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Supercritical Fluid Extraction in Food Engineering

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I. INTRODUCTION

The origins of supercritical fluid extraction (SFE) are firmly rooted in the phenomenon of solute solubility in gases as typified by the classic studies of Hanay and Hogarth in the 1880s (1). However, this curious and somewhat unexpected phenomenon, i.e., the dissolution of solids in such fluids as supercritical ethanol and water, was not exploited for any useful purpose until the midpart of the next century.

From a modern perspective, SFE was first exploited in Russia in the 1950s (2) and later in Germany (3) for the extraction and fractionation of components in natural products. However, it was the appearance of the Zosel patent (4), issued in Germany in the late 1960s, that firmly documented the myriad of possibilities for using supercritical fluids (SCFs) as processing agents. The U.S. version of this patent, entitled, "Process for the Separation of Mixtures of Substances," provided more than 60 examples of applications of super- and subcritical ethylene or carbon dioxide to food processing and other applications. How-

Names are necessary to report factually on available data. However, the USDA neither guarantees nor warrants the standard of the product, and use of the name by USDA implies no approval of the products and the exclusion of other that may also be suitable.

ever, this broad coverage did not deter other parties from similar patent filings over the next 30 years or the industrial exploitation of critical fluids as versatile processing agents.

The classic, often cited applications of SCFs, especially supercritical carbon dioxide (SC-CO₂) or liquefied carbon dioxide, are for the decaffeination of coffee (5) and the processing of hops (6). Thus, there is a historical precedent for using critical fluid media in food engineering, which continues up to this present day. Since the above-cited applications, there has been a plethora of additional applications of SFE to foodstuffs, agricultural raw materials, and associated natural products (7). This has resulted in the development of 32 processing plants worldwide employing SCFs. Currently, most of these facilities are centered in Germany, the United States, France, and Japan. Nations such as Great Britain, Australia, Canada, India, and Italy continue to develop more plant capacity for critical fluid processing; and other nations with a rich litany of natural products will undoubtedly enter the marketplace as users of SCF technology in the future. It should be noted that not all of the new processing schemes employing SCFs will be wholly based on extraction, but may include fractionation schemes or reactions conducted in critical fluid media.

Table 1 shows a list, which is not inclusive, of many users of critical fluid extraction for food and natural product processing throughout the world. Key players in the various market segments are as follows: decaffeination—General Foods, SKW Trostberg, Kaffee HAG, Hermesen; hops processing—HVG Barth (NATECO₂), John Haas, Yakima Chief, Carlton United Breweries, Steiner Hops, English Hops, SKW Trostberg; flavors/spices—Cultor, Quest, Flavex,

Table 1 Organizations Processing or Offering Critical Fluid–Derived Products

Flavex (Germany)	Fuji Flavor (Japan)
Hermesen (Germany)	Kobe (Japan)
HVG Barth (Germany)	Mori Oil Mills (Japan)
Kaffe HAG (Germany)	Ogawa (Japan)
SKW Trostberg (Germany)	Takasago (Japan)
KD-Pharma-IQA (Germany–Spain)	Takeda (Japan)
General Foods (United States)	Cultor (France)
John Haas (United States)	HITEX (France)
Praxair (United States)	Norac (Canada)
Yakima Chief (United States)	Aroma Tech OY (Finland)
Carlton United Breweries (United Kingdom)	Quest (Holland)
English Hops (United Kingdom)	Wells Investment Ltd. (New Zealand)
Steiner Hops (Germany–United Kingdom–United States)	

Norac, Ogawa, Fuji Flavor, Kobe, Mori Oil Mills, Takeda. Many of the processors listed under the generic heading of flavors/spices also produce a variety of other natural products such as specialty oils, natural pigments, and antioxidants. For example, Flavex is also involved in the processing of ginseng among other moieties, and Norac in Canada processes rosemary antioxidants, saw palmetto, kava kava, and other botanicals (8).

Since the early 1990s, an awareness of the potential of critical fluid processing as a viable component for “green” processing has arisen (7). This coupled with an increasing consumer awareness of the identity and use of chemical solvents in food and natural products processing has provided further impetus for the use of benign solvents as SC-CO₂, ethanol, and water. Recently, the use of SC-CO₂ for the processing of certain nutraceutical products (9) has provided additional possibilities for exploiting SCFs. As governments worldwide are also currently making regulations on the use of organic solvents even more strict (10), including the banning of some traditional solvents, environmentally benign SCFs such as SC-CO₂ or non-ozone-depleting fluorocarbons will become even more attractive.

In this chapter, we have reviewed some of the basic fundamentals of SCFs and their use for the extraction and fractionation of food-related materials. The relevant physical and chemical properties of SCFs, particularly SC-CO₂, are initially discussed, followed by the key factors that contribute to successful SFE, namely, the solubility of solutes in SCFs, phase equilibria, and mass transfer considerations. A discussion of the fundamentals required in effectively using SCFs, such as the type of extraction or fractionation, along with choice of solvents, entrainers, and condition of the matrix to be extracted, follows. The various application areas of SCF extraction are discussed at length in following chapters.

II. PROPERTIES OF SUPERCRITICAL FLUIDS

The mathematical modeling, simulation, and design of an SFE process require knowledge of physicochemical properties of compounds of interest. Further interpretation of physicochemical property values can be obtained by an understanding of molecular behavior. For example, the ideal gas law [Eq. (1)] is a prime example of the correlation of properties.

$$PV = NRT \quad (1)$$

Critical temperature and pressure, compressibility, density, heat capacity, dielectric constant, viscosity, diffusivity, and thermal conductivity are important properties, which are needed for the characterization of both solvent and solutes in an extraction process. Pure-component properties as well as mixture proper-

ties are used to describe individual solute and solvent characteristics and how the solute and solvent behave as constituents of mixtures.

A. Critical Constants

The critical point of a pure substance is usually defined as the temperature and pressure at which the gas and liquid phases become indistinguishable. However, in the case of a solid and a liquid, these two phases do not become identical when their densities are equal. Therefore, solid–liquid, solid–gas, and solid–solid equilibrium lines do not end by critical points, as do gas–liquid lines (Fig. 1).

When a substance is compressed and heated to its critical point it enters a phase referred to as “supercritical phase.” The matter that is in the supercritical region is called a supercritical fluid (SCF). Temperature, pressure, and molar volume of a substance at the critical point are defined as the critical temperature (T_c), critical pressure (P_c), and critical molar volume (V_c), respectively. These parameters are collectively referred to as critical constants. Each substance has a unique set of critical constants (Table 2). Applications of SFE in food engineering involve processing of many materials, which contain a number of components. Identification and characterization of natural material components are usually very difficult. Therefore, in the literature SFE often characterizes processes above the critical point of the solvent. In this case, mixture of solvent and solute usually exists as two distinct, partially miscible phases below the critical point of the mixture. Similarly, extraction processes just below the critical point of the solvent are usually referred to as near-critical extraction based on the pure solvent properties rather than that of the mixture.

Critical properties of small molecular weight compounds can be found in standard handbooks (12, 13). Critical properties of many biological materials cannot be determined experimentally due to the fact that these materials will be decomposed before their critical point is reached. Usually, semiempirical methods are used to estimate critical properties of natural products. The group contribution method is also widely used to estimate critical properties of biological materials. Reid et al. (13) reviewed Ambrose, Fedors, and Joback modification of Lydersen’s method in detail. The Ambrose group contribution method is widely used to estimate critical properties of organic materials. In this method, the critical properties are estimated using the following relations:

$$T_c = T_b[1 + (1.242 + \Sigma\Delta_T)^{-1}]; P_c = M(0.339 + \Sigma\Delta_P)^{-2}; V_c = 40 + \Sigma\Delta_V \quad (2)$$

The Δ values for a number of compounds are given in Reid et al. (13). When the compound of interest contains functional groups for which Δ parameters are not available, use of group contribution methods becomes difficult. In such cases, more empirical models are used (14, 15).

