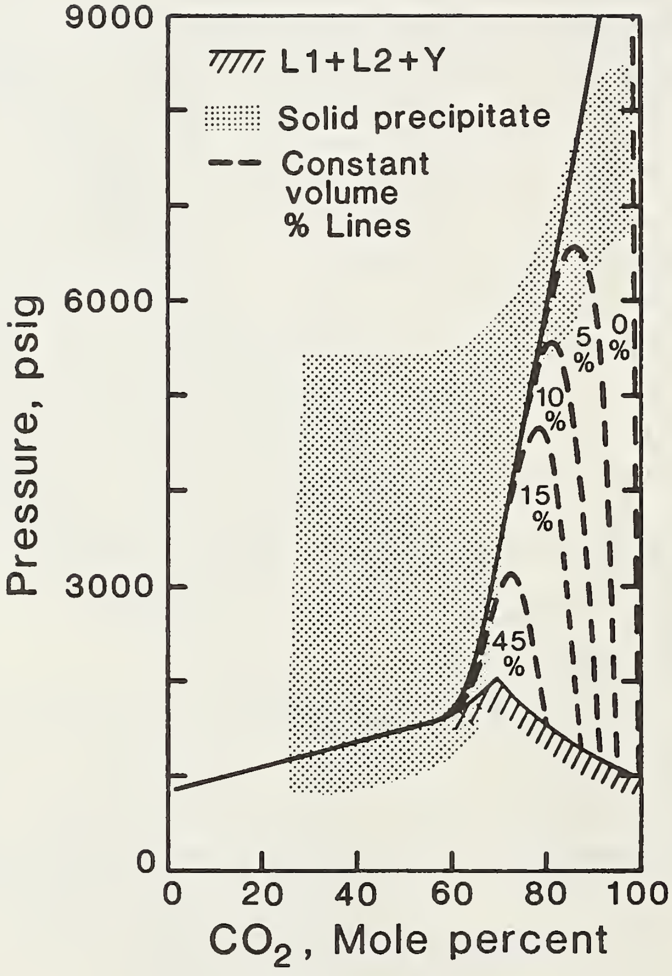

Figure 28. Typical phase diagram of carbon dioxide and a heavy reservoir fluid [72].

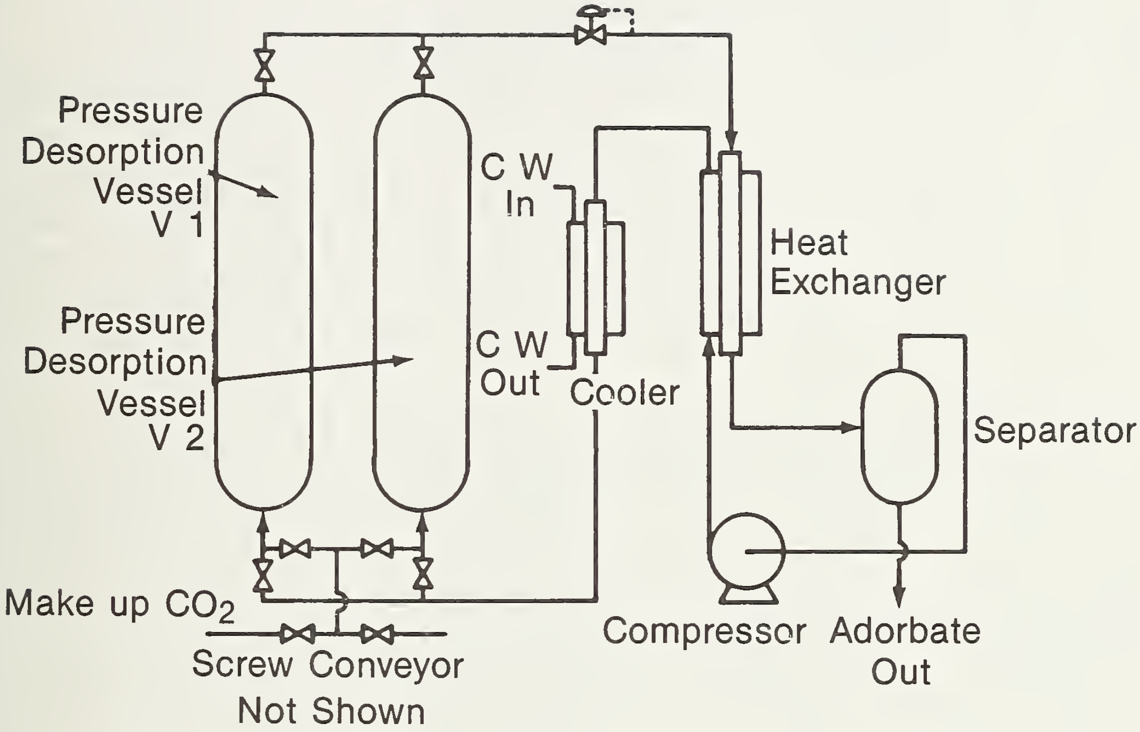

Figure 29. Schematic of a SFE Adsorbent Regeneration System [128].

medium to low volatility in which a distillation separation technique cannot be applied. Many examples of this type of application arise in the food industry. Here, carbon dioxide serves as an ideal extraction agent for it is readily available in large quantities and high purity, has a critical temperature a little above ambient, and does not react in any way with the food constituents. In addition, it is non-flammable, non-toxic, and non-corrosive. As a matter of fact, carbon dioxide is often formed in many common manufacturing processes (i.e., beer, wine, bread). For these reasons, SFE of natural products have so far been processed predominantly with CO_2.

Not all extraction processes have the same purpose. In some, the aim is to obtain an extract and the remaining vegetable substance may be of either no value (e.g., spices) or subjected to further treatment (e.g., hops). In another process, it is the carrier substance that is wanted (e.g., tobacco) while the extracts are of secondary importance.

In addition to applications in the food and drug industry, SFE has been proposed for the separation of low vapor pressure oils, polymers and extraction of organics from aqueous solutions. This latter application may be of special importance in bioengineering processes. Other chemical processing applications include catalyst and activated charcoal regeneration and applications in chemical kinetics.

