Supercritical fluids for extraction of flavors and fragrances from natural products

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T he past decade saw the emergence of several noteworthy trends: enhanced consumer concern for the quality and safety of foods; more stringent government regulations on solvents and allowable residues; and increasing energy costs. In the future, issues such as these will significantly affect the future of many technology-oriented processes, including natural flavor and fragrance extraction.

In view of these influences, processors must be aware of both the positive *and* negative attributes inherent in the extraction of natural products. On one hand, the present popular belief that "everything 'natural' is good" provides positive incentive towards growth. "Mother Nature" is considered a marvelous synthesizer of desirable flavors and fragrances. The subtle nuances and characteristic notes possessed by natural extracts have not yet been equalled by synthetic materials, although significant strides have been made in the compounding of synthetic chemicals. On the other hand, the dual issues of increased government regulation and higher energy costs create a negative environment for growth. Solvent extraction and solvent distillation are common process operations in the production of natural flavors and fragrances, and both are influenced to some extent by the previously mentioned issues.

To minimize the competitive edge of synthetic materials, alternate extraction methodologies that are cost efficient and comply with both consumer preference and regulatory controls must be used. Extraction with supercritical fluids (SCF) is one such method.

SCF extraction uses a clean, inexpensive, nonflammable, nontoxic solvent such as carbon dioxide for the extraction of natural flavors and fragrances. In addition to being clean and safe, the energy costs associated with this novel extraction process are often lower than the costs of traditional solvent extraction methods. This article will discuss applications of SCF extraction in the isolation of flavors and fragrances from natural products. To give an overview of the process, a brief history of its technology and some basic information and theory are included in order.

History

Table I presents, in a nutshell, the long history of supercritical fluid extraction technology. In 1879 Hannay and Hogarth reported their observations on the enhanced solubility of inorganic salts in supercritical ethanol and ether.[1] They found that the solubility of salts such as cobalt chloride and potassium iodide increased with increasing pressure. (Andrews had actually discovered the phenomenon in 1875 but his work was published only after his death in 1887.[2])

In the early 1900s, Buchner and Centnerszwer studied the solubilities of organic materials in supercritical carbon dioxide and ammonia.[3-5] They reported on the solubility of compounds with low volatility, including naphthalene, anthracene, camphor, and substituted phenols. As had previous investigators, these authors also reported that at isothermal conditions, changes in pressure dramatically affected solubility.

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In the 1950s, Francis conducted extensive studies on literally hundreds of organic materials and their solubility in carbon dioxide at conditions just below its critical point.[6-8] During this period, also, various groups in Russia, Germany and the United States began seriously exploring the potential of this novel extraction process. The separation of chemicals and petroleum fractions and the extraction of natural products with near critical liquids and supercritical fluids became the subject of extensive process development effort. Various patents on process applications of near-critical and supercritical fluid phenomenon in the areas of foods, flavors, oils and specialty chemicals began to appear in the late 1960s.

Presently, two commercial scale process applications are known. There is a large plant in Germany for the decaffeination of coffee with supercritical carbon dioxide. The plant is owned by Hag AG, which was purchased by General Foods in 1979. And in Australia, liquid carbon dioxide extraction of hops is now a commercial reality.

Nomenclature and SCF extractants

Various generic descriptions have been coined to describe this separation process. No generally accepted nomenclature presently exists. Common terms used include *destraction*,[9] *dense gas extraction*,[10] *vapor phase extraction*,[11] and *supercritical fluid extraction*.[12] The term *supercritical fluid extraction* (SCF) as it is used in this paper is restricted to those processes that use a fluid phase above its critical temperature and critical pressure. This is to be distinguished from the use of compressed gases at subcritical conditions, because of the different physical state and solvating power of the extractants at subcritical and supercritical conditions.

Various monographs have been written on the critical point phenomena, that is, the disappearance of the miniscus, the equality of liquid and vapor phase densities, and the more intricate physicochemical principles associated with the novel method. The interested reader is urged to explore further.[10,13-16]

Several common chemicals have been tested as supercritical fluid extractants at Arthur D. Little, Inc. and at other laboratories. The critical pressure and temperature for these chemicals are shown in Table II.