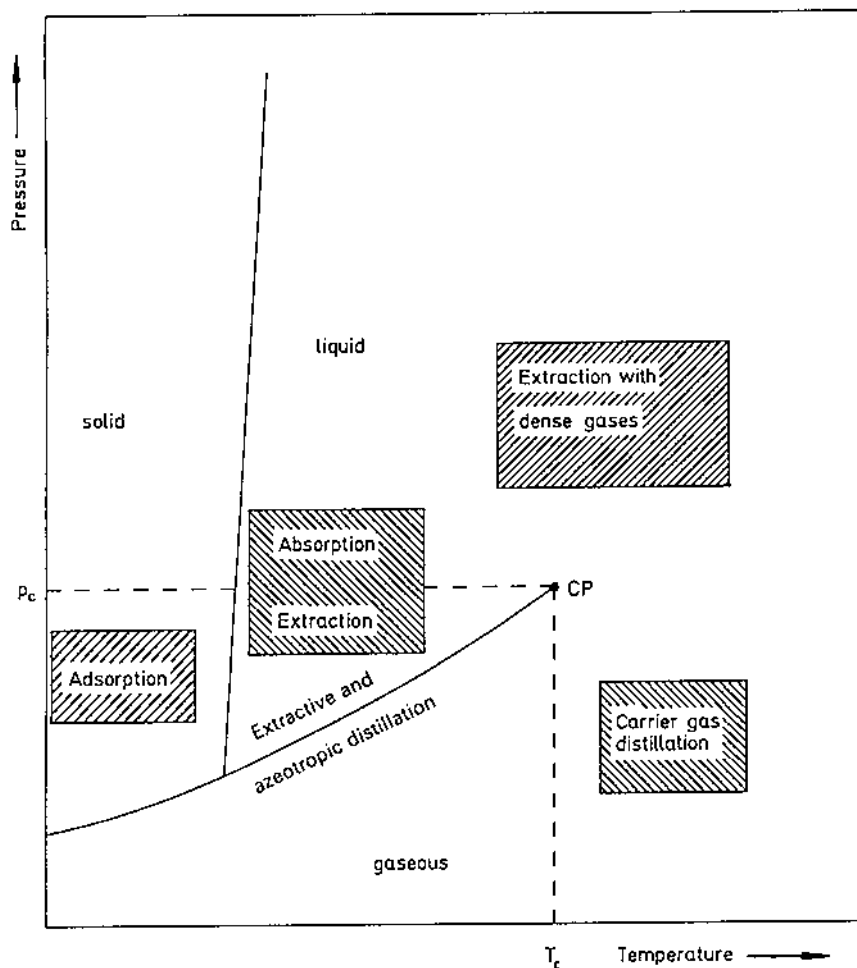


Figure 1 Phase diagram for a pure substance.

B. Physicochemical Properties

A unique feature of the SCF is the adjustability of their density in the supercritical region by regulating the temperature and pressure of the system. An increase in temperature leads to a decrease in density in all cases. Density of a fluid is extremely sensitive to temperature and pressure near the critical point ($P_r = 1$, $T_r = 1$). Reduced density ($\rho_r = \rho/\rho_c$) of a pure compound at reduced pressure 1.0

Table 2 Critical Pressure and Temperature of Common Fluids for SCFE

Fluid	Crit. temp., T_c (°C)	Crit. pressure, P_c ($\times 10^5$ Pa)
Carbon dioxide	31.1	73.7
Chlorotrifluoromethane	28.9	39.2
Ethylene	9.3	50.3
Ethane	32.3	48.8
Propane	96.7	42.4
Propylene	91.9	46.2
Cyclohexane	280.3	40.7
Isopropanol	235.2	47.6
Benzene	289.0	48.9
Toluene	318.6	41.1
<i>p</i> -Xylene	343.1	35.2
Trichlorofluoromethane	198.1	44.1
Ammonia	132.5	112.7
Water	374.2	220.4

can be changed from a value of about 0.1, a gas-like density, to about 2.0, a liquid-like density, by regulating reduced temperature in the range of 0.9–1.2 (Fig. 2, Table 3). As the reduced densities become liquid-like, SCF begins to act like a liquid solvent. However, as the reduced temperature is raised to a value of about 1.6, the fluid becomes gas-like due to the decreased density (expansion of fluid) with increasing temperature. Data on the physical properties of mixtures is scarcer than for the pure compounds. An interesting publication of Magee (16) includes a list of references, which report density calculations for CO₂-rich mixtures from various predictive models or theories.

At high pressures, gases deviate from ideal behavior due to enhanced physical forces between ions, dipoles, induced dipoles, and higher poles, which contribute to the molecular interactions in the system. The potential energy of interaction, E_p , of point charges q_1 and q_2 can be defined as a function of the permittivity of the medium, ϵ , and the distance between the charges, r [Eq. (3)].

$$E_p = \frac{q_1 q_2}{4\pi\epsilon r} \quad (3)$$

The relative permittivity, ϵ_r , also known as dielectric constant of the medium, is defined as follows:

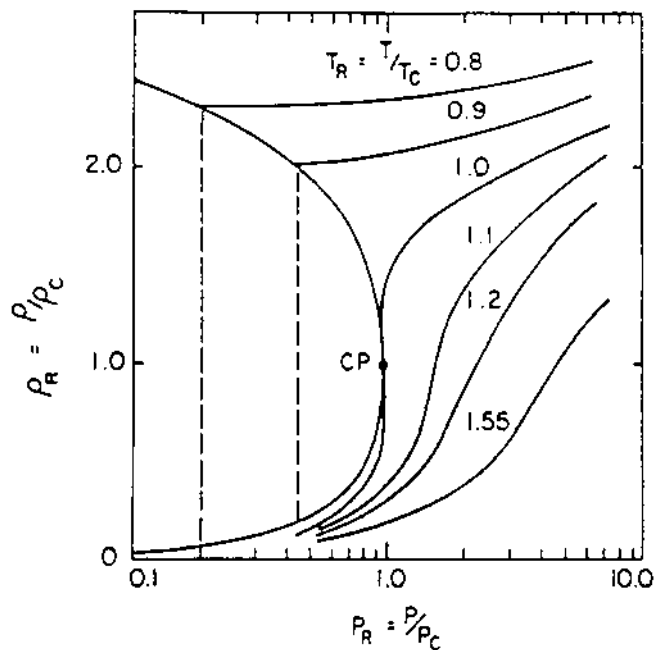


Figure 2 Variation of reduced density of a pure substance in the near-critical region (20).

Table 3 Comparison of Physical Properties of Gas, Liquid, and SCF (98)

Physical property	Gas (1 atm, 15–30°C)	Supercritical fluid		Liquid 15–30°C
		T_c, P_c	$T_c, 4P_c$	
Diffusion coefficient ^a (cm ² /s)	0.1–0.4	0.7×10^{-3}	0.2×10^{-3}	$(0.2\text{--}2) \times 10^{-5}$
Viscosity (g/cm.s)	$(1\text{--}3) \times 10^{-4}$	$(1\text{--}3) \times 10^{-4}$	$(3\text{--}9) \times 10^{-4}$	$(0.2\text{--}3) \times 10^{-2}$
Density (g/mL)	$(0.6\text{--}2) \times 10^{-3}$	0.2–0.5	0.4–0.9	0.6–1.6

^aSelf-diffusion for gas and dense gas; binary mixture for liquid.

$$\epsilon_r = \frac{\epsilon}{\epsilon_0} \quad (4)$$

where, ϵ_0 is the permittivity in a vacuum.

The static dielectric constant (DC) is a useful property to estimate the solvent properties of the relatively polar fluids such as ethanol, methanol, and water. DC is also a density-dependent property and can be changed significantly by modest changes in temperature and pressure of the system. The DCs for SCFs become important because they are a measure of intermolecular force enhancement through dipole–dipole interactions. For example, DC values for CO₂ rise rapidly between 70 and 200 × 10⁵ Pa at 40°C and reach liquid-like values around 200 × 10⁵ Pa (Fig. 3) (17). This partially explains the greater solvent power of SC-CO₂ for low-volatility compounds at elevated pressures.

C. Transport Properties

1. Viscosity

Viscosity is an important property, which is needed for the characterization of momentum, mass, and energy transport within a system. The viscosity of a gas increases with increasing temperature at a moderate pressure whereas that of an SCF decreases (18). This phenomenon is attributed to the higher molecular velocity and increasingly hindered “collision transfer” of momentum at high temperature and pressures. Viscosity of a substance changes by a factor of 3–5 in the critical region rather than orders of magnitude (Table 3). Thus, when pressure is increased, gas viscosity approaches liquid-like value more slowly than does density (19). The viscosity of CO₂ as a function of pressure is shown in Fig. 4. The viscosity of CO₂ is only 0.09 cP even at pressures as high as 300–400 atm, which is an order of magnitude lower than the typical viscosities of liquid solvents (20). As another example, viscosity of supercritical water (Fig. 5) is less than one-tenth of liquid water, and as a consequence its diffusion coefficient and ion mobilities are one order of magnitude greater than those of the liquid water.

Viscosity measurement and relevant estimation techniques for pure and SCF mixtures have been discussed by Vesovic and Wakeham (21) in detail. Magee (16) also reviews the literature related to the viscosity for gas mixtures; however, this kind of information is virtually nonexistent for the SCF-natural product mixtures.

