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Supercritical Fluid Extraction in Citrus Oil Processing

High-pressure CO₂ system concentrates aroma and flavor compounds in citrus oils

F. Temelli, C. S. Chen, and R. J. Braddock

□ CITRUS AND MANY OTHER essential oils consist of mixtures of hydrocarbons of the terpene and sesquiterpene groups, oxygenated compounds, and nonvolatile residues. Advances in instrumental analysis—e.g., gas chromatography and mass spectroscopy—have made it possible to identify more than 150 compounds in cold-pressed citrus oils (Shaw, 1977, 1979a, 1979b). According to Shaw (1979a), cold-pressed orange oil contains about 96% terpene hydrocarbons, which is mostly d-limonene, 1.6% aldehydes, 0.8% alcohols, 0.3% esters, and 1% nonvolatile high-boiling components that cannot be detected by gas chromatography.

Limonene is the principal constituent of the terpene fraction. The terpenes do not contribute much to the flavor or fragrance of the oil. They act largely as carriers of the oxygenated compounds. Since they are mostly unsaturated compounds, they are unstable to heat and light, and rapidly oxidize in air. Consequently, they often decompose to undesirable compounds. In fact, the oxidation of cold-pressed oil has been attributed to autoxidation of limonene which resulted in the formation of carvone and carveol, compounds responsible for terpene-like off-notes (Bernhard and Marr, 1960; Buckholz and Daun, 1978).

It is the oxygenated compounds that provide much of the characteristic flavor of citrus oil. This flavor fraction consists of aldehydes (decanal, octanal, citronellal, dodecanal, neral, geranial, undecanal, nonanal, perillaldehyde, α - and β -sinensal), alcohols (linalool, α -terpineol, 1-octanol), and ketones (nootkatone). Ratios of total aldehydes, esters, alcohols, and organic acids present in the oils were found to be very important to the flavor characteristics of the individual oils (Braddock and Kesterson, 1976). Total aldehydes in orange oil are used as a measure of quality.

It is common industrial practice to remove some of the limonene and other terpenes to concentrate the oxygenated compounds in cold-pressed oils. Folded oils have the advantage of reduced storage and transportation costs because of their smaller volumes. Folded oils are preferred for use in flavoring food products to be heated or in beverages where limonene and oxidation products might be objectionable.

Vacuum distillation (Vora et al., 1983), steam distillation, extraction with solvents (Owusu-Yaw et al., 1986), and adsorption (Kirchner and Miller, 1952; Lijn and Lifshitz, 1969; Vora, 1982; Ferrer and Matthews,

1987) are processes used for folding cold-pressed oils. The drawbacks of all these processes are low yields, formation of degradation products, and/or addition of extracting solvent that must later be removed. There is a difference in the flavor of the product folded with these processes when compared to that of the original expressed oil. Supercritical fluid extraction technology can be a suitable alternative process for folding citrus essential oils.

Supercritical Fluid Extraction

Supercritical fluid extraction (SFE) processes have gained increasing importance in the chemical and food industries in recent years, since they can maximize product recovery and improve product quality while minimizing energy requirements. The fact that compressed gases can dissolve solids has been known since the late 1800s; however, it was not until recently that SFE technology has been the focus of active research which resulted in the publication of a number of review papers (Irani and Funk, 1977; Caragay, 1981; Williams, 1981; Paulaitis et al., 1983; Krukonis, 1985; Rizvi et al., 1986). Some of the motivations to employ SFE technology as a viable separation technique were: (1) increased cost of energy; (2) tightening government regulations on solvent residues and pollution control; (3) consumer concern over the use of chemical solvents in the manufacture of foods; and (4) increased demand for higher quality products which traditional processing techniques cannot meet.

Recent investigation of SFE technology has led to the identification of many possible applications of SFE in food industries. There are at least two commercial applications—one is in the decaffeination of coffee in a plant in Germany (Zosel, 1980) and the other is in recovery of hop extracts in a plant in Australia (Harold and Clarke, 1979). Both of these applications employ supercritical carbon dioxide to replace the conventional liquid solvents such as methylene chloride which is under investigation by the Food and Drug Administration and faces increasing restrictions on its use (Basta, 1985).