Attractiveness of carbon dioxide for fragrance and flavor extraction

The most desirable solvent for the isolation of flavors and fragrances is carbon dioxide. It is an inert, nonflammable, nonexplosive, clean solvent that leaves no solvent residue in the product. It is nontoxic and is generally accepted as a harmless ingredient of foods and beverages. Moreover, carbon dioxide is readily available in large quantities and high purity. It is probably the cheapest solvent next to water; it costs only about 3¢/lb. Other very important physical properties of carbon dioxide that give it very favorable extraction characteristics are its low surface tension and viscosity and its high diffusivity.[16,17] The diffusivity of supercritical carbon dioxide is one to two orders of magnitude higher than those of other liquids. The high diffusivity permits rapid mass transfer and thereby yields a faster rate of extraction than that obtained by conventional liquid extraction.

It should also be noted that the critical temperature of carbon dioxide is only 31°C, which makes this solvent attractive for processing thermally labile natural products such as jasmine, chamomile, and other delicate essences. Moreover, it has been found that the energy associated with the normal heat requirements for distillation and evaporation of conventional organic solvents is often greater than the energy associated with compression of the supercritical fluid extractant. Thus, decreased energy cost is another motivating factor for supercritical fluid extraction processes.

Solubility in supercritical fluids

The strong pressure dependence of solubility of certain solutes in compressed fluids is a key factor in supercritical fluid extraction. As an example, figure 1 shows the effect of pressure on the solubility (in

Table I. Historical perspective on solubility in supercritical fluids

- 1879 – Solubility of Inorganic Salts Reported by Hannay & Hogarth

- 1900's to 1950's – Solubility of Organic Compounds Studied by Various Investigators

- 1955 to Present – Solubility Phenomena Applied to Extraction Processes

- Late 1970's – Commercial Scale Process Applications Emerged

Table II. Critical temperatures and pressures of selected supercritical fluid extractants

Fluid	Pressure, ATM	Temperature, C
Carbon Dioxide	73	31
Ethylene	50	10
Ethane	48	32
Propylene	46	92
Propane	42	87
Sulfur Hexafluoride	37	46
Ammonia	111	132
Nitrous Oxide	71	36

g/liter) of p-iodo-chlorobenzene[18] in ethylene at 25°C (T_c=10°C) and of naphthalene[19] in carbon dioxide at 45°C (T_c=31°C). It is seen that in both cases at low pressures of 1 atm or above, the solutes are virtually insoluble in their respective solvents. However, as the pressure is increased to points beyond the respective critical pressures (50 atm for ethylene and 73 atm for carbon dioxide) a dramatic increase in solubility behavior is observed. The observed enhanced solubility is orders of magnitude greater than that which be due simply to vapor pressure contribution.

Process schematic

Figure 2 shows a schematic diagram of the processing equipment for supercritical fluid extraction. The four primary components needed are a stainless steel extraction vessel, a pressure reduction valve, a separator, and a compressor for recycling the fluid. In this simplified diagram, ancillary equipment such as pumps, valving, fluid make-up source, and other equipment, such as heat exchangers for heating/
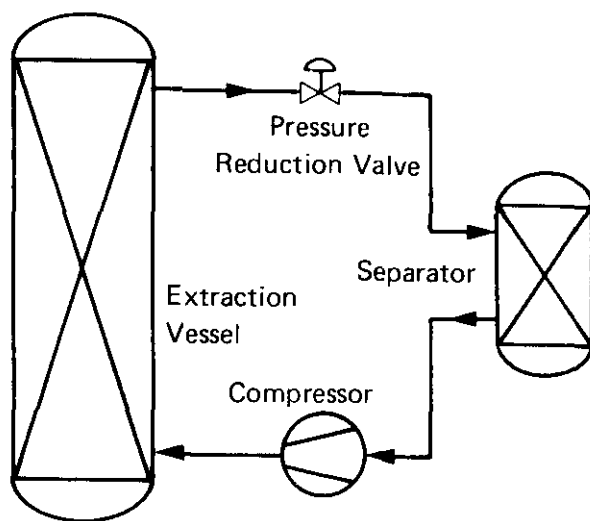