3.2.1 Coffee Decaffeination

The most widely cited example of industrial SFE is the decaffeination of coffee using carbon dioxide. This is the case because thus far it is the only truly commercial application of SFE. The original work of Zosel began in Germany in the early 1970's. The first U.S. patent for coffee decaffeination using supercritical CO_2 was obtained in 1974 by General Foods, Incorporated [86]. In 1981 alone, six U.S. patents were obtained for various supercritical caffeine extraction procedures [87-92]. Four subsequent patents were issued in 1982 [229-232].

The decaffeination process has shown considerable improvement since its introduction, and research is continuing. Following the summary of Paulaitis [93], the first U.S. patent outlined a three-step process for coffee decaffeination in which dry supercritical CO_2 at 29 MPa and 323 K is used to extract the flavor and aroma oils from whole roasted coffee beans in the first stage. The caffeine is then extracted with wet CO_2 and, in the final step, the flavor and aroma oils are added back to the coffee beans. A subsequent patent [91] served to improve the three-step process when it was shown that wet supercritical CO_2 selectively extracts caffeine from raw coffee beans. The caffeine is then recovered from the solvent using (1) pressure reduction techniques, (2) water scrubbing, or (3) adsorption on to activated carbon. In addition to these various processes, various solvent mixtures have been proposed. One U.S. patent [90] describes the use of an entrainer or co-solvent (8 wt. % acetone) with the supercritical CO_2. Liquefied petroleum gas (i.e., propane, butane) has also been utilized to extract caffeine from green coffee beans [92].

3.2.2 Hops Extraction

Hops have been used to make beer for over 2,000 years, but the use of hop extracts in the brewing industry is a more recent development. Conventional hop extraction generally employs dichloromethane to extract the desired soft hop resins containing a mixture of humulones and lupulones. The dichloromethane must then be successively evaporated off to leave a pasty, dark-green residue which contains less than 2.2 percent solvent. One primary motivation for using a supercritical CO_2 extraction is the increasing government scrutiny of traditional industrial solvents, particularly chlorinated hydrocarbons. Several patents describing the extraction of air-dried hops with supercritical CO_2 have been issued since 1972, with the first U.S. patent being received in 1978 [94]. In most cases, the extract is obtained by a single-stage pressure reduction and the analysis shows the extent of extraction of the humulone mixture is almost 99 percent, above the 95 percent minimum. Extract separation by releasing the pressure in several stages is currently being investigated, which would provide a choice of extracts of different compositions.

Recently, two large hop processing plants based using carbon dioxide have been constructed. The Hopfenextraktion GmbH facility uses supercritical CO_2 [95] and the BRF facility uses liquid CO_2 [96]. As pointed out by Vollbrecht [95] the supercritical CO_2 process has the following advantages over conventional solvent extraction.

(1) The extracts are free of organic solvents
(2) Pesticides used in agriculture are not extracted
(3) Oxidation is prevented
(4) Longer shelf life is obtained
and (5) The important ingredients (α-acid) are not polymerized.

3.2.3 Extraction of Nicotine from Tobacco

During the last two decades it has been realized that the nicotine and tar constitutents in tobacco present serious health problems. As described by Hubert and Vitzthum [97] early liquid solvent extraction attempts to remove these compounds had undesirable effects on the extracted tobacco leaves [98,99]. A process utilizing supercritical CO_2 has been shown to successfully reduce the nicotine content to the desired levels with a minimum loss of aroma [100,101]. In this supercritical fluid extraction process, the extraction residue is wanted while the extracted nicotine is of secondary importance. The presence of water (approximately 25 percent) is essential to the extraction of nicotine. In the single-stage process, supercritical CO_2 is passed through the wet material and the dissolved nicotine is separated by either reducing the pressure, changing temperature, or adsorption onto sorbents. Often, the single stage extraction has a detrimental effect on the aroma and a multistage process is more suitable. In the first stage, the aroma is removed from the fresh material and is used to impregnate a previously denicotinized batch. The de-aromatized tobacco is moistened for the second stage, and the nicotine is removed in an isobaric and isothermal recycling operation. The third stage involves a homogeneous distribution of the transferred aroma in the bulk by repeated dissolution and reprecipitation. It has been found that when the treated tobacco is discharged from the extraction unit, a certain expansion of its fibers is observed as a result of the removal of gas residue from the vegetable tissue. Researchers are investigating the effects of moisture content, temperature, and several other parameters on controlling the expansion limits.

3.2.4 Flavors, Aromas and Drugs

There has been a long term effort to isolate and concentrate natural flavors and aromas even though many of the major natural constituents have been synthesized. In spite of this chemical ability, the need for natural extracts has not ceased and there has been a substantial effort to improve extraction technology in this area. Classical liquid extraction has the disadvantages of difficult solvent removal from the extract.

The primary supercritical fluid which has been used for these extractions is carbon dioxide because it is critical at ambient temperatures, available in high purity and non-toxic. Thus far extractions using CO_2 have been reported for black pepper (piperine), nutmeg (essential oil), chilies (capsaicine) [97]; lilac (various fractions); lemon oil (monoterpenes and limonene) and almonds (essential oil) [102].

Stahl and coworkers [103-109] have reported extractions of various natural products using various solvents such as carbon dioxide and nitrous oxide, coupled with thin-layer chromatography. Included in their work are extractions of dyes [103], chamomile [104,105], alkaloids [106], valepotriates [107], sunflowers, opium, glycerides [108] and chrysanthemum roots to obtain pyrethrins and pyrethroids [109]. More recently Caragay has reviewed the extraction of flavors and fragrances [110].

3.2.5 Extraction of Other Natural Materials

Supercritical extraction has been recently applied to two other major groups of naturally occuring materials: wood and vegetable oils. In the case of wood, most early work dealt with the pyrolysis of wood and lignin [111]. More recently, SFE has been applied successfully to extract high boiling materials in much the same way as it has to coal, viz., at temperatures below those required in pyrolysis. Two patents for this type of process have been issued [112,121] and several detailed articles have appeared documenting the procedure and products [111,113-116].