2. Diffusivity

Knowledge of diffusion coefficients in SCF is important to the design and efficient operation of SFE processes. The diffusion coefficient is the proportionality

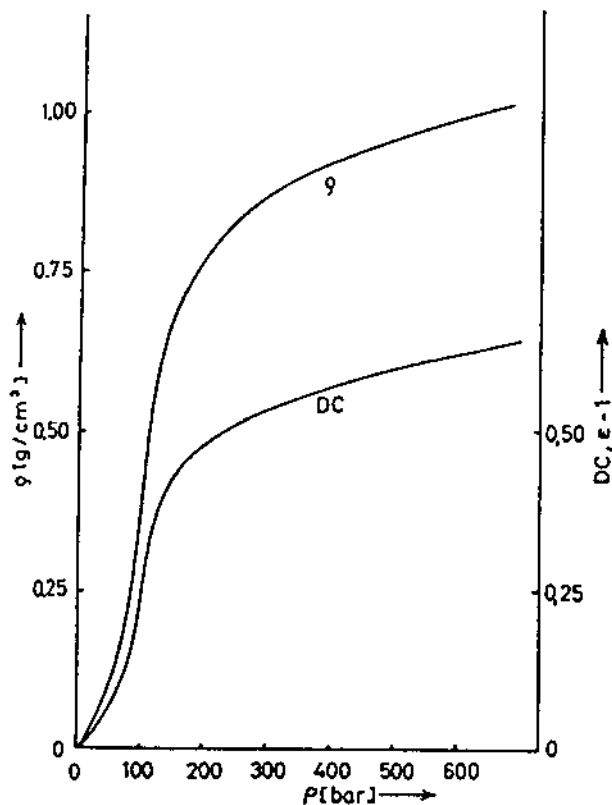


Figure 3 Density and dielectric constant of carbon dioxide as a function of pressure at 50°C (17).

constant between the molecular flux of a compound and its composition gradient. Fick's law defines it as follows:

$$\begin{aligned}
 J_1 &= -D_{12} \frac{\partial C_1}{\partial Z} \\
 J_2 &= -D_{21} \frac{\partial C_2}{\partial Z}
 \end{aligned} \tag{5}$$

where C_1 , C_2 , and J_1 , J_2 are the molar concentrations and fluxes of two components, respectively. Fick's law holds for binary, isobaric mixtures and assumes presence of no external force field. The diffusivity of a pure SCF is orders of magnitude greater than that of a liquid, i.e., liquid CO_2 , which results in im-

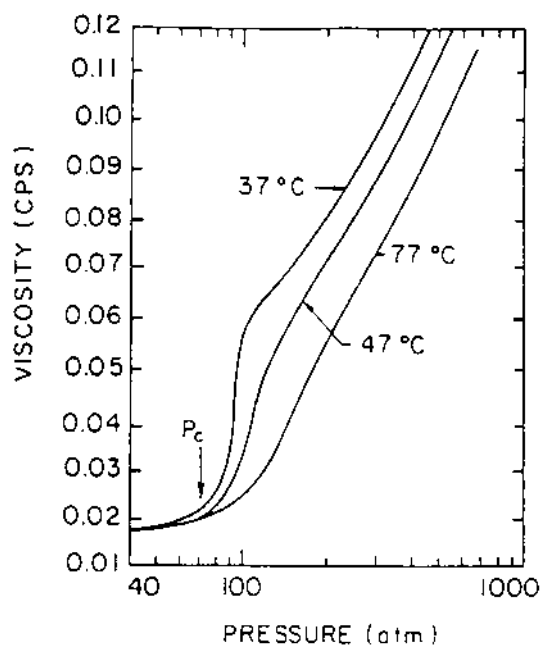


Figure 4 Viscosity behavior of carbon dioxide (20).

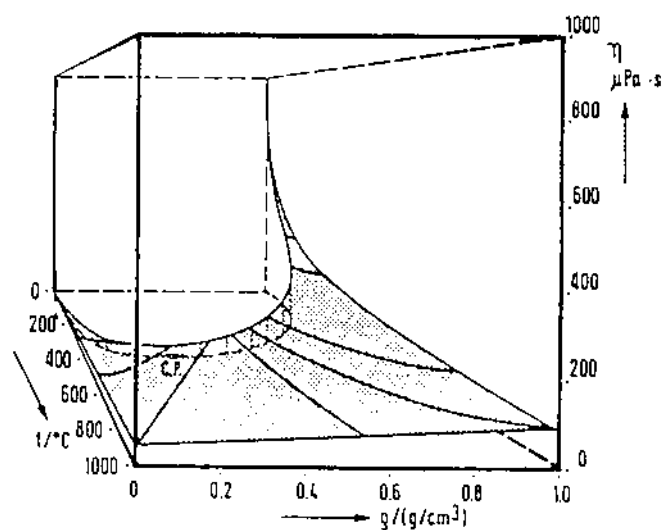


Figure 5 Viscosity of water as a function of density and temperature (18).

proved mass transfer rates during SFE. In general, the binary diffusion coefficient in SCF increases with temperatures and decreases with pressure at constant pressure and temperature, respectively (Fig. 6). Although the effect of composition on diffusion coefficient is quite small at low pressures, it becomes significant at higher densities. Solute diffusion coefficients decrease with increasing solute molecular mass. Furthermore, molecular mobility is hindered if the solute and solvent molecules are significantly different in size.

The experimental methods used to determine diffusion coefficients in SCF

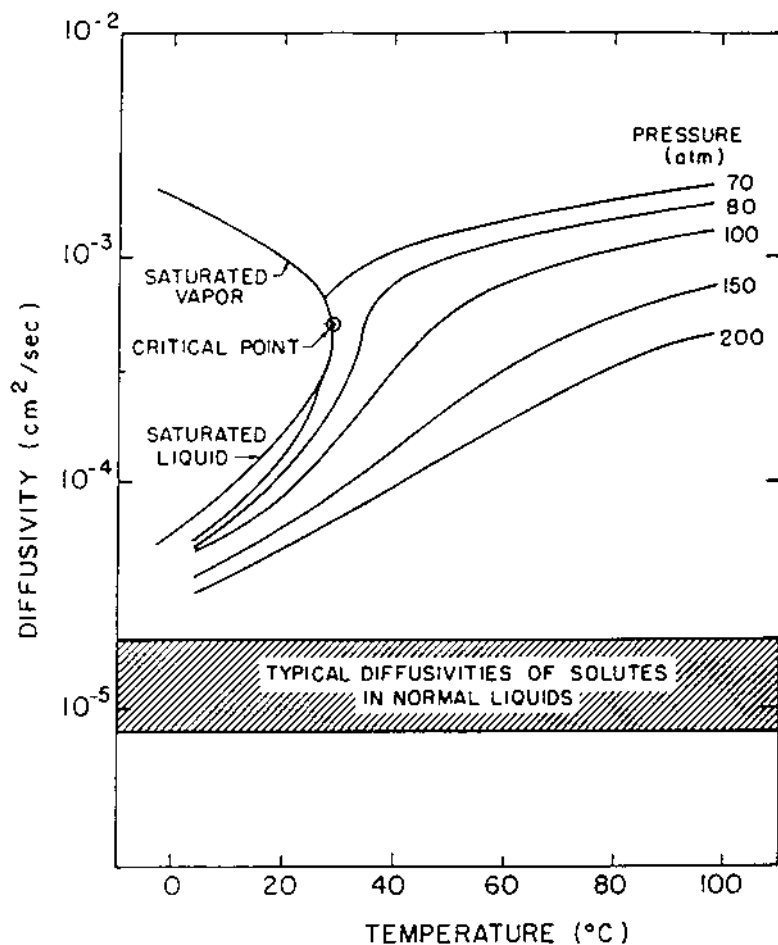


Figure 6 Diffusivity behavior of carbon dioxide (20).

systems, such as solid dissolution, capillary peak broadening, photon correlation spectroscopy, nuclear magnetic resonance, and radioactive tracer response techniques, have been reviewed by Giddings and Seager (22) and Liong et al. (23). Examples of measured diffusion coefficients reported in the literature are for C_{16} fatty acid esters (24), caffeine (25), and C_{18} unsaturated fatty acid methyl esters (26).

3. Heat Capacity and Thermal Conductivity

Heat capacity and thermal conductivity data are needed for the characterization of heat transfer behavior in a system. In the critical region, heat capacity at constant pressure is large and goes through a maximum (Fig. 7) (27). However, heat capacity at constant volume shows only small changes in the critical region (Fig. 7). Angus et al. (28) have reviewed the heat capacity data published up to 1976. Magee and Ely (29) have measured the heat capacity of CO_2 at constant volume, at a larger density range, 0.2–2.5 times the critical density. They also compared their experimental results with those calculated using an extended Benedict-Webb-Rubin equation of state. In general, the measured and calculated heat capacity values agreed well, except that relative errors were higher at the near-critical region. Magee (16) also reviewed the heat capacity data for pure CO_2 and CO_2 -rich mixtures.

