

AOCS Press - Champaign, IL

Chapter 17

Critical Fluids for Oil Extraction

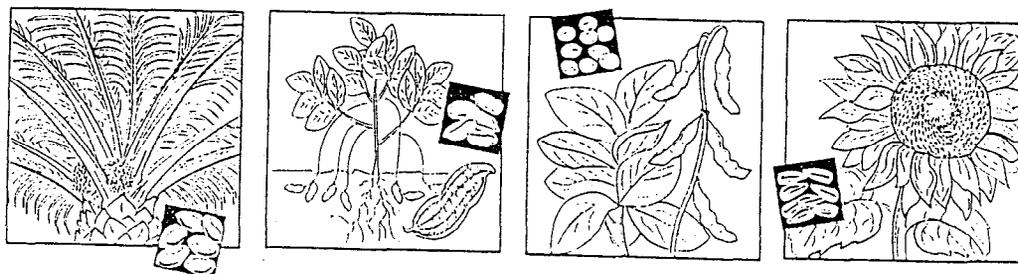
Jerry King

Technology and Solvents for Extracting Oilseeds and Nonpetroleum Oils

Editors

Peter J. Wan

Phillip J. Wakelyn



Chapter 17

Critical Fluids for Oil Extraction

Jerry W. King

Food Quality and Safety Research, National Center for Agricultural Utilization Research,
Agricultural Research Service, 1815 N. University Street, Peoria, IL 61604, USA.

Introduction

The use of supercritical fluids for the extraction of nonpetroleum oils, that is, vegetable and plant-derived oils (1) has now been investigated for over 15 yr. Although earlier citations can be found, the peak for research activity and relevant applications occurred in the early and mid-1980s (2); however, additional activity continues to this day (3). This chapter will attempt to assess the current state of this technology as applied to the extraction of commodity seed oils, drawing heavily from experiences at the National Center for Agricultural Utilization Research (formerly the Northern Regional Research Center)—ARS/USDA in Peoria, Illinois. Considerable research has also been performed on the extraction of specialty plant-derived oils (4), and refining or fractionating oils to isolate extracts containing high-value ingredients (5). These studies will not be cited to any great extent since this book is primarily concerned with alternative solvents for extracting and processing the major seed oils of commercial importance.

In keeping with the practical orientation of this book, most of the discussion of critical fluid extraction utilizes carbon dioxide as the extraction fluid, since this is the most economical, rational, and environmentally compatible fluid for the previously mentioned processes. Discussion is also limited on the use of light hydrocarbon gases, for example propane, either in the supercritical or near critical state, since this is covered in another chapter of the monograph. Such fluids are similar to the liquid hydrocarbon solvents currently being used to extract seed oils and has all of the attendant benefits and disadvantages.

The purpose of this chapter is to separate the facts from the conjectures that often are utilized to reject critical fluid extraction as an alternative technology for processing seed oils. Economic studies for the supercritical fluid processing of seed oils are, for the most part, missing from the open literature. An attempt shall be made to report what is known on this subject, although there is some concern that direct comparison of a hypothetical supercritical carbon dioxide (SC-CO₂) extraction with the established "hexane" extraction technology is not entirely valid. This concern is based on the fact that SC-CO₂ extraction can eliminate costly downstream processes, such as caustic refining and bleaching, that are necessary when using liquid solvents. Hence, a direct comparison of the costs associated

with the entire extraction and refining process when comparing critical fluid to conventional solvent use is probably the more valid comparison.

A particularly strong emphasis has been placed on the optimization of the extraction parameters that will ensure rapid and complete removal of triglyceride-based oils, specialty as well as commodity. Although no critical fluid processing plant has yet been built to extract commodity oils, potential approaches to achieving this end goal will be demonstrated, at least on the pilot-plant level.

Basic Principles of Supercritical Fluid Extraction

The supercritical fluid state for any substance may be defined as when a liquid exists above a specific temperature, known as the critical temperature and a specific pressure, the critical pressure, T_c and P_c , respectively. Its relationship to other states of matter in the case of carbon dioxide is shown in Figure 17.1. In this figure, both T_c and P_c define a critical point on a pressure-temperature diagram, and correspondingly define a critical density; in the case of CO_2 is approximately 0.45 g/cc (6). One of the practical implications of these defined properties is that CO_2 cannot be converted to its liquid state no matter how much pressure is applied, as long as it is held above T_c . As will be demonstrated, this confers some unusual and exploitable properties to critical fluids that can be used to advantage in performing supercritical fluid extraction (SFE). So-called "near critical fluids" have also been used to advantage, by operating the extraction in a temperature range slightly below the critical temperature (usually in the range of 0.85–0.95 in terms of the

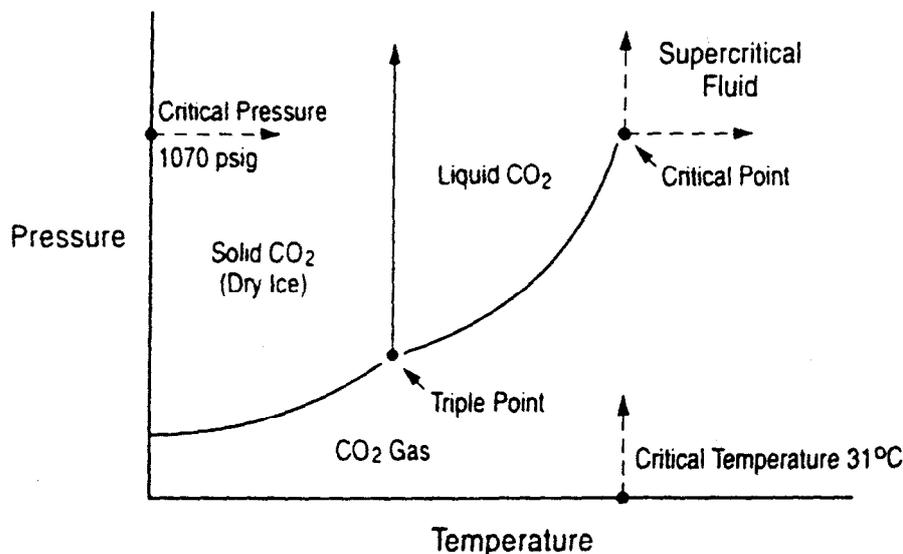


Fig. 17.1. Phase diagram for carbon dioxide.

reduced temperature, $T_r = T/T_c$); in many cases these approximate the liquefied gases discussed in a previous chapter, and seem to offer limited advantage, if any, over supercritical fluids for the processing of seed oils.

From an operational point of view, the thermodynamic-based definitions are rather sterile, and a more useable definition is provided here. Hence, when a fluid meets the previously mentioned criteria, it exhibits physical properties that are intermediate between those of a gas and liquid, and its density can be changed by varying the pressure applied to the fluid. Therefore, when the fluid is in a state of high compression, it takes on a correspondingly high density, approximating that associated with a liquid solvent. Under such conditions, the supercritical fluid has the capability of dissolving a variety of materials just as liquids do. It is for this reason that supercritical fluids become attractive solvents for oil extraction.

In addition, when solutes become dissolved in supercritical fluids, they exhibit a higher diffusivity than they do in liquids, thereby facilitating rapid mass transfer of the solutes from the seed matrix. Also, to a more limited extent, the selectivity of a supercritical fluid can be changed by altering its density, similar to changing liquid solvents in conventional extraction. This has been exploited in specific cases, for example the decaffeination of coffee (7). However at high densities, the extraction selectivity of supercritical fluids is lost and their molecular specificity approximates that found for nonpolar to moderately polar solvents (in the case of CO_2).

A generic SFE process is illustrated in Figure 17.2 where the fluid is compressed to an appropriate extraction density with the aid of a compressor or pump, and then expanded into the supercritical fluid state. Extraction occurs within a pressure-rated vessel at a temperature above the T_c of the fluid in a homogenous one-phase system. The dissolved solute (oil) is then precipitated by inducing a phase separation, usually by either lowering the pressure or raising the temperature (or both) after passage through a pressure reduction valve. At this point, some additional heating is normally applied to overcome the Joule-Thomson cooling that occurs with the decompression of the fluid. The extracted oil is then collected in a separator and can be removed after the extraction, or intermittently, while the decompressed fluid is rerouted back to the pump or compressor for reuse as an extraction solvent.

A considerable change in the solute's solubility in the supercritical fluid can be experienced during this process, as illustrated for naphthalene in Figure 17.2. Here, a solubility of 5.2 mol% is found for naphthalene at a pressure of 300 atm and a temperature of approximately 55°C, corresponding to conditions found in the extractor, E_1 . Separation of the naphthalene from the compressed CO_2 can then be produced in one of two ways as depicted in Figure 17.2. The separator can be kept at a constant pressure (300 atm) and the temperature lowered to 20°C, thereby providing a solubility change of 4.0 mol% at S_2 . An even greater drop in naphthalene solubility in SC-CO_2 can be achieved by dropping both the pressure and temperature at the separator, S_1 . When these conditions are adjusted to 90 atm pressure and 45°C, only 0.1 mol% of naphthalene is left in the SC-CO_2 phase. It should be noted that separator vessels are rarely operated close to ambient conditions because of the energy penalty associ-

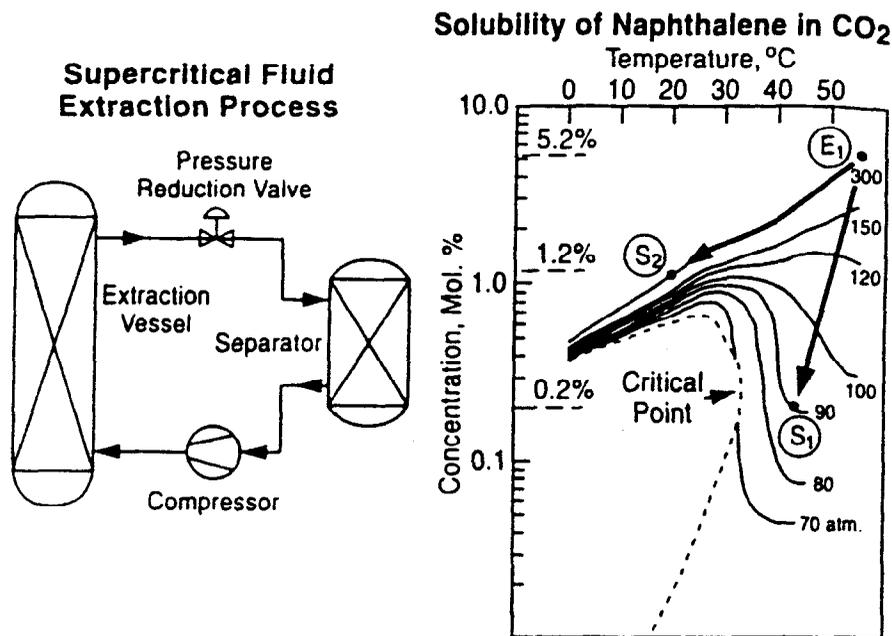


Fig. 17.2. Supercritical fluid process for extracting naphthalene.

ated with recompressing the fluid media. This principle also plays a role in the design of a continuous oil-processing plant using SC-CO₂.