Several patents have been issued since 1972 regarding the deodorization of soybean, palm, and peanut oils with the simultaneous removal of free fatty acids using supercritical CO_2 [19-21,117]. The U.S. Department of Agriculture (Northern Regional Research Laboratories) has reported [118] the use of supercritical CO_2 for extracting oils from soybeans. The results indicate that the extraction yields are comparable with the conventional hexane-extracted oil, and a subsequent distillation/deodorization treatment is not required if supercritical CO_2 is employed rather than hexane. Similar oil extractions from corn and bones, simultaneous hydrogenation and deodorization of fats and/or oils, and the extraction of fats and oils from plant seeds with supercritical gas mixtures are included in this work. In 1975, a U.S. patent was awarded which involved a supercritical CO_2 extraction of cocoa butter and aroma components from cocoa beans [119]. In addition, a process for extracting fats and oils from potato chips and other food snacks using supercritical CO_2 has been developed by Critical Fluid Systems, Incorporated [120].

3.2.6 Extraction of Organics from Aqueous Solution*

The production of chemicals via bio-technology routes is currently the subject of concentrated research at many laboratories. Various commodity chemicals such as ethanol and acetic acid can be produced by fermentation, but at relatively low concentrations in the fermentation broth. Separation of these organics from dilute aqueous solution would require large amounts of energy per unit of product if conventional separation techniques (e.g., distillation) are employed [120]. Extraction with SFE solvents offers a potential for extracting these organic chemicals more energy-efficiently, especially if the distribution coefficients for the organic compounds in the SFE solvent relative to water are favorable.

Separation of water-organic mixtures with supercritical ethylene has been investigated by Elgin and Weinstock [122]. The work shows that compressed ethylene at 288 K can be used to extract organic constituents from water, and the authors propose using SFE solvent extraction with ethylene as a method for dehydrating organic solvents. As an example of such a process they consider the ternary system methyl ethyl ketone (MEK)-water-compressed ethylene. The binary mixture MEK-water exhibits partial miscibility at 288 K and the mutual solubility of these two components can be significantly reduced by adding compressed ethylene to the system. Since MEK and ethylene are completely miscible while water and ethylene are almost completely immiscible, water is "salted out" of MEK-ethylene mixtures. A similar investigation of water-organic-CO_2 mixtures has also been reported [123], which shows a highly unfavorable distribution coefficient for acetic acid in supercritical CO_2 relative to water. Thus extraction of acetic acid from dilute aqueous solutions does not appear economically viable on an industrial scale from the reported data.

Extraction of ethanol from water using both supercritical CO_2 and supercritical ethylene has recently been reported [124,125,2]. Experimental data at various temperatures and pressures were used to compare solvent extraction with atmospheric distillation [124]. The results show that extraction with supercritical CO_2 is more energy efficient than extraction with supercritical ethylene because of the higher ethanol solubilities in supercritical CO_2. Although SFE solvent extraction with CO_2 cannot break the ethanol-water azeotrope, concentration of ethanol-water mixtures using SCF extraction appears competitive with distillation. An efficient process for concentrating dilute aqueous solutions of ethanol in water would be an attractive first step in recovering products from fermentation broths [126]. Measured distribution coefficients at infinite dilution of the organic for various alcohols and esters in liquid CO_2 relative to water are shown in Table 3 [127]. The distribution coefficient for ethanol would fall between those for methanol and n-propanol. These data suggest that SFE solvent extraction with CO_2 would be more favorable for higher molecular weight alcohols or mixtures of alcohols (including methanol and ethanol) compared to supercritical CO_2 extraction of ethanol.

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* This section was written by M. E. Paulaitis [93].

Table 3. Distribution Coefficients at Infinite Dilution for Alcohols and Esters in Liquid CO_2 Relative to Water at 16°C [127].

Compounds	Distribution Coefficient
Methanol	0.40
n-Propanol	0.66
n-Butanol	1.8
n-Pentanol	4.5
n-Hexanol	15.0
n-Heptanol	31.0
i-Propanol	0.35
i-Butanol	1.7
tert-Butanol	0.82
sec-Butanol	1.23
i-Pentanol	5.0
Ethyl Acetate	42.0
Isopropyl Acetate	80.0
Methyl Butyrate	120.0
Butyl Acetate	350.0
Propyl Propionate	370.0
Isoamyl Acetate	850.0

3.2.7 Regeneration of Activated Carbon

A large number of chemicals are manufactured by processes which release contaminated waste waters. These effluent streams must be either treated to eliminate the hazardous materials or disposed of without treatment by methods such as deep well disposal. In the future, untreated disposal may not be permissible due to increased environmental scrutiny by the EPA. Thus, an effective treatment to eliminate hazardous effluents is needed. One process which has been successful in a number of industrial plants is activated carbon adsorption.

Granular activated carbon adsorption is currently in limited use, however, in the chemical industries. The primary reason for its limitation is cost and a large amount of this cost can be attributed to the carbon regeneration step. Currently, the two most common carbon regeneration methods are thermal and liquid solvent extraction. The existing thermal regeneration process using a multiple-hearth furnace is expensive due to high costs of capital, energy, and adsorbent attrition. A liquid solvent extractive regeneration is costly because of solvent removal from regenerated carbon and purification of the loaded solvent for recycle. An appealing alternative process is an extractive regeneration process employing supercritical fluid solvents.

Research and development at Arthur D. Little, Inc. using organics adsorbed on activated carbon confirm that a relatively rapid and effective regeneration can be obtained with a supercritical CO_2 solvent [128]. In addition, an engineering and cost analysis indicates that both capital and operating costs could be significantly less than those for thermal regeneration processes. This type of process was patented in 1979 by Modell [129]. Recently research has been devoted to (1) pesticide screening based on suitability for carbon adsorption and supercritical CO_2 regeneration, (2) model system studies, (3) process development, and (4) process economics. Current development has substantiated the potential of supercritical fluid regeneration of activated carbon for the adsorption of pesticides [128].