There are no solvent problems in the citrus industry. Instead, principal problems are how to produce desirable flavors for processed orange juice and how to minimize undesirable characteristics such as heated flavor or bitterness.

SFE technology offers potentials for extraction and separation of organic compounds at lower temperatures than those being used in the evaporation and distillation processes. Unfortunately, there are no satisfactory techniques that can be used to remove bitterness or cooked flavor. Application of supercritical fluid

Authors Temelli, Chen, and Braddock are employed by the University of Florida, IFAS, Citrus Research and Education Center, 700 Experiment Station Road, Lake Alfred, FL 33850

extraction to citrus essential oil processing has been described in a few literature references (Stahl and Gerard, 1985; Coppella and Barton, 1987; Robey and Sunder, 1984; Gerard, 1984; Hagh, 1986).

The conventional process for the recovery of cold-pressed citrus oils results in the extraction of carotenoids and cuticular wax together with the essential oil, and considerable amounts of essential oil remain in the peel residue. Calame and Steiner (1982) described the extraction of essential oil from lemon peel with supercritical carbon dioxide at 30 MPa and 40°C. They obtained a 0.9% oil yield and its composition was quite different from the commercially available cold-pressed oil. The major differences were in the aldehyde and alcohol contents. The CO₂-extracted oil contained less citral and more alcohols.

Another application of supercritical carbon-dioxide extraction for citrus processing was to remove limonin, a primary bitter component in citrus juices (Kimball, 1987). Using pressures between 21–41 MPa and temperatures between 30–60°C, a 25% reduction in the limonin content was achieved in 60 min with negligible effects on the ascorbic acid, pulp, titratable acidity, and total amino acids.

Recently, a patent (Japikse et al., 1987) was issued for the production of citrus flavor and aroma compositions from orange juice essences using carbon-dioxide extraction. The extract produced was enriched in desirable flavor and aroma compounds responsible for fresh citrus juice flavor. These compounds have a molecular weight less than or equal to that of limonene and some of them are acetaldehyde, ethyl butyrate, and ethyl-3-hexanoate. Carbon dioxide was used as a solvent at a temperature between its critical temperature and 100°C and at a reduced pressure (extraction pressure/critical pressure) between 0.56 and 1.31.

The objectives of this article are to describe a pilot-scale SFE system for study of liquid foods testing and to evaluate the extraction and separation of aroma and flavor compounds from citrus essential oils.

Principles of SFE Technology Using CO₂

The critical temperature of a gas is the temperature above which it cannot be liquefied, no matter how high the pressure. Similarly, the critical pressure of a gas is the pressure below which it cannot be liquefied, no matter how low the temperature. The critical temperature and pressure of CO₂ are 31°C and 7.3 MPa, respectively (88°F and 1073 psi). The supercritical region of CO₂ is shown by dotted lines in Figure 1. In this region, the compressed gas is called a supercritical fluid having characteristics of both gases and liquids. It has the density of a liquid and functions like a liquid solvent, but it diffuses easily like a gas.

The high density of a supercritical fluid allows it to dissolve large quantities of organic compounds that normally have low solubility in the ordinary liquid or gaseous states of the same fluid. However, the solubility of compounds in a supercritical fluid depends on solute and solvent properties.

The dissolved compounds can be recovered from the fluid by decreasing the pressure or increasing the temperature, both of which reduce fluid density and allow the dissolved compound to be separated from the fluid.

Pilot-Scale SFE System

An SFE system consists of four basic components:

(1) a solvent compressor or high-pressure pump; (2) an extractor or pressurized vessel; (3) a temperature/pressure control system; and (4) a separator or adsorber. A Supercritical Extraction Screening System with a 300-mL extraction chamber designed and manufactured by Autoclave Engineers, Inc. (Erie, Pa.) was selected for the study.

Preliminary experiments showed that it was necessary to modify the basic unit for citrus oil applications. After some modifications, the system was used either as a static-cell or as a dynamic-flow apparatus. Figure 2 shows the flow diagram for the modified system.

Main modifications were as follows:

1. The amount of tubing was minimized and only bottom-to-top flow of carbon dioxide through the extractor was made possible. Approximately 30 mL of tubing was removed which was equal to 10% of the extractor volume.