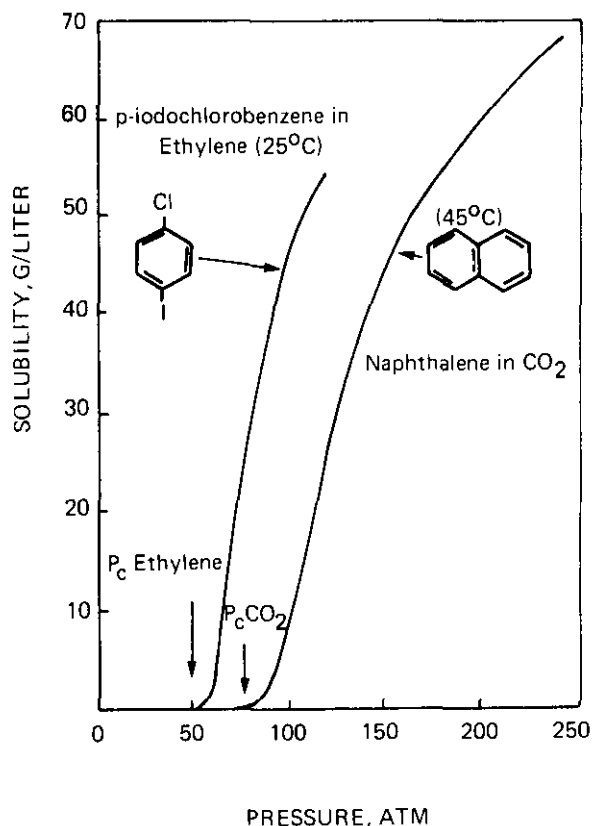Figure 2. Schematic diagram of supercritical fluid extraction process.

Figure 1. Solubility of organics in supercritical fluids.

cooling the fluid, are omitted for clarity. For example, for extracting solids, multiple extraction vessels are used in a batch-continuous system—that is, one or more vessels will be in an extraction mode, while the others will be filled or unloaded.

Figure 3 is a plot of extensive data on the solubility of naphthalene in carbon dioxide as a function of temperature and pressure. When used in conjunction with figure 2, these diagrams illustrate the closed-loop operation of the extraction process. As an example of operating principles, two points are designated on two solubility isobars in figure 3. Point E represents extraction vessel conditions and point S represents separator conditions. Thus, in this example, supercritical carbon dioxide at 300 atm and 50°C is fed to the extraction vessel, where it dissolves or extracts the material. The carbon dioxide-naphthalene stream is expanded to 100 atm via the pressure reduction valve (as indicated by an isothermal path in figure 3 from points E to S) and the napthalene, which now precipitates out due to a decreased solubility during the expansion process, is collected in the separator. The carbon dioxide is recompressed, returned to the extractor and the process continues until all the naphthalene is extracted.

Although the example cited represents a simple case, the principle and process discussed above could be used for the extraction of more complex flavors and fragrances from natural products.
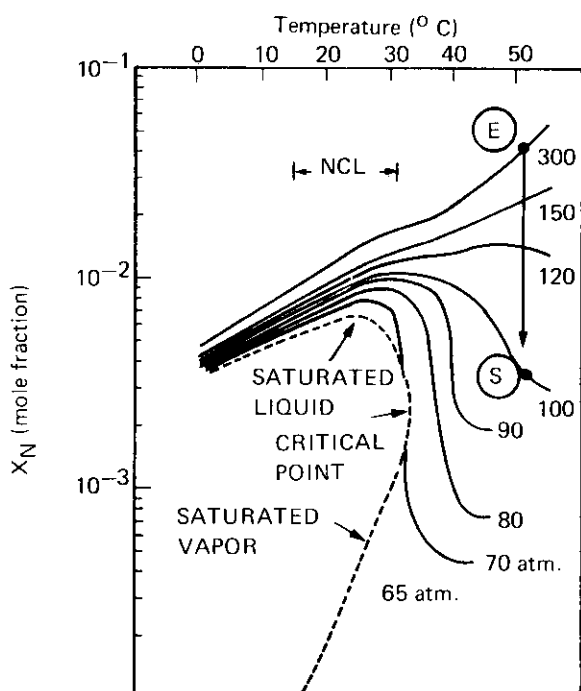
Figure 3. Solubility of napthalene in carbon dioxide.