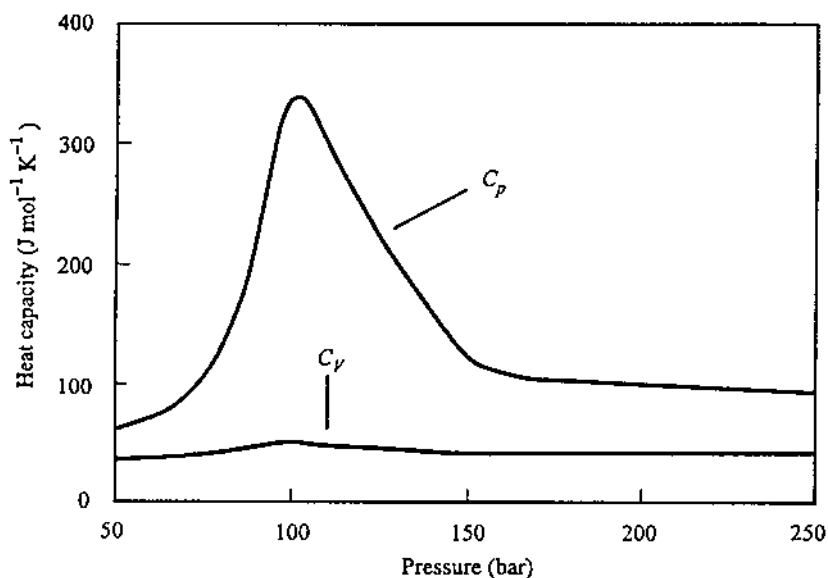


Figure 7 Heat capacities for carbon dioxide at 320 K (27).

Thermal conductivity of fluids has been recognized as an important transport property, which is needed for the design of the SFE process equipment. Thermal conductivity “ λ ” is a proportionality constant between the heat flux, Q , and the temperature gradient that exists in the fluid. The Fourier’s law defines it as follows:

$$Q = \lambda \nabla T \quad (6)$$

For most SCFs thermal conductivity increases with increasing temperature and density of the system. Table 4 shows the thermal conductivity data for water and CO₂ as a function of temperature at several pressures.

The Transient Hot-Wire Technique and The Coaxial Cylinder Method are two techniques that are used to measure thermal conductivity of SCFs over a wide range of conditions (21). Although the Eucken expression and correlations based on the work of Dymond had been used to estimate thermal conductivity of dense fluids, the calculated values did not agree well with the experimental data (21). Nieto de Castro (30) has reviewed the literature on the thermal conductivity in SCF.

III. EQUILIBRIUM PROPERTIES

A. Phase Equilibrium

Process modeling and operating conditions, as well as economic feasibility for an extraction process, require information on phase equilibria between the solute(s) and solvent(s) involved. This information can be obtained experimentally or via phase equilibrium calculations. Phase equilibrium calculations require an equation of state, which describes the mathematical relation between volume, pressure, temperature, and composition in the system. Deviations from ideal gas law are expressed in the equations of state such as van der Waals [Eq. (7)] and Redlich-Kwong (31) or Peng-Robinson equations (32).

Table 4 Thermal Conductivity [λ (mW/mK)] of Some Fluids Used in SCF Technology (21)

	$T = T_c + 20 \text{ K}$		$T = T_c + 100 \text{ K}$		$T_c \text{ (K)}$
	$P = 0.1$ MPa	$P = 10$ MPa	$P = 0.1$ MPa	$P = 10$ MPa	
CO ₂	18.8	51.1	25.5	31.9	304.1
H ₂ O	54.0	67.8	63.7	73.0	647.1

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \quad (7)$$

where a and b are the constants specific for each gas. The van der Waals equation of state assumes that molecules restricted to a volume $(V - b)$ and repulsive interactions cause molecules to behave as small but impenetrable spheres. Attractive forces between molecules reduce the pressure exerted by a real gas. The critical constants can be calculated from the van der Waals equation by setting the first and second derivatives of Eq. (7) with respect to zero to obtain the following relations:

$$V_c = 3b; P_c = \frac{a}{27b^2}; T_c = \frac{8a}{27Rb} \quad (8)$$

Through algebraic manipulation, then, the critical compression factor, Z_c , can be given as:

$$Z_c = \frac{P_c V_c}{RT_c} = \frac{3}{8} \quad (9)$$

In a similar fashion, dimensionless reduced properties of a gas can be expressed as ratios of the respective critical properties, as:

$$P_r = \frac{P}{P_c}; V_r = \frac{V}{V_c}; T_r = \frac{T}{T_c} \quad (10)$$

The “law of corresponding states” (33) states that if reduced variables are used to define the state of gases, all gases show the same PVT behavior; in another words, two different gases, each at the same P_r and T_r , will have the same V_r . Using this analogy, van der Waals’ equation can also be written in terms of reduced variables as:

$$P_r = \frac{8T_r}{3V_r - 1} - \frac{3}{V_r^2} \quad (11)$$

This equation eliminates the constants a and b and provides a more direct method of estimating physical properties. Other equations of state, their mixing rules (13, 34–36) along with PVT surface measurements, and their correlations for a number of fluids (37), are available in the literature.

Models describing equilibria between SCF and condensed phases are classified in two groups: fluid–liquid and fluid–solid equilibria (31, 38–41). Van Konyenburg (42, 43) developed a system for classification of phase behavior for binary fluid mixtures. This system groups the phase behavior of fluid mixtures into six general types, which are distinguished by the behavior of their critical lines (20, 32, 44). Rizvi et al. (32) has reviewed the phase diagrams of

class I and class III mixtures for representative of typical biomaterials of interest to the food industry. Modeling of such phase equilibria shows highly nonideal behavior due to the complexity of these natural products, which vary enormously in molecular size and chemical nature. Despite these complexities, equations of state have been developed to predict phase behavior of natural substances such as fatty acid esters (45), vegetable oils (46), rapeseed oil (47), and limonene (48) in SCFs.

The equations of state calculations require the knowledge of acentric factor, ω , which is defined as follows:

$$\omega = -\log P_{\text{vpr}} - 1 \quad (12)$$

where P_{vpr} is the reduced vapor pressure at $T_r = 0.7$.

The acentric factor is a macroscopic property that measures the extent to which the force field around a molecule deviates from spherical symmetry. The acentric factor is practically zero for small, spherical, or highly symmetrical and nonpolar molecules.

Several experimental and predictive methods for the determination of the acentric factor of compounds have been reported in the literature (13). Araujo and Meireles (45) used Tu's (49) indirect method and correlation of Vetere (50) to estimate the acentric factor for high and low molecular weight fatty acids, respectively. The study showed that acentric factor of the compounds increased with increasing carbon number and linearly decreased with increasing double bond in the chemical structure.

B. Solute Solubility

The development of mathematical models describing the solubility behavior of solutes in SCFs requires an understanding of intermolecular interaction among solute and solvent, as well as solute and solute. Thus, the vapor pressure and the solute-solvent intermolecular interactions are key properties that determine the solubility of a solute in a supercritical solvent. The effect of temperature on solubility manifests itself in the solute's vapor pressure, the SCF's density, and molecular interactions in the supercritical phase. At low pressures, solubility decreases with increasing temperature due to the lower SCF density. However, at higher pressures, the SCF's density is only slightly affected by temperature, so that solute solubility increases with temperature through its effect on solute vapor pressure.

In the highly compressible near-critical region, it is also known that the solvent "clusters" around the solute due to the attractive intermolecular interactions (23). This effect is especially important in entrainer systems because abnormally high local solvent density around the solute may preferentially attract entrainer to the solute. Unfortunately, many solubility models assume infinite

dilution of a solute in a solvent (SCF) and no solute–solute interactions. However, there is experimental and computational evidence that strength of solute–solute interaction may be strong in very dilute solutions (14).

One measure of solvent power (capability of a solvent to dissolve various solutes) of an SCF can be described qualitatively by the solubility parameter approach (51). The concept of solubility parameter was first defined for liquids in the condensed phase by Hildebrand and Scott (51) as follows:

$$\delta = \left(\frac{-E_v}{V_l} \right)^{1/2} \quad (13)$$

where E_v and V_l are heat of vaporization and molar liquid volume, respectively.

A liquid's solubility parameter is theoretically calculated knowing the heat of vaporization and molar volume of the liquid. Relating the solubility parameter to the energy of vaporization for dense gases is conceptually difficult because the heat of vaporization becomes zero at a solvent's critical temperature and the vaporization process cannot occur under supercritical conditions. However, Giddings (52) has combined the van der Waals equation with the theory of corresponding states, to yield an empirical relationship, where the solubility parameter is defined by the following formula:

$$\delta = 1.25 P_c^{1/2} \left[\frac{\rho}{\rho_{\text{liq}}} \right] \quad (14)$$

where P_c , ρ , and ρ_{liq} are critical pressure and density of gas and liquid, respectively.