2. Original pump was replaced with one that has a higher capacity (46–920 mL/h).

3. A preheater was incorporated into the system by making use of the heater around the extractor. A coil was formed from the tubing and it was wrapped around the extractor vessel; then the heater was placed around the extractor and the tubing. This made it possible to use one controller both for the extractor and the preheater.

4. The controller for the heater of the extractor was replaced with one that could be adjusted. This adjustment resulted in a narrower proportional band width which gave better control of the extractor temperature.

5. After disconnecting the original pressure gauge on the extractor outlet line, a new gauge with a range of 20.7 MPa was placed directly on the extractor. This range was sufficient since higher pressures were not necessary when working with citrus oils.

6. Liquid- and critical-phase sampling valves were placed on the extractor cell, facilitating sampling directly from the extractor.

7. The original separator unit was disconnected. Instead, two glass tubes with side arms connected in series were used and they were placed in -25°C propylene glycol bath.

8. The ring of sparger tube at the bottom of the extractor cell was turned over so that the holes in the tube would point downwards. As such, it was possible to operate the system with small amounts of feed material and still have good contact between the oil sample and carbon dioxide.

After these modifications, the system operated as follows under a dynamic mode: Cold-pressed Valencia orange oil samples (10 mL) were placed in a 300-mL extraction chamber and the temperature was adjusted with the use of heaters around the chamber. The high-pressure pump delivered carbon dioxide continuously at a flow rate of 50 mL/min determined at 25°C and 100 kPa. Pressure was adjusted by a back pressure regulator. Carbon dioxide flowed through a preheater to insure that it reached extraction temperature before contacting the oil.

As carbon dioxide entered the extractor, it distributed through the oil solubilizing some of the components. Solubilized material was carried out of the extractor and the pressure was reduced through an expansion valve. The outlet line and valves were wrapped with a heating tape which was connected to a controller. Heating prevented the separation of the

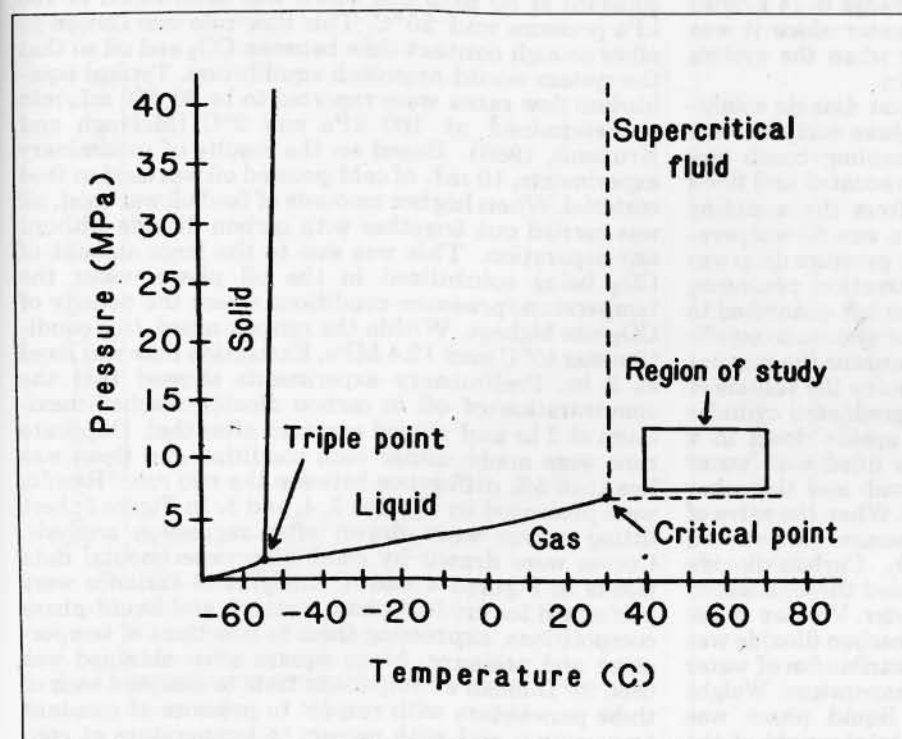


Fig. 1—Phase Diagram of Carbon Dioxide. The supercritical region of CO₂ is shown by dotted lines