Process applications

Several process applications of supercritical fluid extraction are presently known, including a variety of processes beyond the flavor and fragrance industry. The application of interest to perfumers and flavorists will be discussed in the following sections, but the other applications are mentioned as examples of the process applications being pursued extensively in at least three countries: Russia, Germany, and the United States. These processes include regeneration of activated carbon,[20,21] deasphalting of petroleum fractions,[22] extraction of ozokerite from shale,[22] isolation of pharmacologically active materials,[23] fractionation of fuels.[24,25] chemical separations,[26-28] and processing and molecular weight fractionation of polymers.[29,30]

Hop extraction

The use of hop extracts in the production of beer has increased to the point that almost 25% of the world's supply of hops is converted to hop extract. The use of hop extract to adjust the bitterness of beer is not allowed in only a few countries, including Japan and Germany.

The desirable constituents of hops are the soft res-

ins, which consist of the α-acid constituents (humulones) and the β-acid constituents (lupulones). In the brewing process, the α-acids are isomerized to give beer its characteristic bitter taste. Thus, in the production of hop extract, it is necessary that extraction conditions favor the extraction of the soft resins with minimal production of undesirable by-products. In place of the conventional solvent extraction methods with hexane or methylene chloride, extraction of the important flavor components of hops has been carried out by using supercritical[31,32] as well as liquid carbon dioxide.[33-35] The advantages and disadvantages of these two processes have been evaluated.[36] Various patents also cover the use of compressed gases for the extraction of hops.[32,37-40]

Extraction at supercritical conditions affords a more rapid, more efficient, but less selective extraction. The processing conditions used by Hubert and Vitzthum with supercritical carbon dioxide in the temperature range of 35-80°C and a pressure range of 80-300 atm with a single stage pressure reduction have produced an olive green pasty extract with an intense aroma of hops and a high yield of α- and β-acids.[31] The green color and intense hops aroma suggest that chlorophyll and essential oils are coextracted with the valuable soft resins. Investigations on further fractionation of the extract were conducted by releasing the pressure at several stages to effect separation of the dissolved components. This process allows the production of extracts of different composition, ranging in color from green to yellow.

Liquid carbon dioxide extraction of hops is a more selective process that removes only the hop components important in brewing: the α-acids, β-acids, and hop essential oils. The undesirable hard resins and polyphenolic materials are excluded. Another advantage of the liquid carbon dioxide process is that it operates at subcritical conditions—relatively low pressure (<73 atm) compared to supercritical carbon dioxide, which can be equated with lower energy

Table III. Comparison of hops extract produced by three extraction processes

Process	Composition of Extract, Weight %			
	α-Acids	β Acids	Soft Resins	Hard Resins
CH₂Cl₂ Extraction	40	42	82	7
Liquid Carbon Dioxide				
UK	40–60	18–45	70–98	
Australia	45–50	30–35	95–100	–
Supercritical Carbon Dioxide	41	44	85	5

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cost. Liquid carbon dioxide is used for the commercial scale production of hops extract.

The total yield of soft resins by either the use of liquid carbon dioxide, or supercritical carbon dioxide, compares very favorably with the yields of conventional solvent extraction as shown in Table III, based on some reported data.[32,33] It is interesting to note that no hard resins were reported in the liquid carbon dioxide extracts.