There are many advantages associated with the use of SFE for extracting oils. These are as follows:

1. Solvent-free products, both extract (oil) and raffinate (meal), can be obtained for food use;
2. When using CO₂, the extraction process is relatively benign, permitting the removal of heat- and oxygen-sensitive compounds, thereby avoiding molecular alteration;
3. The process causes little pollution of the environment, particularly if CO₂ is used as the extracting fluid; and
4. Carbon dioxide, the principal extraction fluid, is readily available and can be recycled or stored for continual use as the extraction medium.

Early studies on the extraction of seed oils with SC-CO₂ revealed that lighter colored oils and marginally better tasting oils could be achieved with SFE (8). This coupled with zero solvent residue in both the extracted oil and residual meal made for a very appealing, "all natural," alternative extraction process. In addition, the low level of phospholipid components present in many seed oils that are removed in the degumming stage of the refining process showed negligible solubility in SC-

CO₂, even at high pressure and temperature (9). This eliminated the need for the degumming step, or at least lowered lye requirements during refining of the oil, and also lowered oil loss during the refining process overall (10).

Solubility of Seed Oils in SC-CO₂

Considerable information is now available on the solubility of seed oils, pure triglycerides, and lipids in SC-CO₂ over a range of pressures and temperatures (11). Such information is needed along with mass-transport properties, such as diffusion coefficients, to allow modeling and process optimization of the critical fluid extraction of seed oils. Perhaps the most detailed and comprehensive studies are those of Friedrich (12) and Stahl (13), since they encompass the high-pressure and -temperature region in which very high oil solubilities in SC-CO₂ are found. Figure 17.3 illustrates the dependence of soybean oil solubility in SC-CO₂ as a function of temperature and pressure (12). Relatively low weight percent solubilities are recorded in the case of the 40 and 50°C isotherms that do not exceed 5 wt%. As the temperature is increased from 50 to 60°C, there is a pronounced increase in oil solubility at pressures above 800 bar, resulting in solubilities approaching 15 wt%. A further increase in temperature obviously enhances oil solubility substantially as shown in Figure 17.3, resulting in solubilities that exceed 40 wt% at pressures approaching 700 bar.

It is interesting to note that the high oil solubilities recorded at high pressures and temperatures are a result of the so-called "crossover effect" (14) in which oil solubility is no longer dependent on the density of the extraction fluid. This is illustrated in

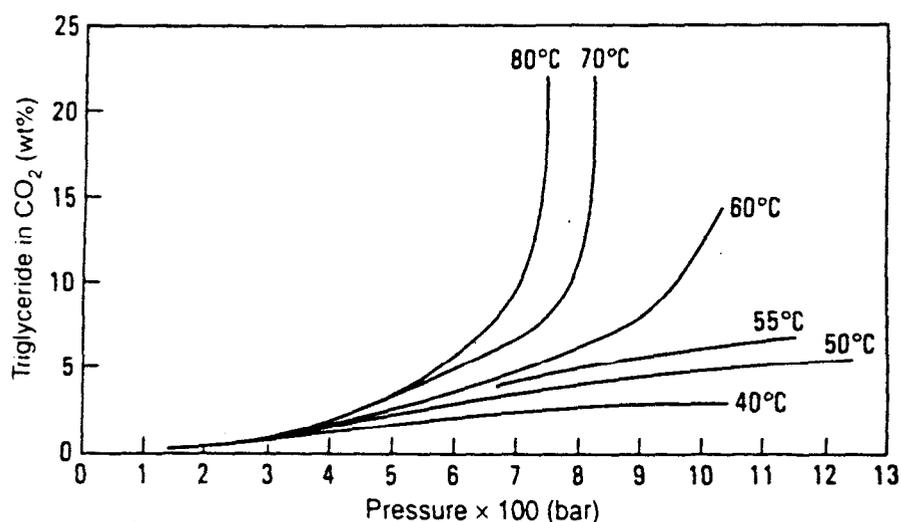


Fig. 17.3. Solubility of soybean oil triglycerides in SC-CO₂ as a function of temperature and pressure.

Figure 17.4 for the region between 300–400 bar in which increasing the temperature not only reduces the density of the supercritical fluid, but also increases the vapor pressure of the solute (triglyceride). This phenomena can be used as a basis for fractionating triglycerides and has been rationalized in terms of the respective cohesive energy densities of solute and solvent (SC-CO₂) as a function of temperature (15). The crossover region is of limited value for the extraction of oils, due to the low seed oil solubilities in that region.

Stahl (16) has shown that solubility maxima occur when SC-CO₂ is used to dissolve seed oils, such as soybean and sunflower. Such maxima occur between

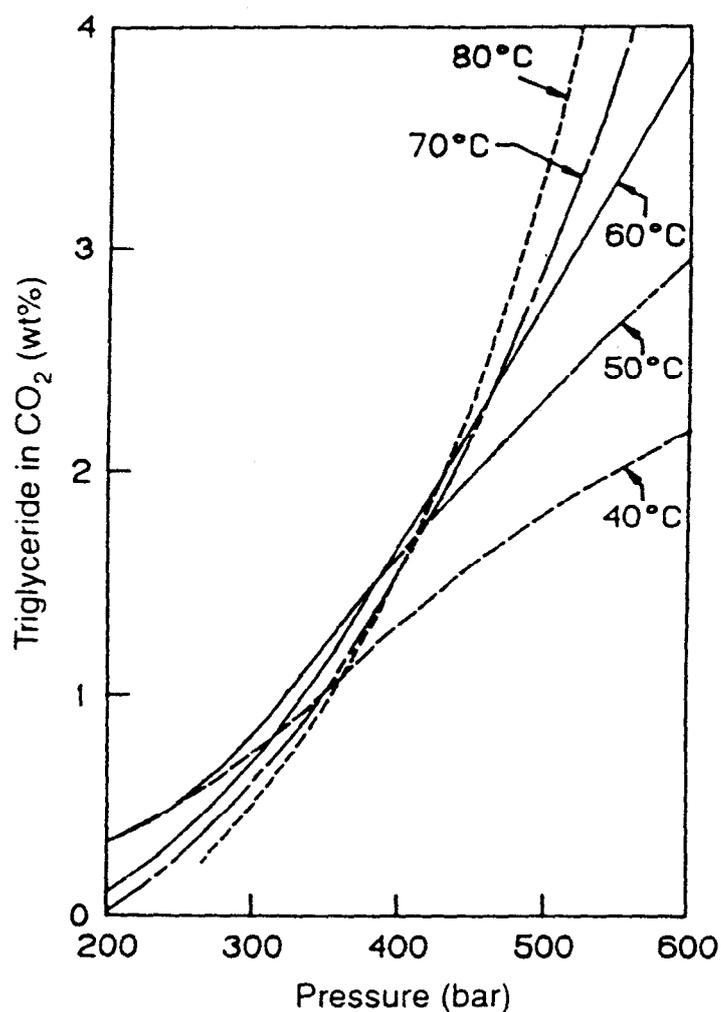


Fig. 17.4. Crossover effect for the solubility of soybean oil triglycerides in SC-CO₂.

800–1100 bar and are of more theoretical interest than of practical utility for processing seed oils. However, the ascent of the solubility curve (i.e., wt% solubility vs. pressure) when approaching this region is important in realizing optimal conditions for extracting seed oils. This fact has been noted by King (15) and used to develop a correlation between the solubility parameter of a solute and the reduced density at which its optimum solubility should be realized in a supercritical fluid. Table 17.1 tabulates these values for lipophilic solutes, such as triglycerides and sterols. The general trend is that higher reduced densities are required to maximize the solubility of more polar lipid species. A reduced density of 2.22 is required to maximize the solubility of triglycerides, the major constituents of seed oils, in a critical fluid.

The solubility data given in Figure 17.3 can be used effectively for the design of oil extraction and precipitation conditions during SFE. As shown in Figure 17.5, substantial drops in oil solubility in SC-CO₂ can be produced by altering the temperature or pressure at the separator stage, similar to that shown for naphthalene in SC-CO₂ (Fig. 17.2). For example, if one keeps the temperature constant (CT) and drops the pressure from approximately 760 to 700 bar, the corresponding solubility drop is 12 wt%. Similar reductions in oil solubility can be achieved by lowering the temperature at constant pressure (CP), for example, at 760 bar, there is a 14 wt% loss in oil solubility by just changing the separator temperature from 80 to 70°C.