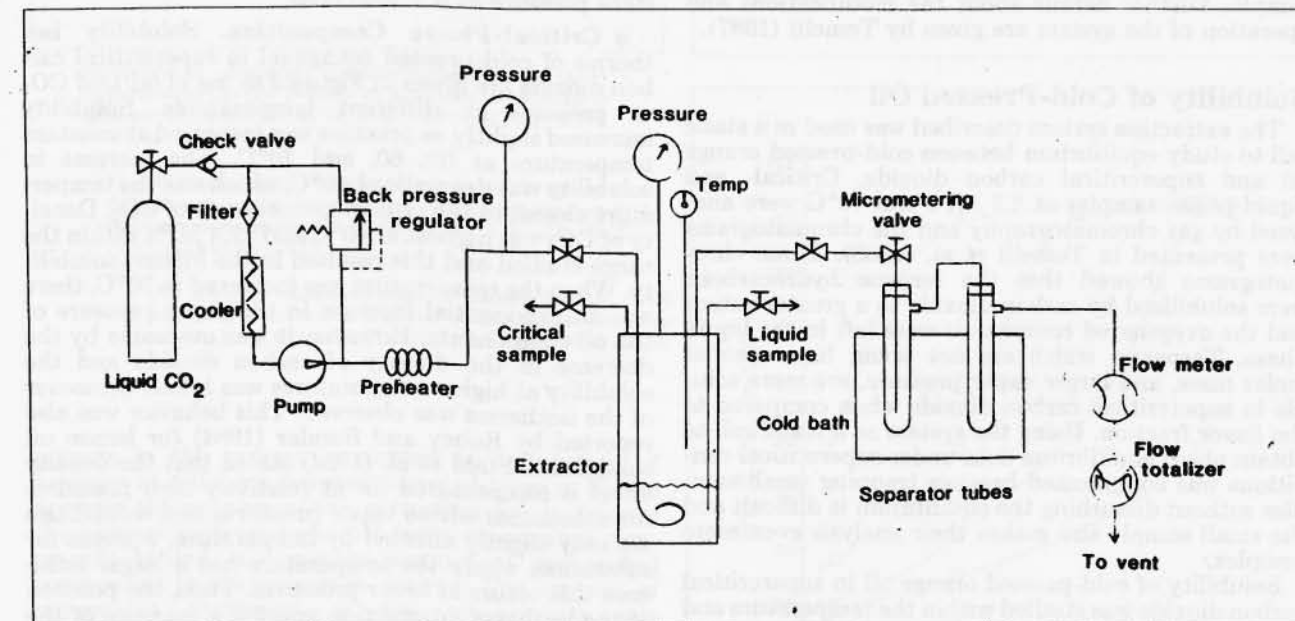


Fig. 2—Flow Diagram of Pilot-Scale Supercritical Fluid Extraction System

extract along the internal surface of the outlet line and freezing of the micrometering valve. Extracts were collected in separator tubes placed in a -25°C propylene glycol bath. The outlet of the micrometering valve was connected to the separator tube with a short vertical tubing so that carbon dioxide had to move downwards after being depressurized and any condensed extract on the walls would drain down into the separator tube. The amount of oil collected in the

separator unit for a given amount of time was determined gravimetrically. After the extract was collected, inlet and outlet openings of the tubes were sealed with polyethylene film immediately to prevent losses from volatilization of the extract during weighing. Then the extract was analyzed by gas chromatography. Corresponding volume of CO₂ was measured with a wet-gas meter. The instantaneous flow rate of the expanded CO₂ was measured with a bubble-flow meter at 100 kPa

and 25°C. The original flow meter (range 0–14 L/min) was replaced with a bubble-flow meter since it was difficult to get an accurate reading when the system operated at a flow rate of 50 mL/min.