One possible design for the commercial application of such a regenerative process is shown in figure 29 [128]. The supercritical CO_2 proceeds through one of the desorption vessels where it picks up adsorbates and is then subsequently depressurized. After expansion, the fluid temperature is altered in a heat exchanger in order to precipitate the solute. The solute is then recovered from the separator and the regenerant is recompressed and reheated in order to obtain the conditions required for desorption. If three high-pressure desorber vessels are used, the regenerant recycle loop can be operated continuously. At any one moment, two vessels are off-stream for loading and unloading while one vessel is on-stream undergoing desorption.

Further research on supercritical fluid regeneration of activated carbon is required before commercial operation can be realized. The process should be tested on a large scale, and a mobile pilot plant could be used for treatability studies at actual waste water producing sites. Current studies should be expanded in order to broaden the range of adsorbates and plant samples. Finally, theoretical models should be developed which verify and predict physical and chemical processes which occur in adsorption and desorption.

4. SFE Technical Difficulties and Commercialization Prospects

Most of the applications of SFE summarized in the previous section are bench scale experiments which have process promise. They might be further studied and scaled up when the necessary engineering technology has developed further. Others, such as coffee decaffeination or hops extraction form the basis for commercial scale processes. In these cases the products are so valuable that process inefficiencies, capital and operating costs are relatively insignficant. Before other applications see commercialization, however, these and other problems must be solved. These problems have been discussed in an excellent review by King and Bott [130] which is summarized in this section.

4.1 Technical Design Difficulties

As discussed in Section 2.3, the basic information required for the design of a large-scale supercritical extraction unit are similar to those required for the design of other forms of separation equipment. This information includes a knowledge of the phase equilibrium and enthalpy data for the system as well as a knowledge of the extent to which equilibrium is actually approached at each point in the system. In addition, however, supercritical fluid extraction also requires knowledge to deal with energy loss in the decompression step, problems with high pressure materials problems and pumps, process control, and safety. Each of these areas will be briefly discussed.

4.1.1 Phase Equilibrium and Transport Properties

There currently exists a lack of physical property data and fundamentally based thermodynamic models which accurately predict supercritical extraction behavior. This has hampered SFE development because process design and economic evaluation are extremely difficult, if not impossible, without these necessary background tools. These technical problems make capital investment a high risk. These risks could be substantially relieved through the initiation of extensive fluid property research (see Section 5).

The systems of interest in gas extraction are usually composed of a comparatively high molecular weight solute mixture contacted with a comparatively low molecular weight gas. The prediction of equilibrium data for this type of system tends to be quite difficult. This is especially true if the solute molecules can form hydrogen bonds with each other. The problem becomes even more complex when a natural product is considered for natural products of different origin may contain constituents which strongly affect their phase behavior. Theoretical models for predicting phase equilibrium behavior in the critical region are, for the most part, only semiquantitative due to a limited understanding of (1) compressible fluid behavior near the critical point and (2) multicomponent mixtures containing dissimilar, highly asymmetric constituents.

In general, gas extraction equilibrium data has been estimated through the use of solubility parameters and the use of equations of state. The solubility parameter approach as presently developed, however, only provides a qualitative indication of the types of substances which will dissolve in a given gas under certain conditions and more work is clearly required. Many times, different equations of state are used to represent the gas and liquid phases so the convergence of the phase behavior at the critical point is difficult to represent and erroneous predictions occur frequently in the critical region. Unfortunately, the best supercritical fluid extraction operating conditions are often in this region.

The situation for transport properties is even worse. Both the pure fluid thermal conductivity and viscosity show anomalous behavior in the critical region which is difficult to model. Since the mass transfer rates must be known to assign an efficiency to the unit and determine the size, residence time, etc., this poses a serious design problem.

4.1.2 Energy Loss in Decompression

Supercritical fluid extraction processes operate at extremely high pressures (5 - 20 MPa). Capital costs for compression equipment are large and the need to operate at elevated pressures usually introduces additional operating costs. In choosing between distillation, liquid-solvent extraction, and supercritical fluid extraction for a particular separation process, energy requirement comparisons are important. In the development of an extract-recovery system it is important that a substantial energy loss is not incurred. Solvent recovery usually imposes a large utility cost in any separation procedure. These utility costs, however, are sensitive to the types of compressors used and the method of supplying heat. The evaluation of capital and energy costs basically involves a comparison between the relative unit costs of power and heat. One method of recovering the extract from an

SFE process is to lower the pressure. Subsequently raising the pressure requires large amounts of energy. Cycles involving complete depressurization and recompression of the gas are usually unacceptable on energy grounds unless the solvent is pumped as a liquid and a high degree of energy recovery is realized. As an estimate, a supercritical extraction process involving a compression ratio of three is roughly equivalent in energy requirements to a distillation operation. A similar energy comparison can be made between SFE and liquid solvent extraction for heat is generally required to recover the solvent in the latter operation. Therefore, supercritical fluid extraction processes are considered economically advantageous only if (1) separation is difficult or impossible by other means or (2) it is possible to effect solvent recovery with small changes in pressure or temperature.

The energy loss from raising the pressure of the recycled gas can be partly recovered by carrying out the initial expansion in a turbine. This arrangement could produce severe erosion due to the deposition of solute and the possible presence of liquid droplets. Several alternative techniques to recompression which warrant further research are (1) adsorption in a fixed bed, (2) washing the gas with a subcritical liquid solvent and (3) solute precipitation through isobaric heating or cooling. An excellent alternative to recompression solvent recovery is the employment of an entrainer.

Little has been published concerning this application. However, in the design of a large-scale separation process which can be operated continuously and economically at constant pressure, we should not be restricted to using a supercritical gas alone as a solvent, but should consider adding a substance to the solvent which has a volatility between the substances to be separated and the supercritical gas. In this system, a regeneration of the gas stream may be realized with a small temperature change alone, which is more feasible from an energy economics point of view than an extensive pressure drop. Although an entrainer complicates the system and will probably make separation equipment more expensive, often the solubility and separation factor are enhanced and, therefore, the operation can proceed at a lower (constant) pressure. In addition, a complete regeneration of the gas phase is possible by a temperature change only, and the gas can be recycled without any marked pressure change. The separation of glycerides using supercritical carbon dioxide with ethanol as an entrainer illustrates well the advantages associated with this type of system [131,132].