Based on the solubility data given in Figures 17.2–17.4, it is readily apparent that there is considerable advantage to conducting oilseed SFE at the optimum temperature and pressure consistent with high oil solubility in the supercritical fluid. King has shown that the conditions most often used for this purpose can be correlated with the aid of a plot of reduced state (17), as shown in Figure 17.6. Most reported oil extraction conditions are clustered at reduced temperatures ($T_r = T/T_c$) between 1.00–1.20 and reduced densities ($\rho_r = \rho/\rho_c$) of 1.5–2.2. From this figure, the corresponding reduced pressures ($P_r = P/P_c$) can be ascertained as well as the extraction pressure, P . It is interesting to note that the quoted upper limit of reduced density for

TABLE 17.1

Solubility Parameters for Lipid Types Found in Seed Oils and the Reduced Densities Required to Optimize Extraction of These Lipid Species

Lipid type	Solubility parameter ^d	Reduced density
Hydrocarbons	8.34	2.08
Carotenoids	8.72	2.17
Tocopherols	8.86	2.21
Triglycerides	8.91	2.22
Ubiquinones	9.08	2.26
Fatty acids	9.10	2.27
Diglycerides	9.45	2.35
Sterols	9.52	2.37
Monoglycerides	10.2	2.54

^dIn units of cal^{1/2}/cc^{1/2}

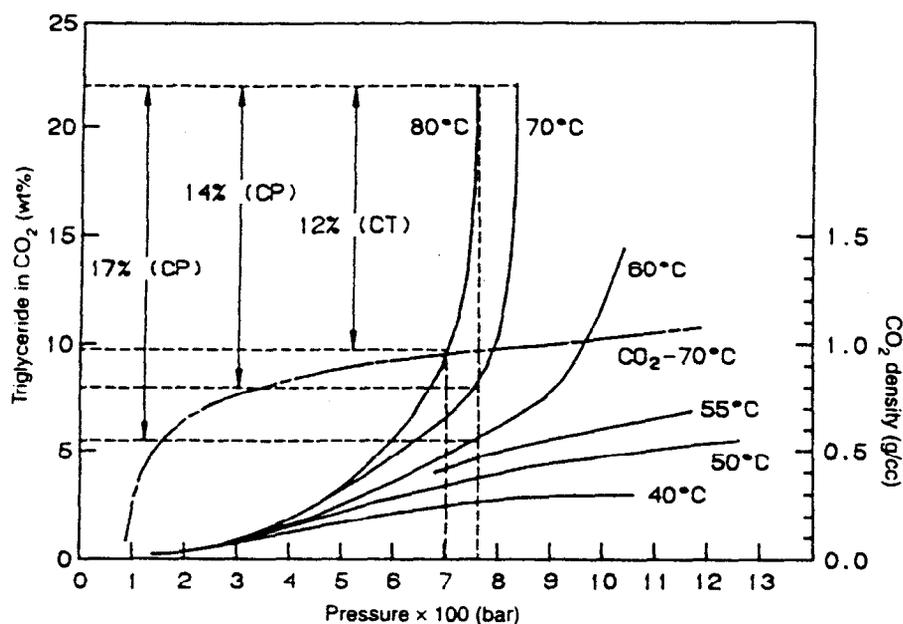


Fig. 17.5. Effect of changing pressure and/or temperature on the solubility of soybean oil triglycerides in SC-CO₂.

oilseed extraction is close to the theoretical value predicted in Table 17.1. Such correlations can be used to optimize the fractionation of oil constituents and deodorization of vegetable oils using their respective reduced state plots.

Extraction of Seed Oils Via SFE

Successful SFE of seed oils not only requires optimized extraction conditions; it also requires properly prepared and optimized seeds to ensure successful extraction. Much has been reported on this latter topic (18–21) for individual oilseed types; this chapter will cover only the major factors that are required to ensure successful extraction.

The kinetics of SFE are not only dependent on the extraction pressure and temperature, but also on the preparation of the seed and its morphology. Extraction rate curves for oil removal by SFE are initially linear and are governed by the solubility of the oil in the supercritical fluid (22). One then sees the onset of a transition region in which the rate of oil removal diminishes, followed by an asymptotic approach as the final amount of oil is removed from the seed matrix. These curves have been modeled by several investigators, including Brunner (23), Eggers (24), Hong (25), Reverchon (26), and Cygnarowicz-Provost (27) among others.

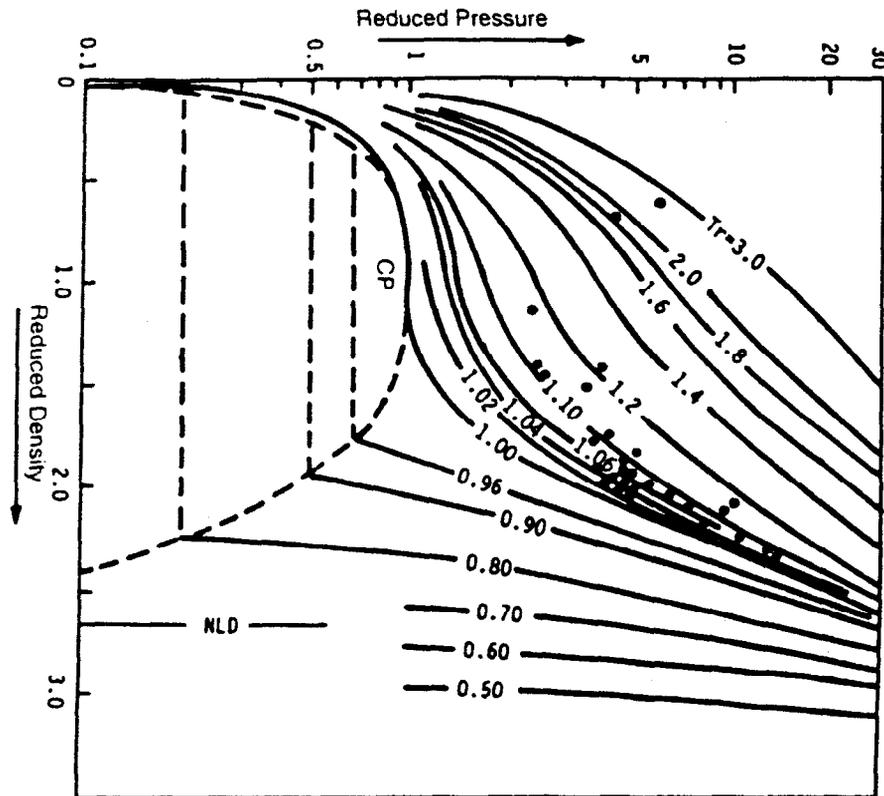


Fig. 17.6. SFE conditions for oil extractions on a plot of reduced state.

The practical importance of extraction pressure and temperature is shown in Figure 17.7; the weight percent solubility of cottonseed oil in the flowing SC-CO₂ phase has been plotted as a function of the mass of SC-CO₂ passed through an extraction vessel. The obvious benefit of extracting at 10,000 psi and 80°C vs. 8,000 psi and 50°C is apparent, since the extraction takes considerably longer at the lower temperature and pressure. Such conditions also require the use of more extracting fluid as depicted in Figure 17.7, where the superimposed vertical dashed lines indicate a mass of CO₂ equivalent to that required to fill the volume of the extractor bed once (2.9 kg). Therefore, extracting the flaked cottonseed at the higher pressure and temperature requires approximately three column volumes of CO₂, while the 8,000 psi and 50°C condition requires more than seven column volumes of extraction fluid.

The processing implications of the trend listed previously is that exceedingly rapid extractions can be facilitated if the pressure and temperature conditions are optimized and are accompanied by a sufficient extraction-fluid flow rate. This is illustrated by the data in Table 17.2; the data have been produced from soybean

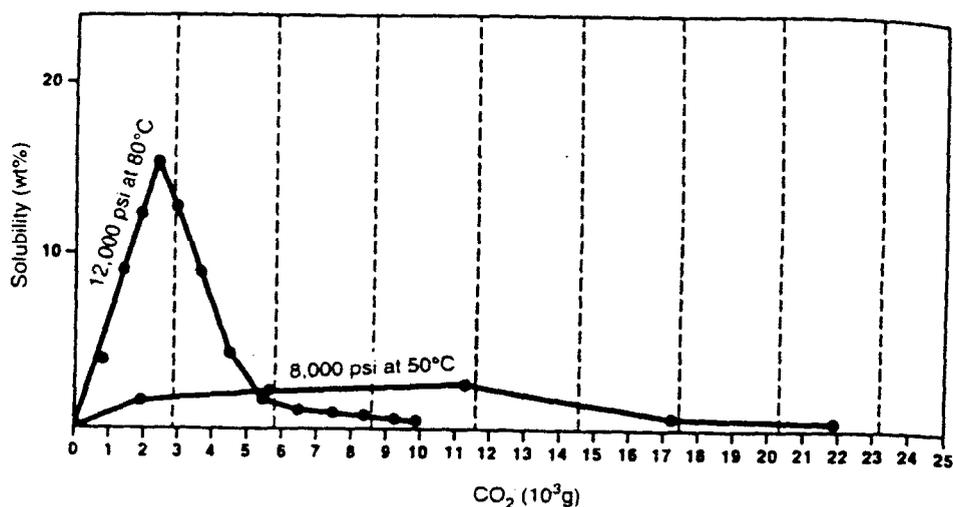


Fig. 17.7. Solubility of cottonseed oil (wt%) vs. mass (g) of CO₂ passed through seed bed.

flakes that have been deoiled at 12,000 psi and 80°C. In this example, a CO₂ flow rate of 1.0 lb/min leads to the removal of most of the oil in a processing time of only 10 min! This data is based on the extraction of 3.5 lbs of soybean flakes charged to a 4-L extractor vessel in the semicontinuous NCAUR pilot plant; the pilot plant will be discussed in this chapter. Hence, very rapid extraction of seed oils can be produced with SC-CO₂ provided that the extraction pressure, temperature, and fluid flow rate are optimized.

Table 17.3 illustrates some of the types of oilseeds that can be extracted by SFE. These seed matrices were all extracted on the NCAUR pilot plant operating

TABLE 17.2
Rapid Extraction of Seed Oils Using SC-CO₂^a

Substrate	Ext. time ^b	CO ₂ flow rate ^c	Oil recovered ^d (wt%)	Residual oil ^e (%)
Soybean flakes	25	0.66	20.1	—
Soybean flakes	15	0.66	19.4	0.8
Soybean flakes	14	0.72	18.3	1.4
Soybean flakes	11	0.92	19.4	0.7
Soybean flakes	10	1.00	18.6	—

^aExtraction Conditions: 12,000 psi, 80°C. Receiver: 2,500 psi, 80°C. Soybean Flake Charge: 3.52 lbs in a 4-L extractor

^bmin.

^clb/min.

^dBased on initial weight of soybean flake charge.

^eBased on weight of residual meal

TABLE 17.3

Substrates Extracted Using the Semicontinuous Pilot Plant Utilizing Carbon Dioxide Recycle

Substrate	% Extracted (based on oil weight in substrate)
Jojoba nut (ground)	47.3
Pressed jojoba meal	13.5
Macadamia nut (diced)	36.3
Roasted peanuts (ground)	42.2
Soybean flakes	19.4
Dry milled corn germ (flaked)	22.8
Flash-dried gluten	3.7
Whole corn distiller's grain	6.9

in the recycle mode using CO₂ as the extraction fluid. Note that the matrices extracted ranged in oil content from a few percent to close to 50 wt% in oil. Besides the listed seed oils, partially deoiled meals can also be treated using SFE, as well as partially defatted products, such as diced macadamia nuts, for use in low-fat food-compounding applications. It should be stressed that each individual matrix may require some adjustment when conducting SFE. For example, when extracting seeds having a high oil content, it has been found advantageous to lower the flow rate of the extracting fluid through the bed to avoid compaction of the spent meal that will inhibit the completion of a total extraction of the oil.