When the solubility parameter defined by Eq. (14) is plotted against pressure, the relationship depicted in Fig. 8 resembles that of density vs. pressure (Fig. 2). At infinite compression, the SCF's solubility parameter in Eq. (14) reduces to:

$$\delta_{\text{liq}} = 1.25 P_c^{1/2} \quad (15)$$

where $\rho = \rho_{\text{liq}}$, approximating the solvent power of a gas in its liquid state.

Returning to Eq. (14), the solubility parameter is a function of density, which is a state variable. The contribution of δ_{liq} to δ is known as the “chemical effect” and is dependent on the choice of SCF, while the contribution of ρ/ρ_{liq} is attributed to the “state effect” (53). Under supercritical conditions, a large δ is obtained when pressure is high and temperature is slightly over the T_c . The solubility parameter of the fluid may vary from zero at low pressures up to liquid-like values $\sim 10 \text{ (cal/cm}^3)^{1/2}$ at ultrahigh pressures. SCFs have solubility parameter values in the range of 0–10 $(\text{cal/cm}^3)^{1/2}$ (53). King and Friedrich (54) utilized the concept of reduced solubility parameter as a measure of the solute–

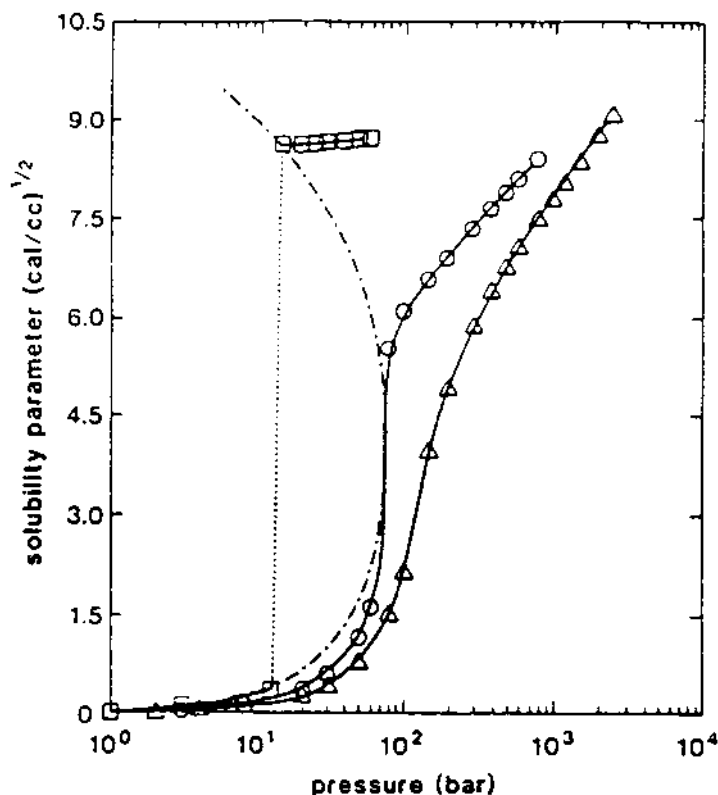


Figure 8 Solubility parameter vs. pressure plot for carbon dioxide (97).

solvent interactions to correlate solubility and distribution coefficients in supercritical and near-critical fluids.

The molecular structure of a solute influences its solubility in an SCF (54, 55). Stahl and Quirin (56) were the first to report that the presence of polar functional groups such as OH, C=O, and COOH in a molecule significantly reduced the solubility of a compound in SC-CO₂. Solubility studies utilizing sterols indicated that increasing the number of carbon-carbon double bonds decreased the solute's solubility in SCF (55).

Substantial work has been carried on the measurement and prediction of solubility of lipid components in SCF, specifically SC-CO₂. The literature on solubility of seed oils in SC-CO₂ has been reviewed by King (56). For example, Eisler and Friedrich (57) used the Fujishiro and Hildebrand equation (58) to

estimate vegetable oil solubility parameters in SC-CO₂ and reported that calculated values compared reasonably well with the experimental literature data. Similarly, Chastiril (14) determined solubilities of a number of lipid components such as stearic and oleic acid, tripalmitin, butylin, and olein. Solubilities of α -tocopherol, cafestol, cholesterol, and water were also measured in pure CO₂ in the range of 40–80°C and 8–25 $\times 10^6$ Pa (14). Chastiril's study (14) has related solute solubilities directly to density of SCF rather than using the equations of state for the prediction. The solubility of relatively polar compounds such as free amino acids, e.g., glycine, phenylalanine, tryptophan, and leucine, and sugars such as D-glucose and D-xylose in pure CO₂ at 40°C and 5–20 $\times 10^7$ Pa were also reported, and solubilities of these compounds were very low, of the order of 10^{-7} – 10^{-8} mole fraction (59).

C. Solvent Selectivity

The selectivity can be defined as the ability of a solvent to dissolve the desired compound to a greater extent than the other constituents of the mixture. Selectivity of an SCF for component 2 vs. component 1 is defined as:

$$S = \frac{y_2}{y_1} \quad (16)$$

where y_1 and y_2 are the binary solute solubility of components 1 and 2, respectively.

The selectivity of an SCF can be tuned by regulating temperature and pressure of the fluid. This phenomenon allows the use of SCFs for selective extraction and fractionation processes.

Selectivity and solubility of a compound are primarily related to the solute vapor pressure and only secondarily to the intermolecular forces in the supercritical phase (55). For example, although the vapor pressure of both cholesterol and ergosterol is negligibly small, selectivity of SC-CO₂ for cholesterol is almost two orders of magnitude higher than that of the ergosterol due to the fact that vapor pressure of ergosterol is lower (10^{-5} – 10^{-6} Pa) than that of cholesterol (10^{-3} – 10^{-4} Pa), showing that selectivity follows the ratio of vapor pressures (55).

D. Enhancement Factor

Frequently in SCF technology, a term called the enhancement factor, E , is utilized to describe the propensity of a solute to partition into a SCF. The enhancement factor normalizes the effect of vapor pressure, allowing an estimate to be made of solute–SCF interactions in the supercritical phase, and is defined as follows (44):

$$E = \frac{y_{\text{actual}}}{y_{\text{ideal}}} \quad (17)$$

and

$$y_{\text{ideal}} = \frac{P_s}{P} \quad (18)$$

where y_{actual} = actual solute solubility in SCF, y_{ideal} = solubility in ideal gas, P_s = vapor pressure of the solid, and P = pressure of the system.

The solubility of a solute in a solvent changes rapidly near the critical region, and this is reflected in the enhancement factor. Enhancement factors of the order of 10^5 – 10^7 are common for solubilization of solutes in SCF. For example, enhancement factors are the same ($\sim 10^7$) for cholesterol, stigmasterol, and ergosterol in CO_2 at 35°C and 200 atm, which indicates that the sterol- CO_2 attractive forces are similar for these sterols (55). Therefore, as noted above, fractionation of the sterols via SFE is basically dependent on the vapor pressure of the components.

IV. MASS TRANSFER

A. Mass Transfer Principles

The economical scale-up and design of commercial SFE processes requires mass transfer data for the system. Even though SFEs have excellent mass transfer properties, such as gas-like diffusivity and viscosity, practically no surface tension contribution at interface, liquid-like density, or pressure-dependent solvent power; SFE processes still have mass transfer limitations. For example, if the rate-limiting step or the largest mass transfer resistance of a separation process is the transfer of the solute from the surface of a solid to the SCF phase, the gas-like diffusivity of a SCF will enhance diffusion and consequently speed up the extraction. However, if the extraction is from a liquid phase into a SCF phase, mass transfer in the liquid phase will be the rate-determining step. Similarly, if the extraction is occurring from within a solid, then the internal solid phase diffusion will control the rate of mass transfer. It has been established by the experimental measurements that initially at high solute concentrations in the solid matrix, the mass transfer rate from a solid matrix into a SCF is constant. This region of the extraction curve is referred to as steady-state or solubility-controlled mass transfer region. However, after a certain amount of material is extracted, this rate starts to decline and the region is called diffusion-controlled mass transfer region (56). A typical SFE curve for oil production from a solid matrix is shown in Fig. 9 (60).