4.1.3 High Pressure Materials and Pumps

Certain SFE processes (especially in the oil and coal industries) employ solvents which require relatively high temperatures as well as elevated pressures. These conditions demand a high quality material of construction with a large vessel wall thickness in order to withstand the severity. The special fabrication of these vessels and piping may be expensive. In addition, a fair number of problems are associated with the pumping of gases near critical conditions due to the combined effects of relatively high pressure and pressure gradients within the pumping system. The difficulties are attributed to the substantial change in the physical properties accompanying pressure changes near the critical point.

In addition to the high pressure aspects of construction materials, SFE solvents may be chlorides or contain hydrogen to effect a stabilization of the extracted material, e.g., in coal liquefaction. The handling of these materials requires a high grade steel which can seriously affect process economics.

4.1.4 Process Control

A key design consideration in SFE is the solvent compressibility. The greater the compressibility, the greater the solvent density at a specified operating pressure. This generally means that the process should operate as close to the critical point as possible. In the critical region, however, process control is difficult because a relatively minor temperature or pressure swing can cause the system to drop into an unfavorable two (or more) phase state. In addition, energy recovery considerations for solvent regeneration will require several unit operations to be closely coupled. This coupling in the critical region will require expensive, state of the art instrumentation and controls which will be a serious process design consideration.

4.1.5 Safety

Although high pressure, high temperature processing is not uncommon in the chemical industry, there are always serious safety considerations. This is especially true in the extraction of materials being produced from mild pyrolysis, e.g., coal or tar sands. At high temperatures material strengths are considerably reduced which presents special problems in the design of seals and valves. Another safety consideration is that of a serious temperature swing in the process which would cause the system to become hydrostatic.

4.2 Commercialization Difficulties

As outlined by King and Bott [130], there are four major problems associated with the commercialization of supercritical fluid extraction: patent problems, capital costs, operating costs and scale up.

4.2.1 Patent Difficulties

An inspection of the Reference section of this report shows a large number of patents dealing with SFE. For example, during the past two years there have been 12 US patents on the decaffeination of coffee. In many other cases patent applications seem to have been filed based on very preliminary laboratory tests with the desire for protection from competition rather than to commercialize the process. An examination of one patent shows more of an attempt to patent physical behavior than to exploit the behavior in a commercial application. From the point of view of commercialization, this use of the patent laws has two serious detrimental effects: it is extremely difficult to determine if infringement is likely and licensing of processes will involve substantially higher front end costs.

4.2.2 Capital and Operating Costs

Contrary to the notion presented by some workers in the field, high pressures are expensive and SFE like any separation process is capital intensive. This expense arises from compressor expense and the need for high pressure vessels. This is especially true in the area of coal liquefaction where temperatures are high.

In conjunction with high temperatures, SFE operating costs can be high due to the need for process energy and maintenance. Energy recovery is essential which in turn increases capital costs.

4.2.3 Scale up Problems

As with any chemical process, there are scale up problems associated with the transition from bench scale to pilot plant to commercial operation. These problems are associated with a general lack of knowledge of the mechanisms governing rate processes and how these mechanisms are affected by physical size and geometry. To minimize the risk in this area, pilot studies will always have to be made which will increase the time and cost before SFE is commercialized.

4.3 Prospects for Commercialization

In spite of the problems outlined in this section, SFE is being commercialized and this commercialization will continue. In the near term these processes will be dealing with the isolation or production of high value, stable priced products required in the specialized food and drug industry. Economic instabilities in the energy and bulk chemical industries will most likely prevent near term commercialization of this process technology. It is likely however that a large amount of bench scale process development will continue and the proliferation of patent protection will become worse.

5. Summary of Current Research and Recommendations

In this section current research activities which bear on the development of SFE are summarized and general recommendations for future research are presented. Generally only a few specific references will be cited, these being to identify the programs and to provide the interested reader a point of reference for investigation. The primary emphasis is on identifying US research facilities which provide basic data and models of interest in SFE.

Five areas have been selected for this summary: phase equilibria, pVT-x measurement and correlation, transport phenomena, supercritical chromatography and kinetics in near critical phases. Other areas dealing with SFE process development such as calorimetric and materials research have been excluded. Industrial research activity has also been excluded since the results are not available in the public domain.

With regard to the first three areas mentioned above, Table 4 summarizes the major university and governmental research facilities in this country. Those marked with single asterisk indicate research programs which are providing data and models which are directly applicable to problems encountered in SFE. The basis for this notation is a set of recent (~5 years) publications in the open literature. In addition, facilities marked with two asterisks indicate (in the authors' opinion) strong thermophysical property research programs, not just dealing with SFE. "Strong" in the sense of this table means more than one professional staff member, a program which includes both theory and experiment and the experimental capabilities to probe the extremes of temperature, pressure and chemical composition. In some cases this program is divided between departments, e.g., chemical engineering and chemistry. The essential point of this table is not whether or not the programs are "strong," rather that the resources for this type of research are limited.

Table 4. Experimental Thermophysical Property Research Facilities in the U.S.[a]

PVT	Phase Equilibria	Calorimetry	Transport Properties	Other[b]
RICE *,**	RICE *,**	TAMU **	RICE *	RICE **
TAMU **	TAMU **	CSM **	CSM *,**	BETC **
CORNELL *,**	CORNELL *,**	CORNELL **	BROWN	NBS **
OSU	OSU	OSU **	OSU	WU
BETC **	NDU *	BYU *	NBS *,**	CSM **
NBS *,**	CSM **	BETC **	BYU *	
BYU	PURDUE	NBS **	UI *	
NDU	RPI	NDU		
PURDUE	BERKELEY *			
WU	OHSU			
	NBS *,**			
	BYU			
	UD *			
	UCLA *			
	UMR			
	UI *			
	MIT *			

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[a] Key to abbreviations: BETC - Bartlesville Energy Technology Center; BYU - Brigham Young University; CSM - Colorado School of Mines; NBS - National Bureau of Standards; NDU - Notre Dame University; OHSU - Ohio State University; OSU - Oklahoma State University; RPI - Rensselear Polytechnic Institute; TAMU - Texas A & M University; WU - Wyoming University; UD - University of Delaware; UCLA - University of California at Los Angeles; UMR - University of Missouri-Rolla; UI - University of Illinois; MIT - Massachusetts Institute of Technology.