When conducting SFE, certain processing problems may arise that can be solved only from experience gained in the laboratory or pilot-plant stage. It should be emphasized that many of these factors are also present during extraction with conventional liquid solvents, such as seed preparation and extractor bed dynamics. The physical morphology of the oilseed has also been found in SFE to be crucial to achieving a thorough extraction, and this factor has been studied in detail by Snyder et al. (28). For example, Figure 17.8 shows the rate of oil removal from both ground and flaked soybean meals. It is apparent that the flake configuration leads to an optimized oil recovery despite the fine grind that has been applied to the soybean meal in the other case. This is probably due to the fact that fine mesh particles tend to compact more readily in the extraction vessel, leading to channeling of the extraction fluid and incomplete oil recovery. Additional studies (28) of the effect of soybean flake thickness on oil recovery are shown in Figure 17.9. It is apparent from this data that increased oil recovery can be produced by using thinner flakes, a result consistent with the improved mass transfer of the oil through the solid matrix.

The moisture content of the seeds can have several effects during SFE, unfortunately most of them are adverse. Water has a small, but finite solubility in SC-CO₂ (29). Therefore water can be extracted along with the target oil, however its removal is often suppressed until the end of the extraction due to the high oil content in the supercritical fluid phase. The presence of turbidity in the oil indicates

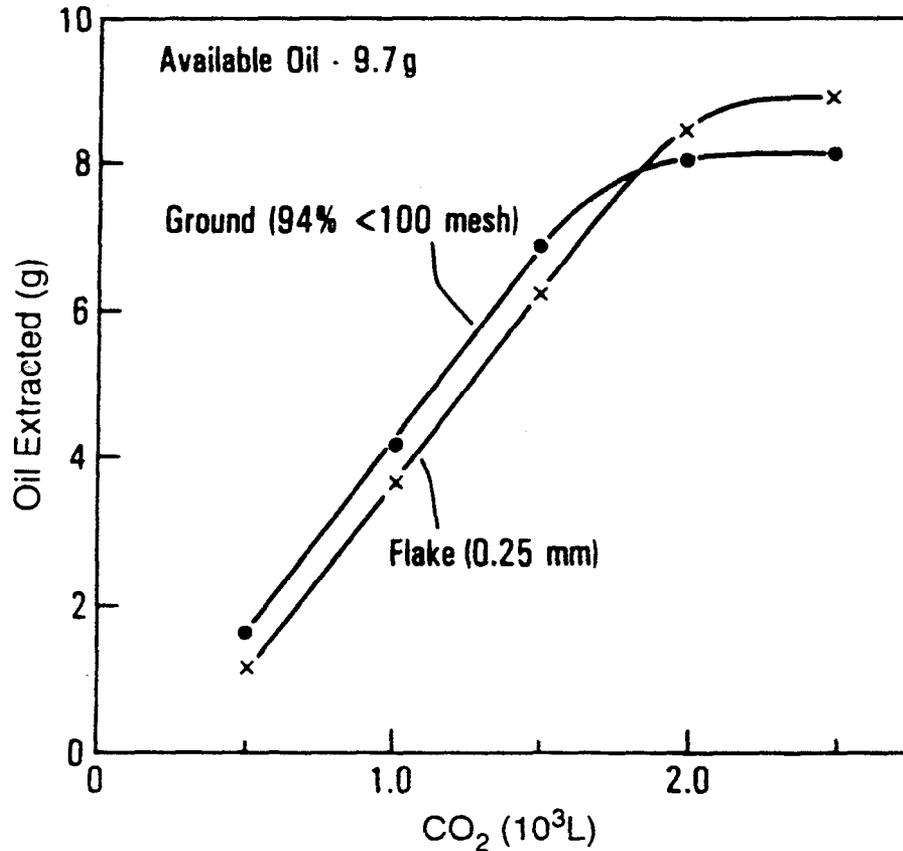


Fig. 17.8. Oil yield vs. liters of CO₂ passed over seeds for a soybean oil extraction (8,000 psi, 50°C).

the presence of water in the extract; it can be removed quite readily by the addition of a filter aid or other sorbent. The presence of moisture during SFE can also be deleterious to extraction vessels and other equipment if the proper materials are not utilized in their construction. It has been found that 316 stainless steel or better inhibits pitting on the inside of the vessel, undoubtedly caused by the formation of carbonic acid during the extraction process. Generally high levels of moisture in a matrix to be extracted by SFE inhibit contact between the SC-CO₂ and lipid-rich regions of the matrix (30). Moisture has been implicated as a swelling agent in some SFE processes and is often cited as an essential factor in the well-known supercritical fluid decaffeination of coffee beans (31).

Physical changes in the extractor bed can also effect the extraction of seed oils. Radial fluid distributors have been found to be critical for evenly distributing

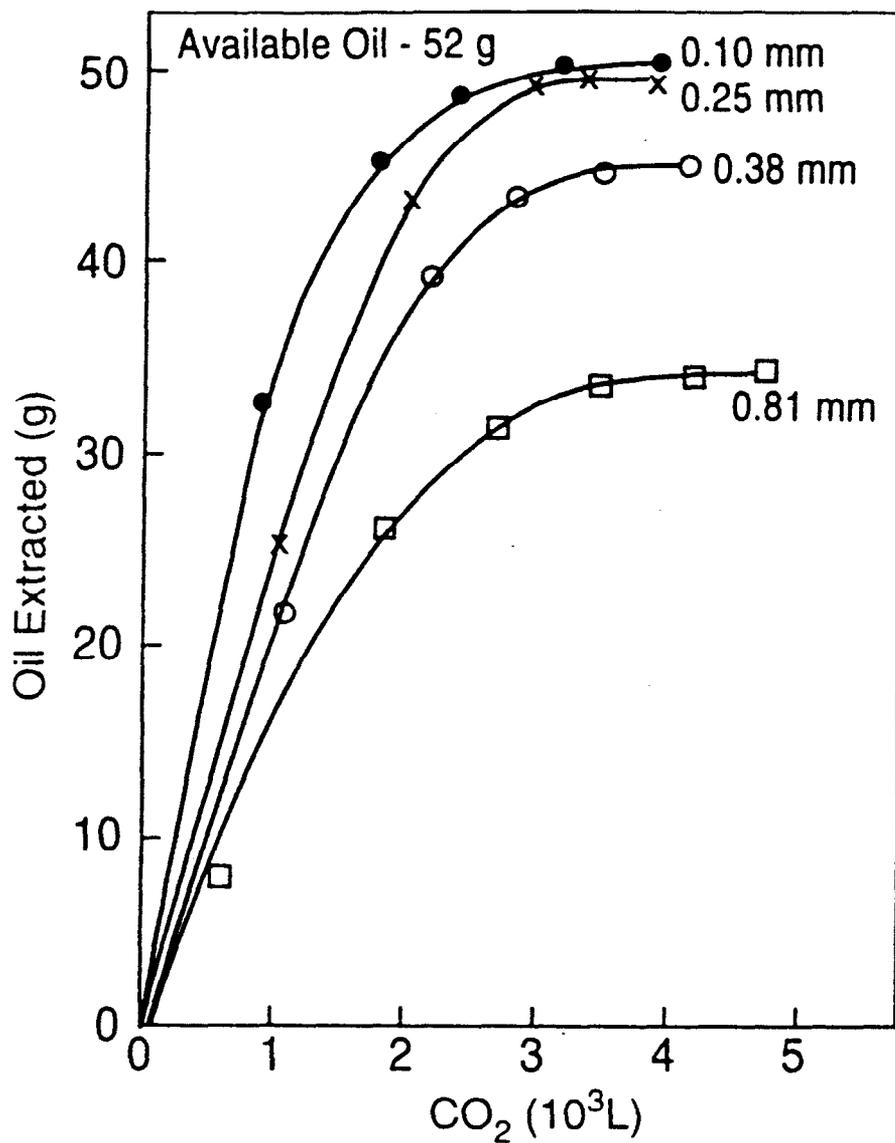


Fig. 17.9. Oil yield vs. liters of CO₂ passed over soybean flakes; effect of flake thickness on oil yield (8,000 psi, 50°C).

the fluid across the cross-sectional area of the extraction vessel. This avoids extraction fluid channeling that leads to incomplete removal of the seed oil. Compaction of the seed bed can also occur during SFE due to the high pressures involved in the process, and can lead to unacceptably high pressures and cessation of flow. This

can usually be avoided by reducing the flow rate of fluid through the extractor vessel. Alternatively, changing the direction of fluid flow usually alleviates any temporary blockage that has occurred in the vessel.

Extraction of desired or unwanted components during the SFE process can simultaneously occur while removing the oil. For example, SFE using SC-CO₂ is a relatively benign process, and the presence of undesired moieties, such as pesticides, will probably be extracted intact along with the vegetable oil. Conversely, phospholipids as previously noted, and inorganic species, such as iron, are relatively insoluble in high-pressure CO₂ and are not removed to the extent recorded for "hexane" extraction of the same seed oil (Table 17.4). This can serve as the basis of a continuous oil-degumming process (32).

Supercritical-fluid-extracted oils with depleted phospholipid contents tend to be susceptible to oxidation; List and Friedrich (33) have documented this phenomenon. This of course can be overcome by adding antioxidants back into the oil proper. Other components are differentially extracted during SFE as evidenced by the improvement in the color of the extracted oil. Favati et al. (34) have documented the differential extraction of carotenoids and lutein during SFE for the express purpose of isolating pigment-rich fractions for food additive purposes.

Oil-Processing Options Using SFE

Perhaps the most vexing problem in SFE of oils is the design of an extraction process that provides a reasonable facsimile of the current solvent-based process used in the industry. This factor plus the resistance to implement a high-pressure process for safety and cost reasons have probably been the factors inhibiting the construction of a seed oil processing plant to date. It is interesting to note that the chemical-processing industry has had considerable experience in constructing and operating high-pressure processes. Table 17.5 lists processes in the multi-thousand psi range that are used to produce products on a billion pounds/yr scale. Supercritical fluid extraction plants of considerable scale have been built around

TABLE 17.4
Effect of Oil Processing on the Phosphorus and Iron Content of Soybean Oil

Processing Step	Hexane		SC-CO ₂ ^a	
	Fe (ppm)	P (ppm)	Fe (ppm)	P (ppm)
Crude	1.45	505	0.3	45
Degummed	0.69	63	— ^b	— ^b
Refined	0.11	28	0.07	35
Refined & Bleached	0.09	25	0.08	25
RBD ^c	0.09	12	0.11	20

^aExtraction conditions: 50°C and 8000 psi.