Interfacial tension (IFT) is an important parameter that influences mass

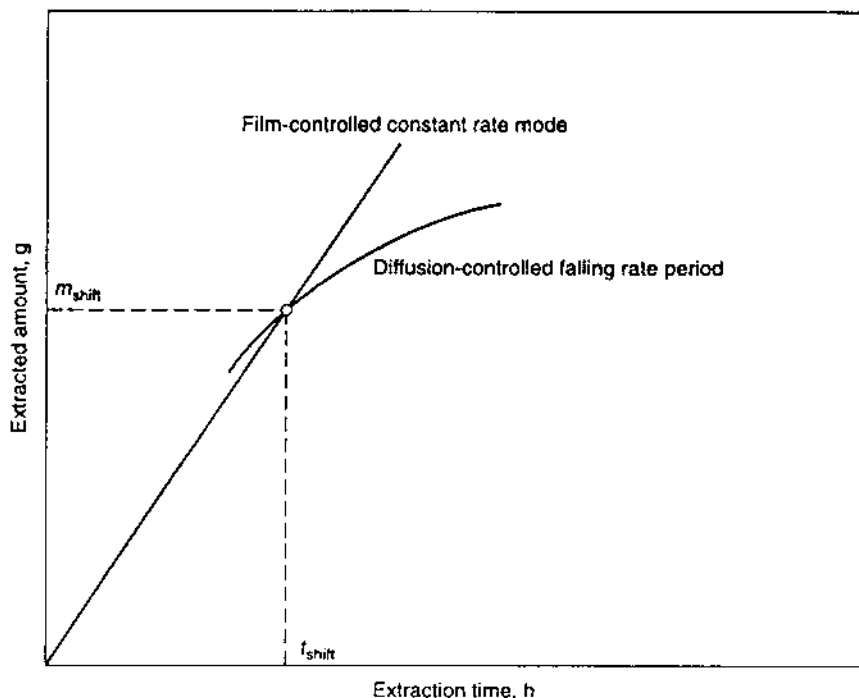


Figure 9 A typical curve for an SCFE process (60).

transfer and solubility of compounds in SCFs. Packed columns have been used for fractionation of liquid mixtures utilizing SCF technology. The design of such systems requires mass transfer data, including the wetting characteristics of the packing surface by the fluid. Literature on the study of IFT in SCF is scarce and usually deals with model systems. However, Simoes et al. (61) reported the data on the IFT of crude and refined corn, coffee, and citrus oils in SC-CO₂. It was shown that IFT of the oils decreased with increasing pressure (61). This phenomenon was explained by the breakup and eventually disappearance of the oil droplets on the packing material surface, with increasing pressure. Experiments carried out with corn oil demonstrated that the decrease in IFT was larger above 20 MPa, and at lower pressures only slight changes in IFT were recorded (61).

B. Mass Transfer Models

Fundamentals of SFE processes for natural materials and food systems are not well defined due to the complex nature of the matrix and difficulty in obtaining

mass transfer data under high pressure. The majority of the SFE mass transfer models published in the literature are based on extraction of oil (60, 62, 63). A number of researchers have attempted to simulate mass transfer rates in SCFs by using different approaches, such as empirical kinetic models, linear driving force approximations, the shrinking core leaching model, and local adsorption-desorption technique. For example, Brunner (64) used dimensionless numbers such as Sherwood, Schmidt, and Reynolds numbers to derive correlations for mass transfer coefficients in various solid fixed-bed SFE processes, i.e., coffee beans and oil seeds. It was shown that extraction rate of whole coffee beans was limited by the diffusion rate of caffeine within the solid matrix. Peker et al. (65) also studied a similar system and developed a mathematical model based on a linear driving force approximation of mass transfer and partitioning of caffeine between the water and the SC-CO₂. A similar approach was applied to spice extraction by Goto et al. (66). In this study, the SFE of peppermint oil was described by a mathematical model that accounted for both local adsorption of essential oil on lipids in the peppermint leaves and mass transfer from a solid matrix to SCF.

Bulley et al. (67) and Lee et al. (68) used a one-dimensional, un-steady-state mathematical model to describe the SFE of a fixed bed of crushed canola flakes. This method assumed plug flow within the seed bed and that axial dispersion was negligible. They calculated canola oil concentration profiles in both SC-CO₂ and solid phases and determined overall volumetric mass transfer coefficients. The model adequately described the constant-rate period of the extraction process. Cygnarowicz-Provost (60) used a similar model but included mass transfer coefficients that represented both constant-rate and diffusion-controlled regimes for the determination of caffeine extraction rates in SC-CO₂. Likewise, the SFE of grape oil has been simulated using a plug flow model, allowing mass transfer coefficients in both solid and supercritical phases to be calculated (69). Another mass transfer model, which was applied to SFE of oils from herbaceous matrices (70), assumed that diffusivity of the solute in the solid matrix was the only variable in the system.

The shrinking core leaching model may be used when the solute to be extracted constitutes a large portion of the solid matrix and is held in the macropores by mechanical or capillary forces as a condensed phase. This model assumes that a sharp boundary exists between a core of material to be extracted, and an outer region, in which only partially saturated SCF exists in the pores. The shrinking core leaching model is valid where the diffusivity of the solute in SCF is much larger than that of the solvent in the solid. Simulation of such a system requires mathematical description of a moving core boundary, which shrinks nonlinearly due to the depleting solute in the pores during the extraction process. Therefore, the following assumptions may be made to simplify the calculations; a pseudo-steady-state diffusion mechanism for extraction from the outer porous layer, negligible fluid velocity at the interface, and the radius of

the core can be determined by a simple mass balance (62). The shrinking core leaching model has applied to ginger oil (71) and freeze-dried mackerel powder (72).

Another example of the mass transfer simulation efforts in food-related systems was published by Dunford et al. (73). They developed a mathematical model to describe the dynamic extraction behavior of oil and water from Atlantic mackerel at different moisture levels. Their model incorporated the interactions between oil and water in the SC-CO₂. This model accurately simulated the experimental data in the solubility-controlled region for the above extraction.

V. ENTRAINER EFFECT

Addition of an entrainer, which is also referred to as cosolvent, or modifier to a mixture containing a supercritical component can modify the extraction selectivity markedly. Entrainers, which are mostly liquids usually having solubility parameters larger than the SCF component, can be used to increase solvent power of an SCF in addition to density adjustment of the extraction fluid. Hexane, benzene, chloroform, isopropanol, methanol, ethanol, acetone, and water have all been used as entrainers. Ethanol is the preferred entrainer for food applications because it is not toxic and is approved as GRAS (generally recognized as safe) status component. Entrainers are usually chosen to interact specifically with targeted solute, through hydrogen bonding, acid–base interactions, or strong dipole–dipole interactions. Entrainers also increase yields, then, by decreasing the pressure and solvent requirements in SFE. Entrainers can affect the extraction process in many ways: by increasing the volatility of the solutes, by increasing the density of an SCF, by potentially dilating a liquid condensed phase, or by enhancing the miscibility of the components. An entrainer normally increases the solubility of nonvolatile compounds in an SCF by shifting the equilibrium of the binary mixture and/or by shifting the critical point of the solvent phase. Entrainers, which as noted previously are more polar compounds than SC-CO₂, can form electron donor–acceptor complexes, i.e., hydrogen bonds, with polar solutes to increase solubilities and selectivities beyond what would be expected based on solubility in the neat SCF. Supporting evidence for the above trend, particularly increasing solute solubility in SCF, was recorded for the addition of a modest amount of cosolvent (less than 10%). For example, Dobbs et al. (74) showed that the solubility of 2-aminobenzoic acid was increased by 600% by the addition of 3.5% methanol into SC-CO₂. Several thermodynamic models have been developed to correlate and in some cases to predict the effects of entrainer on solute solubilities in SCF (3).

In a related phenomenon, when dry almonds are extracted with SC-CO₂ at 40°C and 6×10^7 Pa, an oily extract containing the flavor components is

achieved (75). However, when the extraction is carried out in the presence of ethanol, two phases—an oil phase free of flavors and an ethanol phase containing flavor components with a small amount of oil—were obtained (75). Influence of an entrainer has also been shown for the extraction of caffeine from coffee beans, where neat SC-CO₂ extraction of dry coffee beans cannot efficiently extract the caffeine as a moist coffee bean (5). Another study showed that the pleasant flavor of tea could be extracted with SC-CO₂ in the presence of water; however, isolation of flavors by evaporating the water was not possible since most of the flavor components were removed azeotropically during evaporation (75).

An excellent example of where entrainer-based SCF separations are necessary is in the fractionation of polar solutes from nonpolar moieties using SC-CO₂. Thus, substantial differences in the polarity of molecules, such as neutral oil components (triglycerides) and polar lipids (phospholipids), can be exploited for fractionation purposes with the aid of an entrainer such as a GRAS-approved ethanol. For example, Dunford and Temelli (76) and Montanari et al. (77) studied the extraction of phospholipids from canola and soybean lipids, respectively, using SC-CO₂ and ethanol mixtures. Initially, neutral lipids were extracted with SC-CO₂ and then ethanol was added to SC-CO₂ as an entrainer to enhance the extraction of the relatively polar phospholipids.