To determine the amount of carbon dioxide solubilized in the oil, pressurized liquid-phase samples were taken and analyzed. A 2.5-mL sampling bomb was fabricated for this purpose. It was evacuated and filled with liquid phase under pressure from the sampling valve on the extraction vessel. There was no temperature change during sampling and the pressure drop was from 0 to 5% at low to high extraction pressures, respectively. The sampling bomb was left connected to the extractor for 10 min allowing the system to equilibrate. The bomb was weighed to determine the amount of sample. The system used to determine the volume of CO₂ is described as follows: A 2-L graduated cylinder was filled with water and placed upside down in a bucket of water. Tygon tubing was filled with water and one end was hooked to the bomb and the other inserted into the graduated cylinder. When the valve of the sampling bomb was opened, pressure was reduced resulting in the expansion of CO₂. Carbon-dioxide separated from the oil sample, bubbled through water, and collected in the graduated cylinder. Volume of gas collected was measured. Volume of carbon dioxide was determined after subtracting the contribution of water due to its vapor pressure at room temperature. Weight percentage of carbon dioxide in liquid phase was calculated from its volume and the total weight of the sample. Further details about the modifications and operation of the system are given by Temelli (1987).

Solubility of Cold-Pressed Oil

The extraction system described was used as a static cell to study equilibrium between cold-pressed orange oil and supercritical carbon dioxide. Critical- and liquid-phase samples at 8.3 MPa and 70°C were analyzed by gas chromatography and the chromatograms were presented in Temelli et al. (1988). These chromatograms showed that the terpene hydrocarbons were solubilized by carbon dioxide to a greater extent and the oxygenated compounds were left in the liquid phase. Terpenes, which are not polar, have smaller molar mass, and larger vapor pressure, are more soluble in supercritical carbon dioxide when compared to the flavor fraction. Using the system as a static cell to obtain phase equilibrium data under supercritical conditions was complicated because trapping small samples without disturbing the equilibrium is difficult and the small sample size makes their analysis even more complex.

Solubility of cold-pressed orange oil in supercritical carbon dioxide was studied within the temperature and pressure ranges of 40–70°C and 8.3–12.4 MPa, respectively, and this region is shown in Figure 1. At temperatures above this range, citrus oils begin to suffer thermal degradation. Stahl and Gerard (1985) used pure essential oil components and showed that the solubility of carvone, caryophyllene, and velaranone approached that of limonene at pressures around 12 MPa. So, it is impossible to fractionate citrus oils at pressures above 12 MPa due to increased density of carbon dioxide which results in an increase in the solubility of oxygenated compounds.

The extraction system was also operated under the dynamic mode. Carbon-dioxide flow rate was kept

constant at 50 mL/min which was determined at 100 kPa pressure and 25°C. This flow rate was chosen to allow enough contact time between CO₂ and oil so that the system would approach equilibrium. Typical equilibrium flow rates were reported to be 60–500 mL/min as determined at 100 kPa and 0°C (McHugh and Krukoni, 1986). Based on the results of preliminary experiments, 10 mL of cold-pressed oil was used as feed material. When higher amounts of feed oil was used, oil was carried out together with carbon dioxide without any separation. This was due to the large amount of CO₂ being solubilized in the oil phase under the temperature/pressure conditions where the density of CO₂ was highest. Within the range studied, this condition was 40°C and 12.4 MPa. Extraction time was fixed at 2 hr. Preliminary experiments showed that the concentration of oil in carbon dioxide reached maximum at 2 hr and stayed constant after that. Duplicate runs were made under each condition and there was less than 5% difference between the two runs. Results were presented in Figures 3, 4, and 5. In Figure 3, best fitting curves were drawn after regression analysis. Curves were drawn by combining experimental data points in Figures 4 and 5. Analyses of variance were performed for critical-phase, extract, and liquid-phase compositions, expressing them as functions of temperature and pressure. Mean square error obtained was used for Duncan's comparison tests to compare each of these parameters with respect to pressure at constant temperature and with respect to temperature at constant pressure at $\alpha = 0.05$ level.