[b] For example: dielectric constant, refractive index, sound velocity, etc.

5.1 Phase Equilibrium Measurements, Theory and Models

As was mentioned earlier in this report, it is the solubility enhancement or phase equilibria encountered in the near critical region of mixtures which makes SFE an option for a separation process. The complexity of natural materials (e.g., tobacco, hops, etc.) makes it impossible to systematically study these materials directly. The approach, therefore, is to study model systems which have some of the well defined chemical and physical attributes of the real systems of interest. A detailed experimental knowledge of these systems can then be coupled with a theoretically based model to make engineering design predictions on a real system of interest. The accuracy of these predictions are then limited by the accuracy of the original measurements, theory and current analytical ability to provide a physicochemical characterization of the real system.

5.1.1 Phase Equilibrium Measurements

There are three types of phase equilibria measurements which are of interest in SFE, critical locus measurements, fluid-fluid mutual solubility measurements at high pressures, and solid solubilities in fluids at high pressures. These three types of measurements are not unrelated. They are separated however, because they may be most efficiently performed in different types of apparatus. Even within this gross classification scheme there are over a hundred different types of apparatus which are specialized to a given temperature, pressure or composition range [134].

There have been several excellent reviews of phase equilibrium measurement techniques and data. Rowlinson and Richardson have reviewed solid solubilities in gases [168]. Booth and Bidwell [133] published an early review of solubility measurements in the critical region. More recently Young [134] has reviewed the experimental methods which have been used for phase equilibrium studies. Hicks and Young [135] have also published a review of measured gas-liquid critical properties of binary mixtures. Greer [136] has reviewed liquid-liquid critical phenomena and contains references to many previous reviews. Several symposia at recent AIChE meetings have addressed all aspects of critical phenomena and the relation to SFE [137].

Recently there have been several publications which deal directly with phase equilibria in supercritical fluids. They include the work of Paulaitis at Delaware [138-140], Eckert at Illinois [141,142], Reid at MIT [143,144], Chrastll at General Foods [145] and Holder at Pittsburg [146]. In addition, ongoing programs at Cornell, Rice, Maryland, NBS, Notre Dame and UCLA continue to provide valuable measurements of phase equilibria and critical phenomena.

Major foreign efforts in phase equilibria which bear on SFE seem to be concentrated in Germany in the groups at Karlsruhle [147,148] and Bochum [149-151]. In addition, Knapp at Berlin has a long standing program in high pressure phase equilibria.

5.1.2 Phase Equilibrium Theory and Models

From a thermodynamic point of view the macroscopic laws governing phase equilibria at high pressure are well known. They have been the subject of many reviews [152,153] and can be found in advanced texts on the subject [31]. Research in this area is concentrated on developing the link between microscopic molecular interactions and macroscopic behavior. From an engineering point of view, this link takes the form of an equation of state which relates the pressure of the system to the volume, temperature, composition and molecular parameters. Thus far no totally satisfactory equation of state has been developed, especially for describing critical region behavior. The critical region is especially difficult due to the nonanalytic mathematical relationship between the intensive thermodynamic variables in this region.

Most engineering approaches to predicting phase equilibrium in the near critical region are based on the principle of corresponding states [154]. This principle has rigorous theoretical basis for simple spherical molecules but must be empirically modified to be accurate for complex fluids. There are basically two variants of application of the corresponding states principle. The first uses a universal equation of state whose parameters are determined from pure fluid data and mixing rules. Typical of this approach are the modifications of the van der Waals [155] or Benedict-Webb-Rubin equations [156]. The other approach uses a high accuracy equation of state for a selected fluid (reference fluid) which has been determined from experimental data and scales the temperature and density via molecular parameters and mixing rules [156].

The most common approach in modeling SFE has been to adjust the parameters of a cubic equation of state to agree with measured data over a given range. The equation is then used to provide a smooth extrapolation to the conditions of interest. This approach has been sucessfully applied by Peter and Wenzel [157], Stephan and Schaber [158,169] and King and Bott [130]. The primary problems with this approach are that the cubic equations of state provide a much too simple description of fluid behavior, are analytic in the critical region and must be adjusted to experimental data.

Most recent approaches to phase equilibrium in the critical region use statistical mechanical theory of fluids. Recent work includes the lattice gas models of Wheeler [159], Vezzetti [160] and Kleintjens and Koningsveld [161]; modified Leung--Griffiths theory of Moldover and Rainwater [156,162,163]; and statistical mechanical perturbation theory of Gubbins, Street and Lucas [164,165]. Fox's recent mathematical advances of imposing nonanalytic behavior on an analytic equation of state [166] are currently being exploited in a reference fluid corresponding states theory using a nonanalytic reference fluid [167].

5.1.3 Recommendations for Research

- Automation of high accuracy pressure measurement in thermodynamics experiments.
- Development of high temperature, high pressure phase equilibrium apparatus capable of multiphase (3) measurements.
- Systematic studies of ternary and multicomponent mixture phase equilibria involving polarity and size differences.
- Development of improved/non-intrusive analytical methods for composition determination.
- Fundamental theoretical studies of the critical region of mixtures. Systematic study of the principle of corresponding states for complex fluid mixtures involving different chemical types.
- Molecular dynamics studies of anisotropic/assymmetric mixtures.
- Theoretical studies of mixtures of associating/nonassociating components.