VI. CRITERIA FOR SOLVENT SELECTION

The critical temperature and pressure of a compound are two very important physical properties, when selecting an appropriate solvent for an SFE application. If fluids with high P_c are chosen as solvents, the extraction process will be potentially more expensive due to the higher cost of equipment, which will need to be designed and manufactured for use at high pressures. If T_c of the solvent is exceedingly high, then heat-sensitive materials could be affected adversely during the SFE process.

The chemical stability of the solvent under the processing conditions is another important criterion that should be considered in solvent selection. The chemical decomposition of a number of SCF-entrainer mixtures has been reported in literature (37). As an example, methanol can be very unstable in the presence of stainless steel (37). SFCs should also be inert with respect to the processed raw material to avoid reactions during the extraction process. Low-boiling fluids should be preferred as supercritical solvents for ease of removal after processing. The ideal solvent of choice should also be inexpensive, nonflammable, nonexplosive, noncorrosive, nontoxic, and readily available in high purity. Carbon dioxide fulfills those requirements as a fluid for applications of SFE technology for food processing, and it is preferentially used.

VII. EFFECT OF MATRIX COMPOSITION AND STRUCTURE ON SFE YIELDS AND RATES

Extraction yield is an important parameter, which greatly affects feasibility of a production process. Stahl et al. (78) and Friedrich et al. (79) concurrently reported that the yield of an SFE process is influenced by the size and physical structure of the oilseeds. They showed that oilseeds had to be ground to assure complete extraction of the oil. It was also noted that the shape of the ground seeds as well as their size affected the SFE of oil. Similarly, Snyder et al. (80) illustrated that oil yields were quite low with cracked soybeans; however, theoretical yields were obtained from ground or thinly flaked seeds. Similar results were reported with rapeseed (80) (Fig. 10) and canola (81).

Water is present in all biological materials at varying concentrations and plays an important role in the SFE and mass transfer kinetics. In some cases, a matrix's moisture content determines the surface structure and/or activity of the components, such as enzymes. High moisture content may provide an aqueous barrier inhibiting diffusion of SC-CO₂ into the matrix as well as diffusion of oil out of the matrix. An example of this phenomenon has been demonstrated by King et al. (82). Here it was reported that the yield of fat extraction with SC-CO₂ decreased with increasing moisture content of the beef samples.

The presence of water in the matrix may act as an entrainer and improve the selectivity of SCF for a solute, i.e., caffeine extraction from coffee beans in the presence of water, which was mentioned earlier in this [chapter \(5\)](#). During

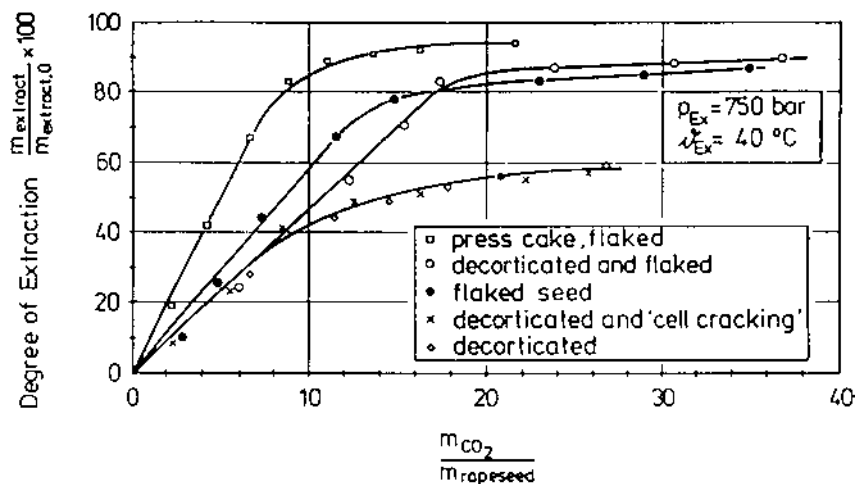


Figure 10 SFE yields as affected by the size of the oilseeds (78).

essential oil extraction, polar component solubilities in SC-CO₂ were improved at higher moisture content in the sample matrix (83, 84). Swelling of plant materials in the presence of water may also be quite significant for extraction because it widens plant cell capillaries, thereby increasing the matrix porosity with subsequent improvement in solute diffusion (85). This phenomenon reduces the extraction time or may even make an extraction possible. It is important to note that water present in the feed material may be coextracted along with the compounds of interest, affecting the quality and purity of the final product. This effect was demonstrated for oil extraction from canola flakes and fish muscle using SC-CO₂ by Dunford and Temelli (86, 87).

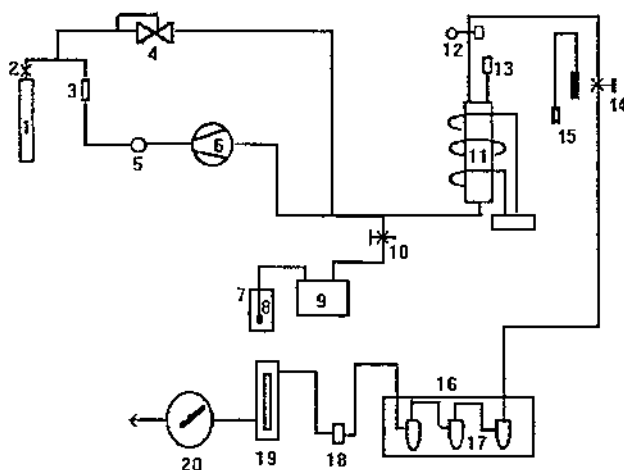
VIII. SCF PROCESSING SCHEMES

A. Extraction

A schematic diagram of a basic SFE process is shown in Fig. 11. As noted in the figure, the major equipment components are the extractor, separators, heat exchangers, pumps, and compressors. If desired, more than one extractor can be connected to the same system. The selection of equipment for a food processing system must ensure a sanitary and safe process. All surfaces, including seals and gaskets, in contact with process fluids and solids must be suitable for food processing and sterilization. Construction materials and fittings must be suitable for the pressure and temperature conditions required by the process.

The solvent, i.e., CO₂, is pumped into the system as a liquid or gas. If the solvent is pumped as a liquid, it will be cooled in a reservoir or it will be kept in liquid phase by cooling the pump head. Depending on the process requirements a system for entrainer addition can be incorporated into the system. Methods for entrainer addition to an SCF system were reviewed by Dunford (88). The fluid is then pressurized and heated to the desired processing conditions. A solvent preheater can be installed into the system to avoid temperature fluctuations due to the solvent being pumped into the system at a lower temperature. In the case of solid feed material processing, the matrix to be extracted will be packed into the extraction cell in a mesh basket or between frits to prevent its being carried from the cell during extraction. Following extraction, the pressure is reduced to precipitate the extract through a control valve. A high-pressure metering valve can control the flow rate of the fluid. The pressure of the system is controlled by the rate of pumping and a back-pressure valve setting. A computer system can be used to control the extraction conditions.

Choosing a continuous process rather than a batch or semicontinuous process may significantly improve the economics of an industrial scale process. Continuous transport of a large volume of solid feed, such as oilseeds, into and out of a high-pressure extractor is costly and difficult. However, advances in



- | | | |
|--------------------------|-------------------------------------|---------------------------|
| 1-CO ₂ tank | 8-filter | 15-temperature controller |
| 2-valve | 9-ethanol pump | 16-cooling bath |
| 3-CO ₂ filter | 10-valve | 17-collection tubes |
| 4-pressure regulator | 11-extractor | 18-silica trap |
| 5-pressure gauge | 12-extractor temperature controller | 19-flow indicator |
| 6-compressor | 13-rupture disc | 20-flow totalizer |
| 7-ethanol reservoir | 14-depressurization valve | |

Figure 11 Typical flow diagram for a SFE process.

high-pressure technology may allow continuous feed of solid materials. Today an extractor design that allows intermittent loading and unloading of solid material through the lock-hopper vessels fitted below and above the extractor while it is pressurized is used in the coffee-decaffeinating plant in Houston, Texas (20). A portion of the solid is discharged to the bottom hopper, while fresh feed is simultaneously charged to the extractor from the top hopper. In the meantime, SCF continuously passes through the extractor countercurrently relative to feed. Such an extractor design has several advantages. Sequencing these operations minimizes raw material feeding and vessel unloading times. The compression costs are lowered since feed loading and unloading are carried out simultaneously while maintaining pressure.

Simulated moving-bed technique has been developed (89) in an effort to approach a countercurrent solid–fluid extraction process. In this method, a single fixed-bed column is subdivided into several zones. The apparent movement of the solid is achieved by switching between valves connected at the junctions

between zones. The solid and extract withdrawal ports are periodically shifted in the direction of the solid movement and opposite to the fluid flow, thus simulating a countercurrent process. This technique has been applied to extraction and fractionation of tocopherol from oleic acid (89) and fragrance and essential oil extraction (90).