Decaffeination of coffee and tea

The decaffeination of coffee with supercritical fluids is an interesting process application not only because it is the largest known commercial operation, but also because several creative variations of the process have been tried. Various patents cover the decaffeination of coffee, which can be performed either on green coffee beans or on roasted coffee beans with no deleterious effect on coffee flavor.[41-48]

In the decaffeination of green coffee beans, one variation consists of charging green coffee beans, presoaked in water, into a pressure vessel and extracting it with carbon dioxide at 160-220 atm. The caffein dissolves in the supercritical carbon dioxide, and the caffeine-rich carbon dioxide stream is allowed to diffuse out of the pressure vessel into a washing tower. In the washing tower, water at 70-90°C acts as an entrainer for the caffeine, and the stripped carbon dioxide is recycled again. The caffeine is recovered by distillation. Coffee beans with a caffeine content of 0.7% to 3% can be decaffeinated to as low as 0.2%.

Another system innovation requires replacing the water scrubber with activated carbon to entrain the caffeine. In a third variation, the green coffee beans are mixed directly with activated carbon pellets of smaller size than the beans. The size of the carbon pellets is such that they fill the space between the beans. The usual ratio, by weight, is one part activated carbon to three parts of coffee beans. Extraction conditions are carbon dioxide at 90°C and 220 atm. The caffeine, dissolved in the supercritical carbon dioxide, diffuses out of the beans and is directly adsorbed by the charcoal. Subsequently, the decaffeinated coffee beans are separated from the charcoal by sieving.

For these process variations using an entrainer, recovery of the caffeine requires further extraction from the activated carbon and subsequent distillation. This is in contrast to process conditions wherein a pressure reduction with or without a temperature change is employed to separate the dissolved material from the extractant. The trade off implemented in these process modifications with entrainers is that the carbon dioxide is not subjected to pressure and temperature changes during the extraction and solute separation modes, thus saving the energy expended in recompressing the recycled carbon dioxide.

Roasted coffee beans can be subjected to a multi-step process to produce decaffeinated coffee beans or caffeine-free instant coffee. Prior to decaffeination, roasted coffee beans or rough ground coffee is first extracted with dry supercritical carbon dioxide to extract the soluble aromatics and coffee oils to avoid loss of these flavor components. Then, decaffeination is carried out with wet supercritical carbon dioxide.* In both steps, a pressure reduction process separates the dissolved solutes from the extracting fluid, which is then recompressed and recycled. The soluble aromatics and coffee oils can be redeposited back into the decaffeinated coffee beans by reversing the fluid flow cycle.

Caffeine-free instant coffee can be prepared by treating the decaffeinated rough ground coffee with water and spray- or freeze-drying the aqueous extract. The coffee powder obtained is aromatized with a portion of the coffee oils derived from the first extraction stage described above.

Liquid and supercritical carbon dioxide have been used to extract coffee aroma, oils, and caffeine. Faster extraction rates are achieved at supercritical conditions.

Caffeine-rich black tea[49] can be produced by a process similar to the multi-step production of decaffeinated coffee. The process can produce caffeine-free tea leaves and caffeine-free instant tea.

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*The carbon dioxide is passed through a water scrubber to dissolve some water.

Table IV. Some natural products extracted with liquid or supercritical carbon dioxide

Natural Product	Constituents Extracted	Extractant Condition
Fruit juices	Alcohols, esters, aldehydes, ketones	Liquid
Black pepper	Essential oil, piperine	SCF
Chili pepper	Essential oil, capsaicine alkaloids	SCF
Cloves	Essential oil, eugenol	SCF
Cinnamon	Essential oil, cinnamic aldehyde, eugenol	SCF
Nutmeg	Essential oil, trimyristin	SCF
Caraway	Limonene, carvone, triglycerides	SCF
Sesame seeds	Sesamin, triglycerides	SCF
Vanilla pods	Essential oil, vanillin	SCF
Peppermint leaves	Essential oil, menthol, menthone	SCF
Roses	Essential oil, geraniol, citronellal	SCF
Chamomile flowers	Essential oil, matricin, herniarin, a-bisabolol, "ene yne dicycloethers"	SCF

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Flavors, spices, essential oils

A large number of natural products have been extracted with liquid or supercritical carbon dioxide to concentrate and isolate the components of interest. Some of these natural products are cited in Table IV along with information on constituents extracted and extractant condition. Flavor-containing liquids, such as fruit juices and vegetable juices, have been extracted with liquid carbon dioxide.[50-55] Liquid carbon dioxide is a highly selective solvent. The alcohols, esters, aldehydes, and ketones that make up the chemical constituents of fruit juices are very soluble, while water has a limited solubility (ca. 0.1% w/w) and the salts, sugars, and proteins are insoluble. Extraction with liquid carbon dioxide minimizes loss of the important volatile flavor components that are primarily responsible for the flavors of the fresh produce.