5.2 Fluid P-V-T-x Measurements and Correlation

In addition to the phase equilibrium needs outlined in the previous section, there is a great need for high accuracy pVT measurements and correlations for both pure fluids and mixtures. This is especially true for SFE where there are large volume flows of a nearly pure solvent in the critical region. Other reasons why these data are needed are as follows:

1) Accurate pVT relations are required for the custody transfer of the solvent.
2) Other regions of the surface are encountered in the solvent regeneration step of a SFE process.
3) Thermal properties such as the entropy and enthalpy, which are needed in sizing energy recovery and compression equipment, depend on volume integrals of the pressure and its temperature derivatives from the ideal gas to the state of interest.

and 4) To perform accurate corresponding states calculations of the phase equilibria, the reference fluid should be chosen so as to be as similar to the mixture as possible. For example, in modelling the phase equilibria in a CO_2 SFE process, the logical choice for the pure reference fluid is CO_2.

As outlined in Table 4, there are five major facilities in the US which are currently making wide range pVTx measurements. Recent systems which have been studied include carbon monoxide, hydrogen sulfide, methanol, methane/hydrogen, methane/ethane, methane/propane, methane/carbon dioxide, and carbon monoxide/hydrogen.

With regard to item (4) listed above, it should be noted that only one highly accurate wide range equation of state for CO_2 has been proposed [170] and that equations of this class for propane, ethylene and water have only recently been developed at NBS [171-173]. To the best of our knowledge, no high accuracy wide range equations exist for toluene, benzene or the halohydrcarbons, which are fluids that are frequently mentioned as candidates for use as supercritical solvents. In light of the fact that current modelling efforts attempt to predict mixture properties from "exact" knowledge of pure fluids, these equations are sorely needed for more complex fluids.

5.2.1 Recommendations for Research

- PVTx measurements for polar/nonpolar mixtures
- PVT measurements for cyclohexane
- Measurements and correlations for equation of state development for benzene, toluene, methanol, and cyclohexane
- Development of apparatus for and measurement of saturated vapor densities.

5.3 Transport Phenomena

The transport properties of fluid mixtures regulate the approach to equilibrium and therefore determine equipment size, residence times, etc. Table 4 shows few facilities which have the capability of making these measurements over a wide range of conditions. Major experimental programs are currently being conducted at Brown, Rice, Illinois, CSM and NBS. In addition, Dymond at the University of Glasgow has recently reported extensive viscosity measurements over a wide range of conditions and Iwasaki in Japan has reported measurements of fluid viscosity in the critical region. Thermal conductivity measurements in the critical region have been reported by LeNeindre at the University of Paris, de Castro in Lisbon and Wakeham at Imperial College. Finally a majority of the world's thermal conductivity and viscosity data prior to 1970 was measured at various facilities in the USSR.

Transport theory in the critical region is especially difficult due to anomalous physical behavior. Sengers, et al. at Maryland have an outstanding research program in this area which has been recently reviewed [174]. Current theoretical work however seems to be concentrated on nonlinear behavior [175]. In addition there is a large amount of work concentrated on molecular dynamics simulations of fluids in nonequilibrium states. Finally, Lucas [176] has recently reviewed the scope of transport properties prediction method, the results of which are summarized in Table 5. In this table CSP stands for corresponding states principle. The interested reader is referred to [176] for references on each of these methods.

5.3.1 Recommendations for Research

- Development of high temperature, high pressure transport apparatus
- Theoretical efforts to describe diffusion in near critical mixtures
- Fundamental studies of diffusion of gases in porous or agregate materials
- Molecular dynamics simulations of nonequilibrium fluids
- Theoretical studies of anomalous transport behavior in the critical region
- Theoretical studies of the contribution of internal degrees of freedom to energy transport in dense fluids.

Table 5. Summary of Transport Prediction Techniques [176].

Property State	Viscosity	Diffusion Coefficient	Thermal Conductivity
Dilute Gas (pure)	Chapman-Enskog-Formula Simple CSP	Chapman-Enskog-Formula Simple CSP	Chapman-Enskog-Formula + Eucken-Correction Chapman-Enskog-Formula + Group Contribution Method
Dilute Gas (mixture)	Simplified Champan-Enskog-Formula Simple CSP+1-Fluid-Approximation	Chapman-Enskog Formula + Empirical Modifications	Simplified Chapman-Enskog-Formula
Dense Gas (pure)	Simple CSP Enskog-Theory	Simple CSP Enskog-Theory	Simple CSP Enskog-Theory
Dense Gas (mixture)	Simple CSP+1-Fluid-Approximation Enskog-Theory	Simple CSP+1-Fluid-Approximation	Simple CSP+1-Fluid-Approximation Enskog-Theory
Liquid (pure, $T>T_b$)	Extended CSP Enskog-Theory	Enskog-Theory	Extended CSP Enskog-Theory
Liquid (pure, $T>T_b$)	Group Contribution Methods Enskog-Theory	Enskog-Theory	Group Contribution Methods Enskog-Theory
Liquid (mixture, $T>T_b$)	Extended CSP+1-Fluid-Approximation Enskog-Theory Empirical Mixing Rules	Empirical Modifications of Stokes-Einstein-Relation	Extended CSP+1-Fluid-Approximation Enskog-Theory Empirical Mixing Rules
Liquid (mixture, $T>T_b$)	Group solution models Empirical Mixing	Empirical Modifications of Stokes-Einstein-Relation	Empirical Mixing Rules

5.4 Supercritical Fluid Chromatography

Supercritical fluid chromatography (SFC) is a relatively new type of chromatographic science in which compressed gases, near or above their critical temperatures, are used as mobile phases. The technique was devised and first applied by Klesper, Corwin and Turner [177] in an effort to separate mixtures of porphyrin derivatives. In their pioneering study, chlorfluoromethanes were used as mobile phases at pressures up to 140 bar.

Since this first work, the development of the technique was relatively slow until the mid-1970's. The reason for this is partly due to the explosive growth of normal pressure gas chromatography, and of high performance liquid chromatography. A more important reason for the slow development of SFC was the extreme lack of advanced knowledge of thermophysical behavior required to fully exploit the great potential of the technique [179]. Since the mid-1970's there has been substantial research activity in this area. This work has been reviewed at timely intervals by several authors [9,178-184]. As pointed out in these reviews, most of the earlier work (after the discovery by Klesper, et al.) was concerned with SFC from the practical point of view, i.e., separation and analytical instrumentation [185-188]. Work on this aspect of SFC has recently concentrated on the separation of various mixtures containing polynuolear aromatic compounds [189-192] and the separations of polymeric materials [193-201]. Instrument developments included a flame detector [202,203], a means to interface SFC with mass spectrometry [192,204] and the development of pressure and/or density programming [205,206].