^bDegumming not required for SC-CO₂ extracted oil.

^cRefined, bleached, and deodorized.

TABLE 17.5
Some Industrial Chemicals Produced by High-Pressure Processes

Chemical	Process Pressure (psi)	Volume (lbs/yr)	Use
Ammonia	3,000–5,000	32,000,000,000	Fertilizers
Urea	3,000–5,000	6,000,000,000	Fertilizers
Polyethylene	30,000–50,000	15,000,000,000	Plastics
Methyl alcohol	3,000–5,000	8,000,000,000	Chemical
Ethyl hexyl alcohol	3,000–5,000	400,000,000	Plasticizer
Hexamethylene diamine	4,000–6,000	1,000,000,000	Nylon products

the world and in the United States, particularly in the processing of food ingredients, such as coffee, hops, and spices. These range from the large General Foods decaffeination plant in Houston, Texas to the more modest extractors in quaint Yakima, Washington, in the United States

For the SFE of seed oils to be effective, the following principles must be observed for designing, constructing, and operating a plant:

1. The solubility of seed oil triglycerides in SC-CO₂ exceeds 40 wt% in the pressure range of 11,000–12,000 psi at 80–90°C. Therefore the plant must have a high-pressure rating to achieve high oil solubilities which will also reduce the processing time and costs substantially.
2. The amount of oil that can be extracted from the seed is limited by the relative amount of available oil and CO₂ in the extraction vessel. Hence, there must be sufficient CO₂ passing through the vessel to ensure rapid extraction, which argues for high flow rates.
3. Batch extractors that have been used for many preliminary SFE operations are inherently more time- and labor-intensive. So-called "batch-continuous" systems are more efficient and have become the rule in most modern SFE processing.
4. There are even more advantages to conducting SFE in a continuous countercurrent or cocurrent mode, but most of these systems are currently practiced on a pilot scale, although more full-scale implementation will occur in the near future.

An example of batch-continuous pilot-plant operation utilized at the National Center for Agricultural Utilization Research is displayed in Figure 17.10 (35). Here the entire system is filled with SC-CO₂ before the start of the extraction, so that a total initial mass of CO₂ is continuously used to remove the oil. Vessels A, B, and C are scaled at 4-L internal volume, accommodating approximately 3.5 lb of soybean flakes each. A compressor (or alternatively a pump) supplies the CO₂ to the extraction vessels; the vessels can be extracted in a sequence that permits filling or discharge of one vessel while the others are either being pressurized or extracted. This creates a form of semicontinuous operation that has been used in other SFE operations.

An auxiliary compressor is used to supply CO₂ that is lost through normal operation or when the product oil is removed from the receiver vessel, R. The CO₂

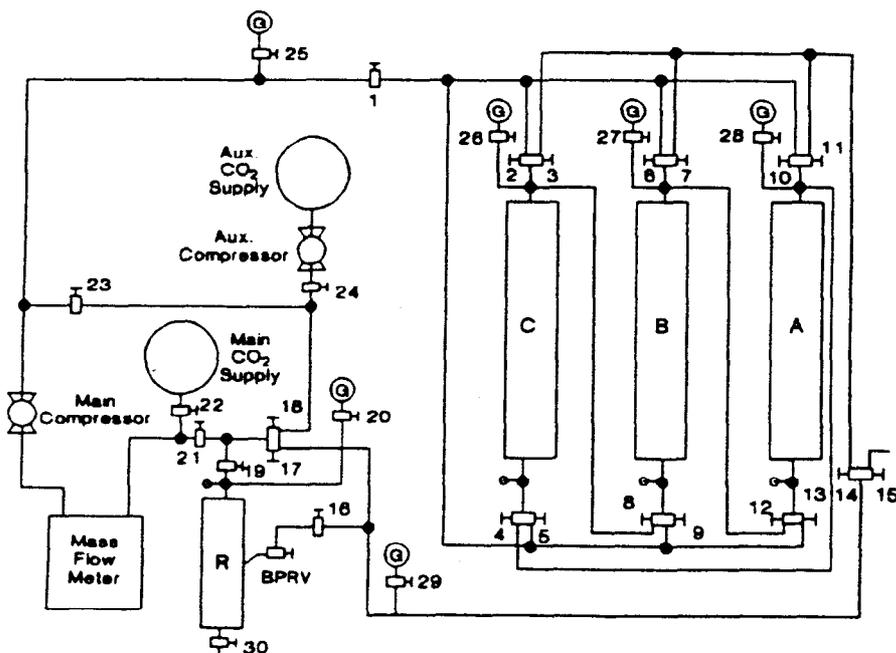


Fig. 17.10. NCAUR batch-continuous SFE pilot plant.

loss for an entire deoiling of 13.5 lb of soybean flakes is less than 1% of the initial mass of CO₂ charged to the pilot plant. It is easy to see by tracing out the valving sequence, how the extractions can be conducted in a sequential fashion. Pressure upstream of the receiver is maintained with the aid of a heated back-pressure relief valve (BPRV). It has been found that for extractions conducted in the 10,000–12,000 psi range and at 80°C, it is advantageous to drop the pressure in the receiver to approximately 2,500–2,800 psi and 80°C. This precipitates the bulk of the seed oil in the receiver vessel, since only about 0.1 wt% oil remains in the SC-CO₂ under these conditions. This allows the CO₂ stream to be maintained above the critical pressure and temperature of the extraction fluid and avoids the large energy penalty commensurate with larger pressure and temperature reductions. Using the listed operational format and conditions, results such as those in Table 17.2 are possible.

Another way of approaching the continuous SFE of seed oils is shown in Figure 17.11. Here the principle of the lock hopper or rotary lock is invoked to continuously feed seeds into the top of a vessel under high pressure (36). The extraction fluid is introduced into the bottom of the vessel and travels upward, countercurrently contacting the seed particles moving in the opposite direction. The operation of the CO₂ recycle loop is very similar to that discussed for Figure 17.10. The problem with implementing this concept at the desired processing pressures is that no suitable lock

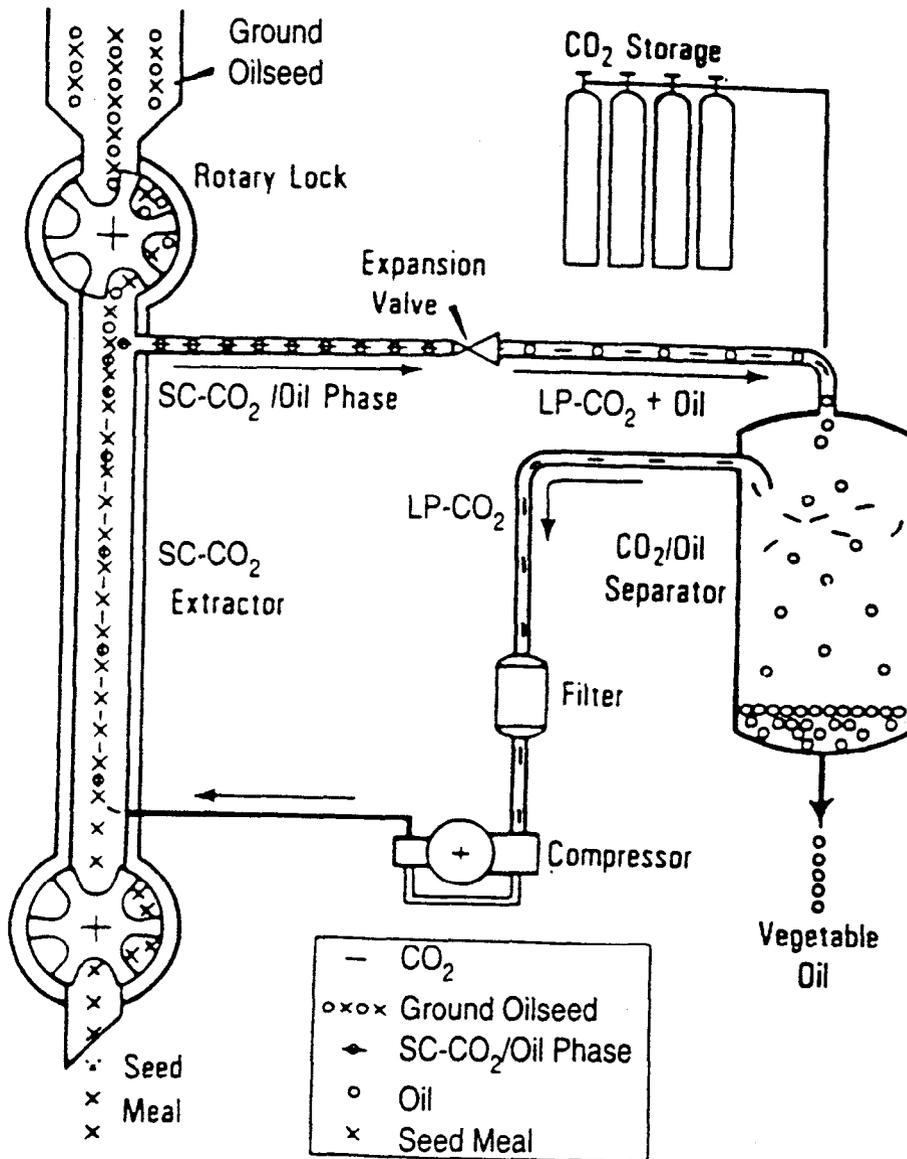


Fig. 17.11. Conceptualized continuous lock feed of oilseeds into supercritical fluid extractor.

hopper exists that will operate continuously in the pressure region approaching 10,000 psi. Special lock hoppers have been designed and experimentally tested for operation up to 4,000 psi in the coal industry, but equipment is lacking to implement the approach advocated in Figure 17.11.

A similar, but somewhat different approach to that discussed in the preceding paragraph, has been designed and tested by Eggers' research group at the Department of Chemical Engineering at the University of Hamburg-Harburg (37). Here the oilseeds are injected into the high-pressure extractor via a screw conveyor that creates a pressure seal along the axis of the charging press as pictured in Figure 17.12. This unit has been successfully operated at pressures exceeding 300 bar for the continuous deoiling of rapeseed. Baffling is provided inside the extractor to ensure contact between the seed particles falling downward and the pressurized CO₂ entering from the bottom of extraction vessel. Spent or deoiled meal is then conveyed out of the extractor via an auger at the bottom.