• **Critical-Phase Composition.** Solubility isotherms of cold-pressed orange oil in supercritical carbon dioxide are given in Figure 3 as mg of oil/L of CO₂ vs pressure at different temperatures. Solubility increased slightly as pressure was increased at constant temperature at 50, 60, and 70°C. The increase in solubility was dramatic at 40°C, which was the temperature closest to the critical temperature of CO₂. Density of CO₂ was highest at 40°C and 12.4 MPa within the range studied and this resulted in the highest solubility. When the temperature was increased to 70°C, there was an exponential increase in the vapor pressure of the oil components. However, it was overcome by the decrease in the density of carbon dioxide and the solubility at higher temperatures was lower. Crossover of the isotherms was observed. This behavior was also reported by Robey and Sunder (1984) for lemon oil solubilities. Stahl et al. (1984) stated that the density effect is compensated for at relatively high pressures for substances whose vapor pressures and solubilities are only slightly affected by temperature, whereas for substances where the temperature has a larger influence this occurs at lower pressures. Thus, the position of the isotherm intersection point is a measure of the effect of temperature on solubility. Statistical analyses showed that there were no significant differences between the solubilities at different pressures at 50, 60, and 70°C at $\alpha = 0.05$ level. Solubility at 40°C and 12.4 MPa was significantly higher than that at other conditions studied.

• **Extract Composition.** Compositions of the extracts were analyzed by gas chromatography and triplicate injections were made from each sample. To compensate for day-to-day variation of the gas chromatograph, 99.67% limonene was used as an external standard. Weight percent of all the oxygenated com-

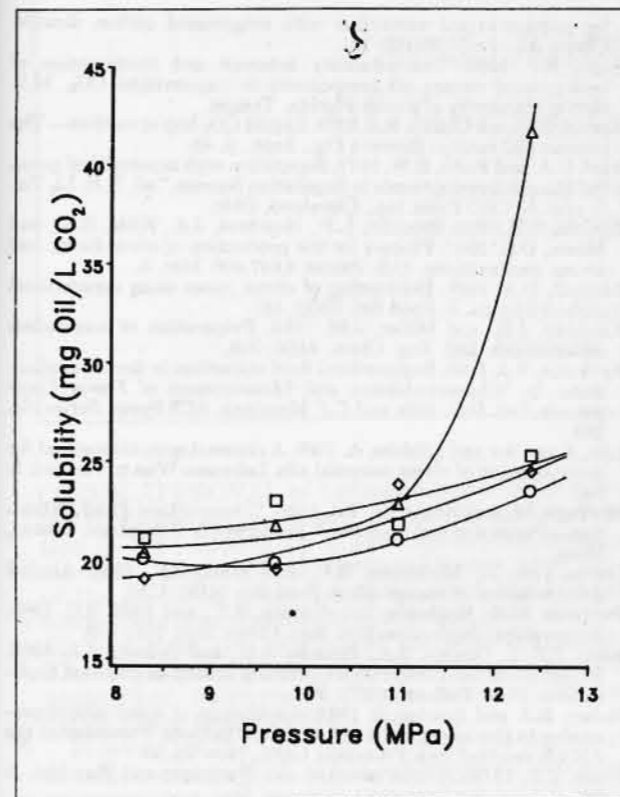


Fig. 3 (above)—Solubility of Cold-Pressed Orange Oil in Supercritical Carbon Dioxide as a function of pressure at different temperatures: 40°C (Δ-Δ), 50°C (□-□), 60°C (◇-◇), and 70°C (○-○)

Fig. 4 (above right)—Weight Percent of Oxygenated Compounds in the Extract as a function of pressure at different temperatures: 40°C (Δ-Δ), 50°C (□-□), 60°C (◇-◇), and 70°C (○-○)