From the point of view of supercritical fluid extraction an interesting development in SFC has been the application of the instrument to physicochemical measurements. Early work on the use of conventional gas chromatography, (GC) as a thermophysical property measurement apparatus was reviewed by Kobayashi, et al. [198] is now well established [208,209]. For example, measurements of GC retention volumes allow determination of infinite dilution activity coefficients [210], partition coefficients [211], molecular association constants [212], enthalpies of vaporization [213], and second virial coefficients [214] . Using gas-solid chromatography, thermodynamic parameters of adsorption can be measured [215]. Two chromatographic methods have been developed to measure diffusion coefficients in gases [216,217], one of which was later extended to liquids [218].

Although physicochemical applications have only occured recently, the results are exciting. Pressure dependence of the partition coefficient allows one to extract partial molar volumes of solutes in the supercritical phase [179,34]. The importance of these quantities was discussed in Section 2 of this report. In addition to the partial molar volumes, the limiting slope of the partition coefficient pressure curve provides second virial coefficients [179,214,218]. Finally diffusion coefficients which are of importance in mass transfer calculations have been measured via SFC [219-221]. Further developments in this area should greatly benefit the development of SFE.

5.4.1 Recommendations for Research

- Further development of SFC as a physicochemical measurement technique
- Development of the theory of the instrument which will allow more reliable determinations of partial molar volumes
- Wide range diffusivity measurements
- Development of new measurement techniques, especially at elevated pressures

5.5 Chemical Reactions in Supercritical Fluids

Chemical kinetics in the critical region is a relatively unexplored area of research although it has been briefly discussed [6,9,93]. Eckert [222] has reviewed high pressure reaction kinetics in solution and should be consulted for detailed references. It is possible that supercritical fluids may be able to enhance chemical kinetics with regard to (1) reaction rates and (2) selective reactant/product solubilities. Work on supercritical chemical kinetics has been primarily focused on these two applications.

Temperature effects on reaction rates have been studied in detail, but at moderate pressures, the pressure dependency on the reaction rate is insignificant. In fact, substantial changes of reaction rates in liquid solvents usually become evident only at extremely high presures (i.e., $\sim$ 1000 atm). At the pressures encountered in SFE ($\sim$ 100 atm), however, these pressure effects may become very significant due to strong partial molar volume, solvation effects, and viscosity. These particular dependences have been discussed by Luft [223] and Theis [224].

Simmons and Mason [225,226] studied the dimerization of chlorotrifluorothylene at temperatures and pressures near the critical point of the reactant. Appreciable changes in the activation volume near the critical region were observed which could be correlated with changes in the partial molar volume of the transition state. Using the Redlich-Kwong and fourth-order virial equations of state, they suggest that transition-state theory can describe quantitatively the pressure effects on reaction rates in compressible fluids. Similarily, Menshutkin type reactions in supercritical isopropanol and methanol at various conditions have been studied to ascertain the dependence of the volume of activation upon temperature and pressure [227]. Krichevskii, et al. [228] have measured the dimerization of NO_2 in supercritical CO_2 near its critical point and observed that dimerization increased as temperature increased within five degrees of the critical temperature. Current research at the University of Delaware involves determining the effect of supercritical solvents on the global rates of reaction in several pyrolysis reactions [93].

Understanding the relationship between reaction rates and supercritical operating conditions is very important. As mentioned, reactions may be either enhanced or inhibited by operating near the critical point. Thus, there are two important implications. In a system where the primary objective is supercritical chemical reaction, the desired reaction may be enhanced while unwanted side reactions could be inhibited. In a system where the primary objective is supercritical separation, insignificant chemical reactions may become more pronounced.

It is also possible that supercritical fluid solvents may be used to control solubilities of reactants and products in order to improve reaction selectivity and yield. A supercritical solvent exhibits liquid-like loading capacity due to its high density. Therefore, the ability of the solvent to selectively reduce the concentration of a particular species (reactant or product) may be more pronounced. In addition, the selectivity could be easily altered during a process for small changes in pressure or temperature will produce significant solubility variations in a supercritical fluid. Some possible selective solvent applications with supercritical fluids include (1) catalyst recovery in homogeneous reactions and (2) mixing dissimilar reactants which are only partially miscible as liquids. Theis [224] has discussed the product selectivity which is possible in high pressure reactions using pressure as the controlling factor. Some examples of this work include the reaction of CO_2 and aniline to give 3-phenyl-2, 4-quinozoline dione (vs. diphenylurea), diels-alder reactions, the synthesis of hexamethylacetonoxime from hexamethylacetone, and the increased yield of 2-nitro-1, 3-xylol from m-xylol.

A supercritical solvent may also provide a new reaction scheme or path. In this case, the fluid acts as both a reactant and solvent. Some systems in which the supercritical solvent is not inert and influences the reaction products are (1) the isomerization of normal paraffins, (2) the decrease in asphaltene products in coal liquefaction, and (3) the conversion of sulfur and nitrogen to H_2S and NH_3 in the treatment of hydrocarbons [6].

5.5.1 Recommendations for Research

- Coupled kinetic-thermodynamic effects in supercritical phases
- Pyrolysis reactions in the presence of supercritical fluids

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During the past ten years there has been intense interest in the application of dense gas separation techniques to various chemical processing problems. An example is known as supercritical fluid extraction. The purpose of this report is to summarize various aspects of supercritical fluid extraction including a definition of the phenomena, current industrial applications, technical difficulties and, where possible, the identification of areas where further research would be of value. In addition, processing aspects which impact on the cost effectiveness of supercritical fluid extraction are considered.

Current research which bears upon the development of supercritical fluid extraction is presented and recommendations for certain high risk research activities are summarized. In addition, a brief review of supercritical fluid chromatography is presented and chemical kinetics in supercritical phases are briefly discussed.

12. KEY WORDS *(Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)*

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