Since the extraction of oilseed particulates poses the problems discussed previously, we have examined more recently the feasibility of applying the supercritical fluid fractionation process to pre-extracted vegetable oils in a packed column has been examined (32). A schematic of the device is shown in Figure 17.13, in which the refining vessel represents a 4-L vessel packed with segmented Goodloe wire mesh packing to promote contact between the SC-CO₂ and the vegetable oil. The apparatus requires a high-pressure-rated liquid pump that can reproducibly deliver a constant amount of seed oil against high column back pressures (i.e., the extraction pressure). Carbon dioxide comes into the refining vessel at the bottom where it begins contacting the oil phase. As can be seen in Figure 17.13, provisions have been made to collect the refined oil on a continuous basis and for continuous recycle of the initial CO₂ charge through the refining vessel. In practice, it becomes necessary to sometimes "scrub" the CO₂ with a sorbent in order to prevent odoriferous materials from building up in the refining vessel and thereby contaminating the extracted oil.

It may be rightly questioned whether the previous processing concept is valid in lieu of its following a conventional extraction step. This process is rationalized on the basis that it provides the advantages of SC-CO₂ processing (i.e., elimination of the conventional degumming step) as well as eliminating the use of bleaching clay before the final deodorization polishing. This refining process has produced an oil suitable in color and other physical properties so that it can be taken right to the final deodorization stage, thereby eliminating several steps in the conventional oilseed-refining process and avoiding the waste streams associated with these processes. It should be noted that a lecithin-rich sludge concentrates in the bottom of the refining vessel and can be isolated by a conventional solvent wash or by jettisoning the CO₂ pressure on the refining vessel and spraying the lecithin concentrate into a collection vessel. A similar refining approach, even incorporating a cosolvent, has recently been presented by Rizvi (38) for the continuous processing of palm oil.

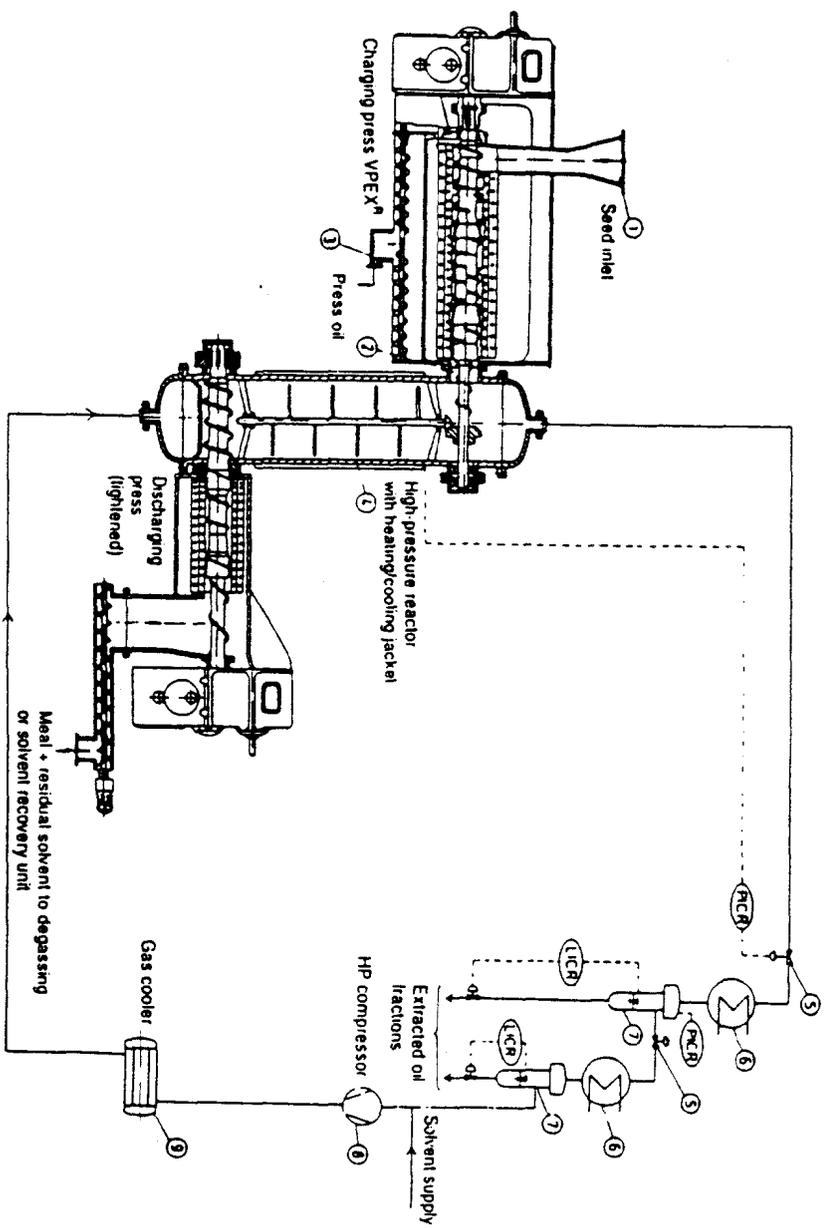


Fig. 17.12. TUHH screw cage press for continuous feeding of oilseeds into a supercritical fluid extractor.

TABLE 17.6
Effects of Processing on Cottonseed Oil Lovibond Color^a Ratings Flavor Scores

Process	Crude		Ref. ^b		% Excess	Bleached		Deodorized		Flavor score ^c	
	Y	R	Y	R		Y	R	Y	R	0	4-Day
PP/Solvent	70	20	70	8	0.5	70	4	20	2.5	7.9	7.7
PP/Solvent	70	20	70	16	0.3	20	9	20	5.0	8.2	6.4
PP/Solvent	70	20	70	20	0.2	20	16	20	6.0	8.1	7.4
CO ₂ ^d	70	7.6	70	3.5	0.1	30	2	20	1.0	7.6	7.1

Abbreviations: PP = Prepressed, Y = Lovibond Yellow Rating, R = Lovibond Red Rating.

^aHexane-extracted oils Lovibond taken at 1 in. tube, all others 5 1/4 in. tube.

^bReference oil: 10% lye, bleached with 0.5% activated clay at 80°C, vacuo 15 min, deodorized 3 h at 210°C.

^c10 point scale: 10 = bland, 1 = extreme.

^dComposite oil from SC-CO₂ extraction at 40–80°C, 8–15,000 psi.

ratings being equivalent for all three oils after the extraction, bleaching, and deodorization stages of refining. The SC-CO₂-extracted oil also shows similar color ratings, but the R-rating is substantially smaller than the R-rating for prepressed/solvent-extracted oils. The improved red ratings are also found in oils processed with supercritical fluids vs. expeller-derived oils when color fixation studies between 104–150°F were conducted for periods as long as 30 days (35,40). Flavor scores were also marginally better for the CO₂-extracted oil, both initially and after 4 days of storage.

Chemical analysis of the minor constituents in cottonseed oil also indicate pronounced differences between the SFE oil and the prepressed/solvent-extracted and expeller-derived oils. Table 17.7 shows that the CO₂-extracted oils, regardless of the extraction conditions chosen, give consistently lower iron content than the conventionally processed cottonseed oils. Likewise, the unsaponifiable content was reduced via supercritical fluid processing, as well as slight reduction in tocopherol content. Perhaps the most dramatic difference between the extraction procedures occurs in the gossypol content; the SC-CO₂-derived oils have approximately 1% of the gossypol of either expeller or prepressed/solvent-extracted oils.

TABLE 17.7
Effect of SC-CO₂ Extraction Conditions on Minor Cottonseed Oil Constituents

Oil Type	CO ₂ Extraction		Iron (ppm)	Unsap. %	Tocopherols %	Gossypol %
	Temp	Pressure				
PP/Solvent	—	—	1.8	0.87	0.092	0.18
Expeller	—	—	1.9	0.76	0.095	0.12
SC-CO ₂	50	8,000	0.2	0.51	0.072	0.003
SC-CO ₂	50	15,000	0.2	0.53	0.046	0.004
SC-CO ₂	80	8,000	0.2	0.52	0.053	0.007
SC-CO ₂	80	15,000	0.6	0.52	0.053	0.004

Abbreviation PP = Prepressed

In the prior section, a supercritical fluid refining option applicable to liquid oils was described. Table 17.8 lists some of chemical properties of the CO₂-refined oil vs. the starting feedstock and the final deodorized oil. Samples taken during the refining operation (#1-7) show a lowering in the free fatty acid (FFA) content, including the final composite oil relative to the starting oil. Note that the composite FFA value of the CO₂-extracted oil is equivalent to that found for the final deodorized oil. The oil refining does not appear to affect the peroxide value (PV) to any great degree, but the phosphorus content is substantially lower due to the insolubility of phospholipids in the SC-CO₂. As the refining operation proceeds, there appears to be some extraction of the P-containing moieties as evidenced by the higher P values in samples #5-7. The iron content of the starting oil is also reduced via the SC-CO₂ process as shown in Table 17.8. Additional data on the oxidative stability and sensory properties of the SC-CO₂-refined oil are also available (32). It is interesting to note that recently Kuk and Hron (41) have studied cottonseed oil extraction with SC-CO₂, with and without cosolvents, on a very small scale.

Alternative Critical Fluid Solvents

As noted previously, CO₂ is by far the most preferred solvent for conducting SFE on edible oils. Besides the properties and benefits already alluded to in previous sections, CO₂'s price of approximately \$0.03/lb makes it economically attractive for consideration as an extraction solvent. Other supercritical fluids that have been explored at the research stage for the SFE of seed oils include nitrous oxide (42), sulfur dioxide (43), fluorocarbons (44), propane (45), and propane/carbon dioxide mixtures (37). The higher costs associated with these fluids, as well as other objectionable properties, including ease of use, have made these less desirable than CO₂. A compelling argument can be made for the use of propane, since its oil-carrying

TABLE 17.8
Physical/Chemical Properties of Soybean Oil from SC-CO₂ Continuous Countercurrent Degumming Process^a

Sample	% FFA	PV	P (ppm)	Fe (ppm)
Starting oil	0.49	0.53	737	1.91
1	0.28	0.45	1.5	0.61
2	0.40	0.43	2.0	0.54
3	0.40	0.54	8.3	0.57
4	0.26	0.51	9.5	0.54
5	0.46	0.51	10.8	0.53
6	0.41	0.51	10.2	0.49
7	0.53	0.60	25.0	0.51
Composite	0.22	0.54	9.8	0.42
Deodorized oil	0.22	0.29	—	—

Abbreviations: FFA = Free Fatty Acid, PV = Peroxide Value, P = Phosphorus, Fe = Iron.