Extraction of fruit juices such as apples, oranges, peaches, pineapples, berries, and pears has been investigated extensively by Randall and Schultz and coworkers.[50-52] As an example of achievable effects,

figure 4 shows the gas chromatograms obtained by head space analysis of the feed material, fresh Bartlett pear juice (5 cc vapor), and the derived carbon dioxide extract (1 cc vapor). Note that the attenuations for the carbon dioxide extract chromatogram are generally higher than those used for the feed material. The chromatograms clearly demonstrate the concentrating power of carbon dioxide extraction. Moreover, the chromatograms show that the chemical components are effectively extracted by liquid carbon dioxide without significant disproportionation.

Schultz compared the extraction of organic volatiles from commercial Delicious apple essence by extraction with liquid carbon dioxide, isopentane, diethylether, and a fluorocarbon solvent.[50] The carbon dioxide extract as obtained was an oil and all the other extracts were concentrated to an oil by distillation. The resulting oil from the carbon dioxide extraction contained less than 1% residual solvent, while the oil phase from all other extraction solvents contained as much as 40% to 55% residual solvent. The oil from the four extraction systems was analyzed by gas
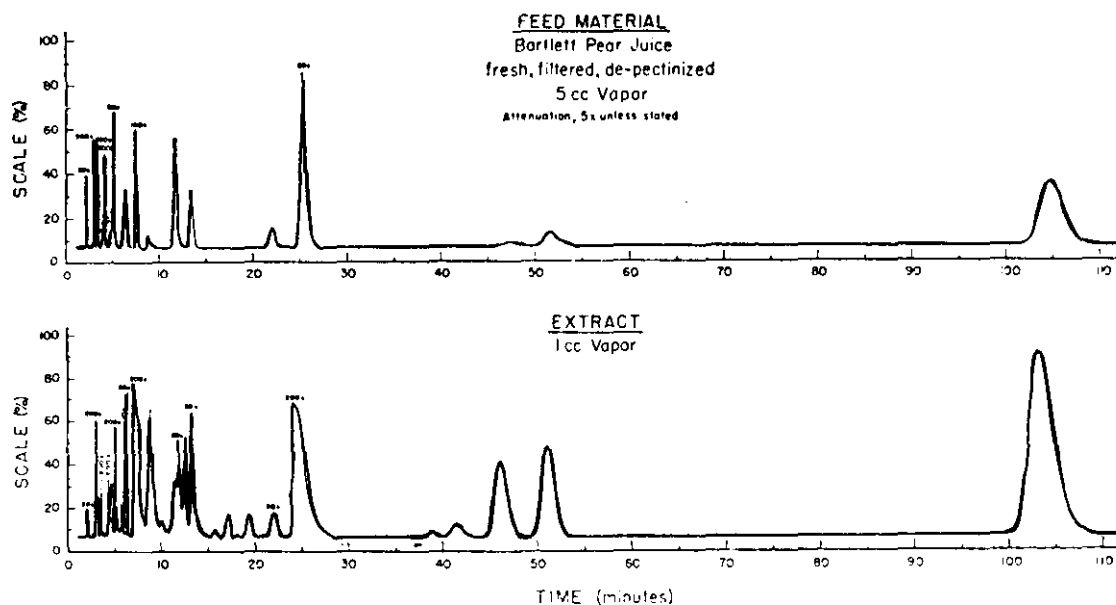

Figure 4. Gas-liquid chromatography comparison of feed and extract from Bartlett pear juice.
Reprinted from Confructa, **16**, No. 1, 16, 1971.