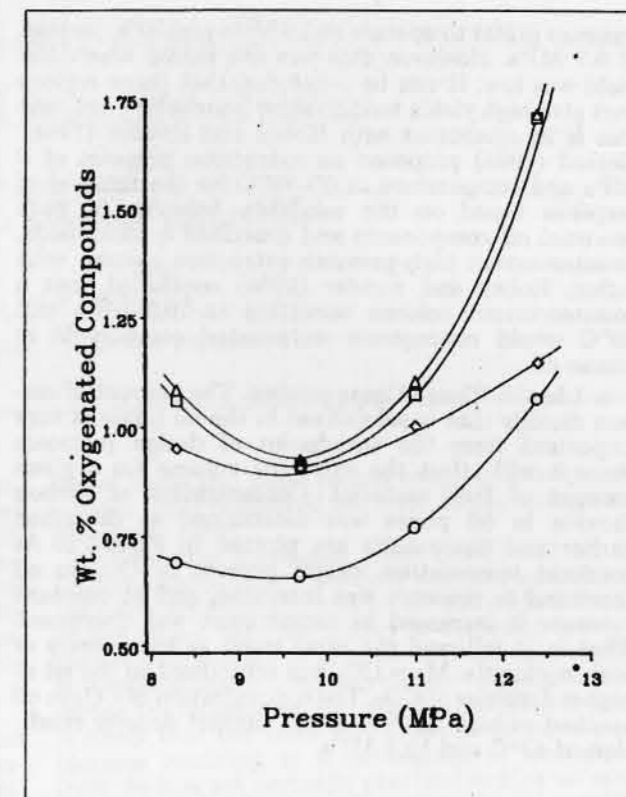
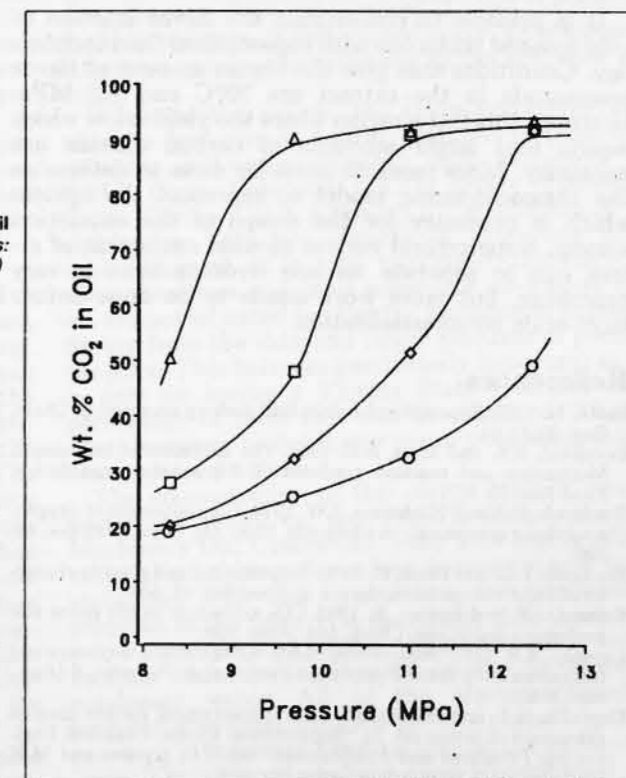


Fig. 5 (right)—Concentration of Carbon Dioxide in Oil Phase as a function of pressure at different temperatures: 40°C (Δ-Δ), 50°C (□-□), 60°C (◇-◇), and 70°C (○-○)



pounds in the extract is plotted as a function of pressure at different temperatures and given in Figure 4. Since the purpose of the extraction was to remove the terpene hydrocarbons and leave oxygenated compounds behind, a minimum amount of oxygenated compounds in the extract is desired. The amount of oxygenated compounds decreased as the temperature was increased. However, this decrease was not statistically significant for 40, 50, and 60°C at pressures of 8.3, 9.7, and 11.0 MPa. The amount of oxygenated compounds in the extract was significantly lower at 70°C than that at other temperatures. At constant temperature percentage of oxygenates passed through a minimum of 9.7 MPa, but this minimum was not significant. A pressure of 12.4 MPa gave the highest amount of oxygenates which was statistically significant at all temperatures. As a result, the condition that gave the lowest amount of oxygenated compounds was 70°C and 9.7 MPa. Concentration of oxygenated compounds in the extract at 8.3 MPa was not significantly higher than that at 9.7 MPa at 70°C. An important factor in

determining the extraction pressure is related to economic considerations, since construction and operating costs increase with higher system pressures. Therefore

one may prefer to operate at 8.3 MPa and 70°C instead of 9.7 MPa. However, this was the region where the yield was low. It can be concluded that those regions that give high yields tend to show poor selectivity, and this is in agreement with Robey and Sunder (1984). Gerard (1984) proposed an extraction pressure of 8 MPa and temperature of 60–70°C for the removal of terpenes based on the solubility behavior of pure essential oil components and described a continuous, countercurrent high-pressure extraction column with reflux. Robey and Sunder (1984) concluded that a countercurrent column operating at 10.3 MPa and 60°C would concentrate oxygenated compounds in lemon oil.