^aProcessing conditions: 8,000 psi, 74°C, oil solubility approximately 3.7 wt%.

capacity is significantly larger than CO_2 's (46). However, the use of propane raises the same concerns of solvent flammability associated with the commercial hexane-extraction processes. Nonetheless, a commercial process utilizing propane for the extraction of seed and marine oils, called the Solexol process (47), has existed for many years, although its application to bulk vegetable oil refining has not been significant.

Liquified or near-critical CO_2 is also another possible extraction solvent that has been used in specific cases for the extraction of hops (48) on an industrial scale as well as flavors and spices (49). Stahl (50) has also studied the extraction of seed oils by liquid CO_2 , however the inferior mass transport properties and solute fluxes realized under such conditions would seem to indicate that this is an inadequate approach for oilseed processing. In addition, King (51) has noted that there is no economic incentive in the near-critical CO_2 process.

Economic Considerations

As indicated previously, there is a paucity of studies on the economics of extracting seed oils with supercritical fluids. Often these studies have focused on just one aspect of the entire extraction and oil-refining sequence, ignoring operational credits in the refining sequence due to the incorporation of SC- CO_2 at the extraction stage. To be sure, SFE entails higher capital equipment costs that must be overcome through reduced operational costs and ultimately a less expensive product in order to displace the existing solvent-extraction methods. Environmental legislation favors consideration of SFE as a viable alternative, but improved plant engineering on existing and new solvent-extraction plants to "cap" emissions represents another practical alternative.

Eggers (52) has been most prolific in addressing certain aspects of the cost issue associated with SFE as applied to seed oils. Generic information on plant-design criteria have been noted by Eggers (53) as well as energy considerations (54). Separate evaluations of both 35 and 70 MPa operations as a function of temperature for the extraction of 1 ton of rapeseed in the caged screw press process (Fig. 17.12) have shown that:

1. High-pressure extraction of oilseed requires considerably more mechanical energy than does conventional hexane extraction;
2. Enthalpy requirements favor separation under supercritical conditions, since heat may be introduced directly into the system from the heat of compressing the fluid; and
3. The energy requirements for cooling required by the supercritical fluid process are higher than the hexane extraction process.

Eggers notes that only at an operating pressure of 75 MPa (10,875 psi) do the energy costs for conducting oilseed extraction become comparable to those using hexane. Another advantage for a 75 MPa process over a 35 MPa process is that the extracted oil:water ratio from the seed matrix is considerably higher.

A rather generic approach to estimate the costs associated with critical fluid extraction has been offered by King et al. (55). Besides the advantages associated with operating a large versus small production plant, he notes that CO₂ replacement costs can make a significant contribution to total extraction and recovery costs. Pressure reduction of the extraction fluid in such a plant also taxes the overall economics due to the additional energy required and other charges associated with operating the recycle compressor. In the case of an extraction performed on a solute having low solubility in near-critical or liquid CO₂ (e.g., rapeseed), the energy and capital costs associated with the recompression cycle become a major economic factor. A specific case is cited and rigorously documented for the near-critical fluid extraction of rapeseed at 25°C and 65 bar pressure. King concludes that for the stated process, the computed minimal extraction cost is equivalent to the current market price for rapeseed oil, hence making near-critical fluid processes unattractive.

A most interesting and relevant economic analysis of seed oil extraction using SC-CO₂ has been performed by Cygnarowicz-Provost (56), based on data initially presented at a conference on food engineering (57). This flowsheet model includes estimates for equipment and operating costs of extractors, separators, compressors, and heat exchangers; the model has undergone several iterations by the author. Nonlinear programming was used to determine designs that minimize the annualized cost/kg of product, including both the case of batch and semicontinuous operation. It was found that the lowest oil-selling price (for canola oil) was obtained with semicontinuous operation employing high extraction pressures and low fluid-flow rates. This was partly due to the use of a relative low flow rate that reduced the size and cost of the compressors and heat exchangers. For this particular iteration, the supercritical-fluid-based process yielded a \$1.40/kg price for the canola oil vs. \$0.44/kg for the *n*-hexane-extracted product. It should be noted that the SFE figure was for operation at 880 bar pressure at which point, canola oil solubility is very high and included credits for sale of the canola meal.

An interesting related cost analysis has been performed by Vijayan et al. for the deoiling of potato chips (58). His economic analysis concludes that if the capital equipment costs are in the range of 4–6 million dollars, and the estimated selling price of oil-reduced chips can be supported by the market, then the SFE process is a viable route for producing low-fat potato chips. Similarly, Passey (59) has presented an elegant cost analysis for the production of reduced calorie peanuts using a 16,000-L plant capacity that he forecasts would meet 2% of the future market demand for this product. This case envisions batch-semicontinuous operation on partially humidified peanut feedstock in order to limit kernel breakage; total plant capacity would be spread between four 4,000-L extraction vessels with the estimated plant cost would run 6.10 million dollars. Passey notes the sensitive of economic analysis to the cost of the raw material feedstock and selling price of product which can vary considerably on an annual basis. It should also be appreciated that for the case cited, a significant dual credit comes from both extracted

products (oil and extracted peanuts)—a factor that is often overlooked in economic forecasts for a commodity seed oil processed via SFE. Passey's economic analysis is far too detailed to discuss in length in this review; however, this author believes the method should serve as a template for anyone attempting the same exercise for commodity seed oil/meal production using SFE.

Conclusion

There is considerable literature describing SFE bench-scale studies of seed oil extraction. The process is relatively well understood in terms of thermodynamics, phase equilibria, and oil solubility in SC-CO₂, although mass-transport properties are still somewhat lacking. Data exists on pilot-plant studies above a 10-L capacity exist for batch, semicontinuous, and continuous operation. For large-scale extraction with SC-CO₂, there exists limited literature on design optimization and economic cost analysis. The lack of a continuous solid feed process operable at high pressure coupled with an unfavorable cost analysis would appear to make SFE using SC-CO₂ an undesirable option for large-scale processing of oilseeds. However, this situation radically changes for seed oils having higher potential market value (60), or an oilseed-extraction process in which both oil and meal have relatively high market value.

This outlook should not deter individuals from considering supercritical-fluid-based processes for other oil- or lipid-based materials. Application to higher value lipid extractives (61), such as tocopherols, sterols, and phospholipids, by employing fractionation techniques hold considerable promise. Likewise, reaction chemistry of lipid species in supercritical fluids may someday be coupled with SFE, or its fractionation analog, to produce unique materials for both food and industrial use.

Disclaimer

Names are necessary to report factually on data; however, the USDA neither guarantees nor warrants the standard of the product. The use of the name by the USDA implies no approval of the product to the exclusion of others that may be suitable.

References

1. Hierro, M.T.G., and Santa-Maria, G. Supercritical Fluid Extraction of Vegetable and Animal Fats with CO₂—A Mini Review. (1992) *Food Chem.* 45: 189–192.
2. Mangold, H.K. Liquefied Gases and Supercritical Fluids in Oilseed Extraction. (1983) *J. Am. Oil Chem. Soc.* 60: 226–228.
3. King, J.W., and List, G.R. (1996) *Supercritical Fluid Technology in Oil and Lipid Chemistry*, American Oil Chemists' Society Press, Champaign, IL.
4. Favtai, F., King, J.W., and Mazzanti, M. Supercritical Carbon Dioxide Extraction of Evening Primrose Oil. (1991) *J. Am. Oil Chem. Soc.* 68: 422–427.
5. King, J.W., Favtai, F., and Taylor, S.L. Production of Tocopherol Concentrates by Supercritical Fluid Extraction and Chromatography. (1996) *Sep. Sci. Tech.* 31: 1843–1857.

6. Klesper, E. (1980) in *Extraction with Supercritical Gases*, Schneider, G.M., Stahl, E., and Wilke, G., Verlag Chemie, Weinheim, Germany, pp. 94, 117.
7. McHugh, M.A., and Krukonis, V.J. (1994) in *Supercritical Fluid Extraction, 2nd edn.*, Butterworth-Heinemann, Boston, MA, pp. 294–299.
8. Friedrich, J.P., and Pryde, E.H. Supercritical CO₂ Extraction of Lipid-Bearing Materials and Characterization of the Products. (1984) *J. Am. Oil Chem. Soc.* 61: 223–228.
9. Friedrich, J.P., List, G.R., and Heakin, A.J. Petroleum-Free Extraction of Oil from Soybeans with Supercritical CO₂. (1982) *J. Am. Oil Chem. Soc.* 59: 288–292.
10. List, G.R., Friedrich, J.P., and Christianson, D.D. Properties and Processing of Corn Oils Obtained by Extraction with Supercritical Carbon Dioxide. (1984) *J. Am. Oil Chem. Soc.* 61: 1849–1851.
11. Bartle, K.D., and Clifford, A.A. (1992) in *Advances in Applied Lipid Research, Vol. 1*, JAI Press Ltd., London, pp. 217–264.
12. Friedrich, J.P. U.S. Patent 4,466,923 (1984).
13. Stahl, E., Quirin, K.-W., and Gerard, D. (1987) in *Dense Gases for Extraction and Refining*, Springer-Verlag, Heidelberg, pp. 82–102.
14. King, J.W., and France, J.F. (1992) in *Analysis with Supercritical Fluids*, Wenclawiak, B., Springer-Verlag, Berlin-Heidelberg, p. 37.
15. King, J.W. Generalized Extraction Conditions for the Critical Fluid Processing of Oils and Oleophilic Compounds. (1983) *J. Am. Oil Chem. Soc.* 60: 711.
16. Stahl, E., Quirin, K.-W., and Gerard, D. Solubilities of Soybean Oil, Jojoba Oil and Cuticular Wax in Dense Carbon Dioxide. (1983) *Fette-Seifen Anstrichmittel* 85: 458–463.
17. Del Valle, J.M., and Aguilera, J.M. An Improved Equation for Predicting the Solubility of Vegetable Oils in Supercritical CO₂. (1988) *Ind. Eng. Chem. Res.* 27: 1551–1553.
18. Klein, T., and Schulz, S. Measurement and Model Prediction of Vapor–Liquid Equilibria of Mixtures of Rapeseed Oil and Supercritical Carbon Dioxide. (1989) *Ind. Eng. Chem. Res.* 28: 1073–1081.
19. Goodrum, J.W., and Kilgo, M.B. Peanut Oil Extractions with SC-CO₂: Solubility and Kinetic Functions. (1987) *Am. Soc. Agric. Eng. J.* 30: 1865–1868.
20. Tilley, K.D., Chaplin, R.P., and Foster, N.R. Supercritical Fluid Extraction of the Triglycerides Present in Vegetable Oils. (1990) *Sep. Sci. Tech.* 25: 357–367.
21. Calvo, L., Cocero, M.J., and Diez, J.M. Oxidative Stability of Sunflower Oil Extracted with Supercritical Carbon Dioxide. (1994) *J. Am. Oil Chem. Soc.* 71: 1251–1254.
22. Stahl, E., Quirin, K.-W., and Gerard, D. (1987) in *Dense Gases for Extraction and Refining*, Springer-Verlag, Heidelberg, p. 6.
23. Brunner, G. Mass Transfer from Solid Material in Gas Extraction. (1984) *Ber. Bunsenges. Phys. Chem.* 88: 887–891.
24. Eggers, R. (1996) in *Supercritical Fluid Technology in Oil and Lipid Chemistry*, King, J.W., and List, G.R., American Oil Chemists' Society Press, Champaign, IL, pp. 35–64.
25. Hong, I.K., Rho, S.W., Lee, K.S., Lee, W.H., and Yoo, K.P. Modeling of Soybean Oil Bed Extraction with Supercritical Carbon Dioxide. (1990) *Korean J. Chem. Eng.* 7, 40–46.
26. Reverchon, E., and Osseo, L.S. (1993) in *I. Fluidi Supercritici e le Loro Applicazioni*, Reverchon, E., and Schiraldi, A., Ravello, Italy, pp. 69–79.
27. Cygnarowicz-Provost, M., O'Brien, D.J., Boswell, R.T., and Kurantz, M.J. Supercritical Fluid Extraction of Fungal Lipids: Effect of Cosolvent on Mass Transfer Rates and Process Design and Economics. (1995) *J. Supercrit. Fluids* 8: 51–59.