chromatography and organoleptic methods. The organoleptic analysis indicated that the principal flavoring components were extracted from the aqueous essence by the various solvents. Gas chromatographic analysis showed that the organic volatiles extracted include acetaldehyde, hexenal, several esters, and C_1

to C_6 alcohols. The liquid carbon dioxide extract appeared to be more similar to the ether extract as shown in Table V. Despite the differences observed in the composition of the various extracts, the organoleptic characterization indicated that the principle flavoring constituents were extracted from the
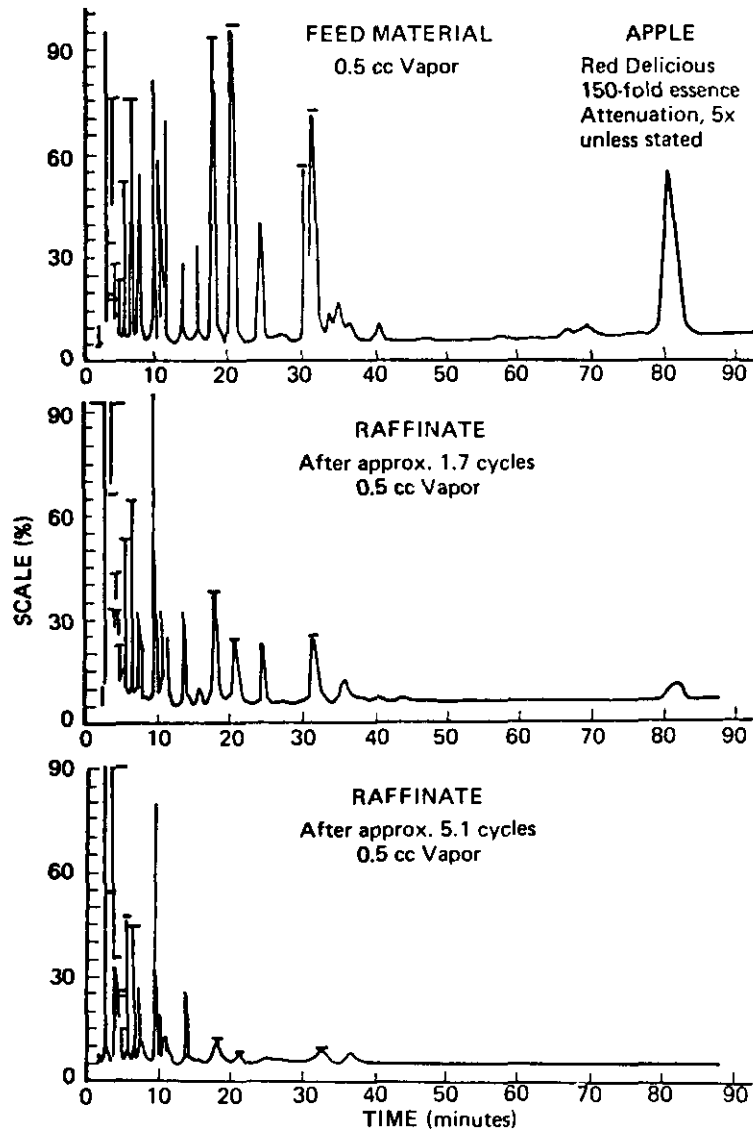

Figure 5. Effect of carbon dioxide volume or extraction time on extraction of Delicious apple essence. Reprinted from Food Technology, **24**, 1283, 1970. Copyright © by Institute of Food Technologists.

aqueous essence by the various solvents.

The three gas chromatograms in figure 5 indicate trends in the liquid carbon dioxide extraction of Red Delicious apple 150-fold essence. It shows gas chromatograms obtained by head space analysis of the feed material and raffinates at two stages of extraction. The complete extraction of the flavor components or organic volatiles depends on total volume of carbon dioxide, i.e., number of cycles or extraction time. Note that the components with retention times greater than 10 minutes appear to be more favorably extracted than the earlier eluting components. The important compounds for apple aroma—ethyl-2-methyl butyrate, trans-2-hexenal, and hexenal—are effectively extracted. Sensory panelists described the carbon dioxide extract as more pleasant and more fragrant than the original feed.