B. Fractional Extraction

Fractionation of components of a mixture can be achieved by various modes of fractional extraction. One fractional extraction method is to collect fractions as a function of time throughout a semicontinuous process. In such a case, the extract composition changes over time due to the changes in the composition of residual material in the extractor. Components that have higher solubility under the initial processing conditions will be selectively extracted in the beginning. Then, as these components are depleted from the matrix, the extraction selectivity will shift to other components. A good example of this behavior would be during SFE of oilseeds. Friedrich and Pryde (91) showed that the amount of phospholipids extracted from full-fat soybean flakes with SC-CO₂ increased in the fractions collected toward the end of the extraction process.

Fractional extraction can also be achieved by increasing solvent density over time. This mode of extraction using incremental pressure programming has been applied to fish oil ethyl esters (92), rice bran oil (93, 94), and phytosterol recovery from vegetable oil deodorizer distillates (95). Fractional extraction using an entrainer in the supercritical phase is another approach, which was discussed earlier in this chapter (76, 77).

C. Column Fractionation

SFE from a liquid phase can be performed utilizing a vertical column. This process is also frequently referred to as supercritical fluid fractionation (SFF). The feed may be a liquid mixture or a solution containing solutes that are solids under extraction conditions or at slurry of solid particles. The column is usually filled with a packing material or has an internal structure such as trays or baffles to increase the contact area between fluid solvent and feed material and to enhance mass transfer. The process can be carried out in semicontinuous or continuous mode. The feed and solvent could be in the batch and continuous modes during the semicontinuous and continuous processes, respectively. Continuous column operations tend to be more efficient and the feasibility of the operation can be improved. Countercurrent operations are inherently more efficient than concurrent operations due to the larger concentration difference between solvent and feed stream, which results in better mass transfer rates.

A schematic diagram of a typical countercurrent SFF process is shown in Fig. 12. The feed is pumped into the column near the top, or at a point between the column top and base, or from the bottom of the column. Because of their relative densities, the liquid phase descends while SCF phase rises through the column during a countercurrent operation. The stream leaving the top of the column contains the extract and the liquid leaving the bottom of the column is the raffinate. The column can be operated at constant temperature, or a temperature gradient can be imposed above the feed entry point. Thermal gradient imposed on the column causes condensation of larger molecules in the extract

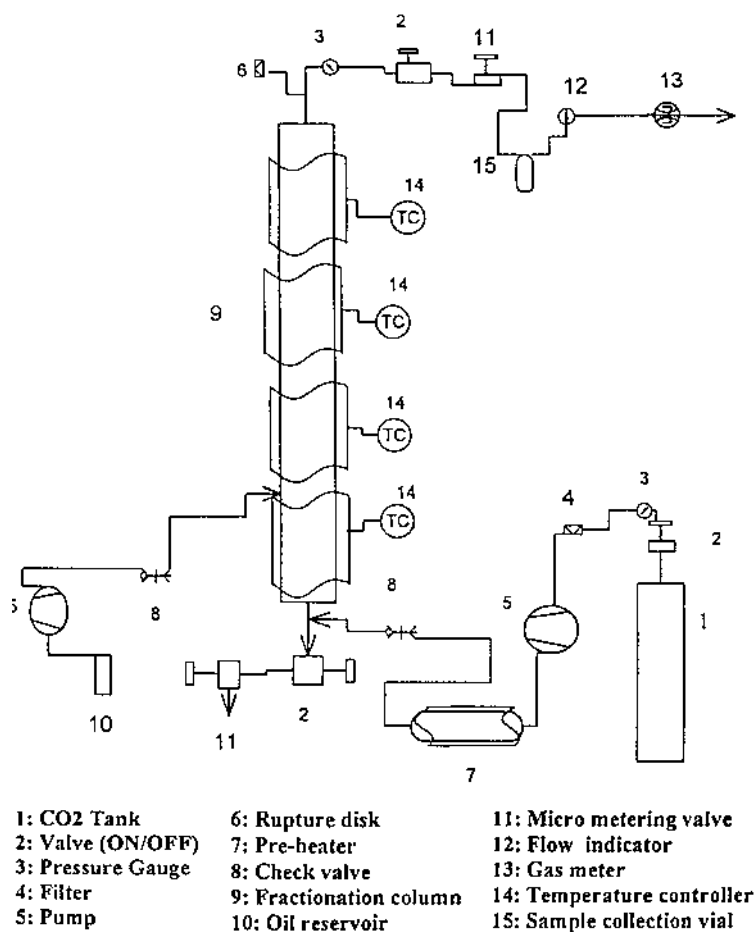


Figure 12 Flow diagram for a SFF process.

stream upon their encountering the lower solvent density at higher temperatures upward in the column under isobaric conditions, thus creating an internal reflux in the column. This process is similar to liquid–liquid extraction with reflux and fractional distillation. Refluxing can improve the extract purity if the process is designed properly. Analogous to terms used in distillation and liquid–liquid extraction process with reflux, the lower and upper parts of the SFF column are referred to as stripping and enrichment sections, respectively. The book by Clifford (27) is an excellent reference for a discussion of the fundamentals and mathematical modeling of SFE and SFF processes.

IX. EXTRACT AND SOLVENT RECOVERY

Recovery of extracted compounds is usually done by lowering the pressure. Hence, high molecular weight solutes in an SCF can usually be precipitated or phase separated at higher collection pressures than more volatile substances. Fractional separation of extracted solute mixtures can also be achieved in a series of collection vessels by successively lowering pressure on each vessel. This method has been successfully applied to essential oils and spice extracts by Reverchon (96) and Nguyen et al. (8), respectively.

Increasing the extract temperature at constant pressure may be another alternative for extract recovery. This method can be used if the solubility of a compound decreases with increasing temperature. This is what occurs mostly with nonvolatile compounds. This method also improves the feasibility of an SFE process by eliminating recompression of the solvent for recycling.

Solute recovery by partial depressurization might not be very successful if the solute is a very volatile compound. In such a case, adsorptive recovery methods might be more effective. For example, the solute may be adsorbed on silica, alumina, or active carbon and then separated from the adsorbent at a higher pressure or by thermal desorption, among other options. Use of molecular filters such as zeolites is another method for extract recovery from SCF. In such a case, pore size of the filter media is chosen such that only fluid passes through the filter (permeate) and extracted solute is recovered as retentate (27).

Solvent separated from the solute by means of one of the methods mentioned above can be either vented out to atmosphere or recycled to the system depending on the size of the operation. For small-scale equipment such as laboratory scale SFE units, solute-free gas is vented to the atmosphere due to the higher cost of installing a recycling system as compared with the cheaper gas cost. If the solvent is to be recycled, which is the case for pilot and industrial scale operations, it is usually passed through an adsorbent bed before it is pumped back into the extractor.

X. CONCLUDING REMARKS

As was noted in this chapter, SCF extraction offers considerable versatility for the extraction of food-related products and raw materials. In general, the overall SFE process is simple, embodying many of the principles inherent in other extraction processes. New approaches for the continuous handling of solid and liquid materials, in and out of extraction vessels, continues to evolve, and improved equipment design and operational dynamics are making SFE processes much more efficient and competitive. However, in some product applications, SCF technology faces competition from conventional techniques such as molecular (vacuum) distillation, a time-honored technique, although greater selectivity is potentially available from SFE using the described methods.

In closing, we would like to offer the following short list of “critical” references that will supplement the material discussed in this chapter. Although this list is not inclusive of all available literature resources, it should assist the reader wishing to learn more about this novel technology and abets the formal references cited in this chapter.

NOMENCLATURE

P	pressure
V	volume
N	number of moles
R	gas constant
T	temperature
T_c	critical temperature
P_c	critical pressure
V_c	critical volume
Δ_T	group contribution constant at constant temperature
Δ_P	group contribution constant at constant pressure
Δ_V	group contribution constant at constant volume
P_r	reduced pressure
T_r	reduced temperature
T_b	boiling temperature
ρ	density
ρ_c	critical density
ρ_r	reduced density
a	van der Waals constant
b	van de Waals constant
δ	solubility parameter
E_v	heat of vaporization

E_p	potential energy of interaction
ϵ	permittivity of the medium
ϵ_r	relative permittivity, or dielectric constant
ϵ_0	permittivity in a vacuum
q_i	point charge for compound i
r	distance between the charges
J_i	molar flux for compound i
C_i	molar concentration for compound i
D_{ij}	binary diffusion coefficient for component i
V_l	molar liquid volume
ρ_{liq}	liquid density
δ_{liq}	liquid solubility parameter
S	selectivity
y_i	binary solubility of component i in the supercritical phase
E	enhancement factor
P_s	saturation pressure of solvent
M	molecular weight
S	solubility
Q	heat flux
ω	acentric factor
P_{vpr}	reduced vapor pressure
Z_c	critical compression factor
λ	thermal conductivity
∇T	temperature gradient

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