28. Snyder, J.M., Friedrich, J.P., and Christianson, D.D. Effect of Moisture and Particle Size on the Extractability of Oils from Seeds with Supercritical CO₂. (1984) *J. Am. Oil Chem. Soc.* 61: 1851-1856.
29. Evelein, K.A., Moore, R.G., and Heidemann, R.A. Correlation of the Phase Behavior in the Systems Hydrogen Sulfide-Water and Carbon Dioxide-Water. (1976) *Ind. Eng. Chem. Process Dev.* 15: 423-428.
30. King, J.W., Johnson, J.H., and Freidrich, J.P. Extraction of Fat Tissue from Meat Products with Supercritical Carbon Dioxide. (1989) *J. Agric. Food Chem.* 37: 951-954.
31. Peker, H., Srinivasan, M.P., Smith, J.M., and McCoy, B.J. Caffeine Extraction Rates from Coffee Beans with Supercritical Carbon Dioxide. (1992) *AIChE J.* 38: 761-770.
32. List, G.R., King, J.W., Johnson, J.H., Warner, K., and Mounts, T.L. Supercritical CO₂ Degumming and Physical Refining of Soybean Oil. (1993) *J. Am. Oil Chem. Soc.* 70: 473-476.
33. List, G.R., and Freidrich, J.P. Oxidative Stability of Seed Oils Extracted with Supercritical Carbon Dioxide. (1989) *J. Am. Oil Chem. Soc.* 66: 98-100.
34. Favati, F., King, J.W., Friedrich, J.P., and Eskins, K. Supercritical CO₂ Extraction of Carotene and Lutein from Leaf Protein Concentrates. (1988) *J. Food Sci.* 53, 1532-1536.
35. List, G.R., Friedrich, J.P., and King, J.W. Supercritical CO₂ Extraction and Processing of Oilseeds. (1989) *Oil Mill Gaz.* 95(6): 28-34.
36. Mounts, T.L. Perspectives on Processing Methods, Equipment and Procedures. (1983) *J. Am. Oil Chem. Soc.* 60: 453-456.
37. Eggers, R. High Pressure Extraction of Oilseeds. (1985) *J. Am. Oil Chem. Soc.* 62: 1222-1230.
38. Ooi, C.K., Bhaskar, A., Yener, M.S., Tuan, D.Q., Hsu, J., and Rizvi, S.S.H. Continuous Supercritical Carbon Dioxide Processing of Palm Oil. (1996) *J. Am. Oil Chem. Soc.* 73: 233-237.
39. Favati, F., King, J.W., and List, G.R. (1996) in *Supercritical Fluid Technology in Oil and Lipid Chemistry*, King, J.W., and List, G.R., American Oil Chemists' Society Press, Champaign, IL., pp. 267-287.
40. List, G.R., Friedrich, J.P., and Pominski, J. Characterization and Processing of Cottonseed Oil Obtained by Extraction with Supercritical Carbon Dioxide. (1984) *J. Am. Oil Chem. Soc.* 61: 1847-1849.
41. Kuk, M.S., and Hron, R.J., Sr. Supercritical Carbon Dioxide Extraction of Cottonseed with Cosolvents. (1994) *J. Am. Oil Chem. Soc.* 71: 1352-1356.
42. Brunner, G., and Peter, S. On the Solubility of Glycerides and Fatty Acids in Compressed Gases in the Presence of an Entrainer. (1982) *Sep. Sci. Tech.* 17: 199-214.
43. Zosel, K., U.S. Patent 3,969,196 (1976).
44. Sakaki, K., Yokochi, T., Suziki, O., and Hakuta, T. Supercritical Fluid Extraction of Fungal Oil Using CO₂, N₂O, CHF₃ and SF₆. (1990) *J. Am. Oil Chem. Soc.* 67: 553-557.
45. Brunner, G. Anwendungsmöglichkeiten der Gasextraktion im Bereich der Fette und Ole. (1986) *Fette-Seifen Anstrichmittel* 84: 464-474.
46. Rice, P.N., Abrishamian, R., and Meitsinger, A.E. "Extraction of Oilseeds with CF Systems' Process." paper presented at the 78th Annual Meeting of the American Oil Chemists' Society, New Orleans, LA, May, 1987.
47. Norris, F.A. (1982) in *Bailey's Industrial Oil and Fat Products, Vol. 2, 4th edn.*, Swern, D., John Wiley & Sons, Inc., p. 289.
48. Gardner, D.S. (1993) in *Extraction of Natural Products Using Near-Critical Solvents*,

28. Snyder, J.M., Friedrich, J.P., and Christianson, D.D. Effect of Moisture and Particle Size on the Extractability of Oils from Seeds with Supercritical CO₂. (1984) *J. Am. Oil Chem. Soc.* 61: 1851-1856.
29. Evelein, K.A., Moore, R.G., and Heidemann, R.A. Correlation of the Phase Behavior in the Systems Hydrogen Sulfide-Water and Carbon Dioxide-Water. (1976) *Ind. Eng. Chem. Process Dev.* 15: 423-428.
30. King, J.W., Johnson, J.H., and Freidrich, J.P. Extraction of Fat Tissue from Meat Products with Supercritical Carbon Dioxide. (1989) *J. Agric. Food Chem.* 37: 951-954.
31. Peker, H., Srinivasan, M.P., Smith, J.M., and McCoy, B.J. Caffeine Extraction Rates from Coffee Beans with Supercritical Carbon Dioxide. (1992) *AIChE J.* 38: 761-770.
32. List, G.R., King, J.W., Johnson, J.H., Warner, K., and Mounts, T.L. Supercritical CO₂ Degumming and Physical Refining of Soybean Oil. (1993) *J. Am. Oil Chem. Soc.* 70: 473-476.
33. List, G.R., and Freidrich, J.P. Oxidative Stability of Seed Oils Extracted with Supercritical Carbon Dioxide. (1989) *J. Am. Oil Chem. Soc.* 66: 98-100.
34. Favati, F., King, J.W., Friedrich, J.P., and Eskins, K. Supercritical CO₂ Extraction of Carotene and Lutein from Leaf Protein Concentrates. (1988) *J. Food Sci.* 53, 1532-1536.
35. List, G.R., Friedrich, J.P., and King, J.W. Supercritical CO₂ Extraction and Processing of Oilseeds. (1989) *Oil Mill Gaz.* 95(6): 28-34.
36. Mounts, T.L. Perspectives on Processing Methods, Equipment and Procedures. (1983) *J. Am. Oil Chem. Soc.* 60: 453-456.
37. Eggers, R. High Pressure Extraction of Oilseeds. (1985) *J. Am. Oil Chem. Soc.* 62: 1222-1230.
38. Ooi, C.K., Bhaskar, A., Yener, M.S., Tuan, D.Q., Hsu, J., and Rizvi, S.S.H. Continuous Supercritical Carbon Dioxide Processing of Palm Oil. (1996) *J. Am. Oil Chem. Soc.* 73: 233-237.
39. Favati, F., King, J.W., and List, G.R. (1996) in *Supercritical Fluid Technology in Oil and Lipid Chemistry*, King, J.W., and List, G.R., American Oil Chemists' Society Press, Champaign, IL., pp. 267-287.
40. List, G.R., Friedrich, J.P., and Pominski, J. Characterization and Processing of Cottonseed Oil Obtained by Extraction with Supercritical Carbon Dioxide. (1984) *J. Am. Oil Chem. Soc.* 61: 1847-1849.
41. Kuk, M.S., and Hron, R.J., Sr. Supercritical Carbon Dioxide Extraction of Cottonseed with Cosolvents. (1994) *J. Am. Oil Chem. Soc.* 71: 1352-1356.
42. Brunner, G., and Peter, S. On the Solubility of Glycerides and Fatty Acids in Compressed Gases in the Presence of an Entrainer. (1982) *Sep. Sci. Tech.* 17: 199-214.
43. Zosel, K., U.S. Patent 3,969,196 (1976).
44. Sakaki, K., Yokochi, T., Suzuki, O., and Hakuta, T. Supercritical Fluid Extraction of Fungal Oil Using CO₂, N₂O, CHF₃ and SF₆. (1990) *J. Am. Oil Chem. Soc.* 67: 553-557.
45. Brunner, G. Anwendungsmöglichkeiten der Gasextraktion im Bereich der Fette und Ole. (1986) *Fette-Seifen Anstrichmittel* 84: 464-474.
46. Rice, P.N., Abrishamian, R., and Meitsinger, A.E. "Extraction of Oilseeds with CF Systems' Process," paper presented at the 78th Annual Meeting of the American Oil Chemists' Society, New Orleans, LA, May, 1987.
47. Norris, F.A. (1982) in *Bailey's Industrial Oil and Fat Products*, Vol. 2, 4th edn., Swern, D., John Wiley & Sons, Inc., p. 289.
48. Gardner, D.S. (1993) in *Extraction of Natural Products Using Near-Critical Solvents*,