Extraction with carbon dioxide has also been used to concentrate flavors of vegetable materials including tomatoes, carrots, celery, and watercress. Schultz and coworkers of the USDA Western Regional Research Laboratory described a pilot plant for liquid carbon dioxide extraction of liquid foods and aqueous essences; a companion unit is used to process solid or macerated materials.[53]

Extracts of spices or oleoresins are important industrial ingredients. In comparison with dried or ground spices, the oleoresins offer several advantages such as freedom from microbial growth and easier standardization and processing. Supercritical fluids have been used to extract the aroma and flavor components of spices to produce spice extracts with a natural com-

Table V. Comparison of composition of extracts from delicious apple essence by various solvents

Compounds Found	Carbon Dioxide	Isopentane	Ether	Fluorocarbon
C_1–C_5 Alcohols	25	3	28	2
C_6 Alcohols	18	12	21	9
Acetaldehyde	3	–	tr	4
C_6 Acetaldehyde	24	50	30	45
Esters	28	33	19	38

— — Percent Composition, Solvent-Free Basis — —

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position and free of solvent residues.[56] The essential oil components of the spices, their active principles, and the triglycerides were found to be extracted. The composition of various spice extracts prepared by supercritical carbon dioxide extraction and by conventional solvent extraction, usually with methylene chloride, is shown in Table VI. The composition data have been limited to a few key components for which assay values were available; color of extracts is also indicated. Carbon dioxide extraction compares very favorably with conventional solvent extraction in terms of yield, product quality, and processing cost.

Essential oils from flowers present another interesting application of supercritical fluid extraction, since most of the essential oils from flowers are susceptible to thermal degradation. Extraction of roses and chamomile flowers have been investigated. German chamomile has been extracted with supercritical carbon dioxide and nitrous oxide.[57] The terpene hydrocarbons were extracted from the chamomile flowers as well as the biologically active components such as bisabolol, herniarin, and matricin. The extraction rate of these components depends on pressure, and thus separation of the various constituents can be carried out by stepwise extraction.

Conclusion and outlook

The key points that have been elucidated in this discussion follow.

- Carbon dioxide is an inert and ideally clean solvent

for food use.
- Most flavor and fragrance constituents are soluble in liquid and supercritical carbon dioxide.
- Supercritical fluid extraction is advantageous for extracting thermally labile materials.
- Extracts obtained by extraction with liquid or supercritical carbon dioxide compare favorably with, and are often superior to, conventional solvent extracts.

In view of the impact of tightening government regulations on allowable solvent residues in foods and increasing energy costs associated with conventional processes, further exploration of commercial applications of this novel process is to be expected. In fact, there is already increasing evidence that a number of flavor and fragrance establishments have begun investigating applications of this emerging technology.

The applications discussed in this article have been limited only to flavor and fragrance extraction. It should be noted, however, that supercritical fluid extraction has a much wider range of applications. It can compete directly with two widely used separation processes—distillation and solvent extraction. Various research groups are studying theoretical and practical aspects of this novel technology. For example, in our laboratories, studies are under way to develop applications pertaining to fuel processing, activated carbon regeneration, fractionation of specialty chemicals, fats and oils extraction, and isolation of pharmacologically active materials.

Table VI. Comparison of composition of extracts: Carbon dioxide extraction vs. conventional solvent extraction

| Natural Product | Selected Component Extracted | Carbon Dioxide | | Conventional Solvent |
		% Composition	% Extraction Efficiency	% Composition
Pepper	Piperine	44	98	41
	Essential Oil	13	81	15
	Color of Extract	Yellow		Olive Green
Chili	Capsaicine	4.9	97	4.7
	Color of Extract	Red		Red
Nutmeg	Essential Oil	19	99	20
	Color of Extract	Whitish Yellow		Yellowish Brown
Cloves	Eugenol	64	98	NA
	Color of Extract	Yellowish-Brown		
Cinnamon	Cinnamaldehyde	39	~100	NA
	Eugenol	6	~100	
	Color of Extract	Yellow		

NA   Not Available

Sources: Hubert, P. and Vitzthum, O., Angew. Chem. Intl Ed. Engl. 17, 710 (1978).
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