• **Liquid-Phase Composition.** The amount of carbon dioxide that is solubilized in the oil phase is very important from the standpoint of design purposes since it will affect the extractor volume for a given amount of feed material. Concentration of carbon dioxide in oil phase was determined as described earlier and the results are plotted in Figure 5. At constant temperature weight percent of CO₂ in oil increased as pressure was increased, and at constant pressure it increased as temperature was decreased. That is, it followed the same trend as the density of carbon dioxide. More CO₂ was solubilized in the oil at higher densities of CO₂. The concentration of CO₂ in oil reached as high as 93% at the highest density condition of 40°C and 12.4 MPa.

Need for Further Research

It is possible to concentrate the flavor fraction of cold-pressed citrus oils with supercritical fluid technology. Conditions that give the lowest amount of flavor compounds in the extract are 70°C and 8.3 MPa. However, this is the region where the yield is low which means that larger amounts of carbon dioxide are necessary. More research must be done to determine the thermodynamic model to represent the system which is necessary for the design of the extraction system. Supercritical carbon dioxide extraction of citrus oils to separate terpene hydrocarbons is very promising, but more work needs to be done before large-scale commercialization.

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Maintaining Flavor and Nutrient Quality of Aseptic Orange Juice

Storage temperature is one of the primary factors affecting stability

C.E. Sizer, P.L. Waugh, S. Edstam, and P. Ackermann

□ THE APPROVAL of hydrogen peroxide as a chemical sterilizing agent by the Food and Drug Administration in 1981 opened up a new market for chemically sterilized, aseptic plastic cartons. Orange juice was one of the products which benefited from the regulation since it was thus possible to pasteurize, cool, aseptically fill, and store the product at ambient temperatures. The aseptic product was positioned as an alternative to pasteurized, refrigerated orange juice which had a better flavor than hot-filled juice.

However, in the six years following the introduction of aseptic orange juice, it has not achieved the consumer acceptance and market penetration which was initially predicted. Although aseptic processing produced a high-quality product, the product as received by the consumer was not always as good as it could have been. Loss of quality due to deterioration of the orange juice under the conditions of storage and distribution was responsible for the deterioration of the product.

The purpose of this article is to examine the factors which influence the product quality and report on new research which may be used to improve quality and extend the shelf life of aseptic orange juice in plastic cartons.

Raw Materials and Thermal Processing

In the production of an acceptable finished product that can withstand the rigors of processing, packaging, and distribution, raw material selection has been regarded as a key factor. Since more than 95% of the aseptically packed orange juice is made from reconstituted orange juice concentrate, the selection of the appropriate orange juice concentrate is important. The type of oranges processed and, of course, their maturity at the time of harvesting must be considered. If the aseptic packer is working with U.S. raw material, then a blend of a 50–60% midseason and 40–50% Valencia varieties should be considered. A higher percentage of Valencia is always desirable, but, owing to the susceptibility of this variety to freezes, it is not practical. It would therefore be advisable to purchase USDA-graded orange concentrate which has been scored for flavor, color, and defects.

For United States consumption, the most desirable ratio will be a brix/acid ratio of 16–17:1. To work with ratios greater than this can increase the chances of

higher mold and yeast counts owing to a tendency for quicker deterioration of the fruit during storage at the processing plant.

Concentrate purchased from Brazil will be made predominately from Pera-type oranges, and the average ratios are generally around 13–15:1. Most Brazilian groves do not have the luxury of irrigation systems so they rely on rainfall to provide the necessary moisture. It is critical that citrus trees receive adequate moisture during the blossom set and should rainfalls not occur, it is likely that the trees will produce an out-of-season blossom resulting in a percentage of out-of-season fruit. As it is not normally practical to pick an orchard more than once in the season, there is a possibility of this immature fruit being mixed in with the deliveries to the processors. If this should occur, an aftertaste of bitterness can be characteristic of the resultant product.

Wherever the source, the citrus-processing industries are fortunate in having available to them highly efficient and well-engineered juice extractors from F.M.C. Corp., Lakeland, Fla., or Brown International Corp., Covina, Calif. Although quite different in principle, they both are capable of extracting all the available juice. It is very important, therefore, that these machines and their respective air-loaded finishers are not adjusted too tightly, resulting in extraneous flavors from the skin and larger amounts of pectins in the juice. This becomes particularly important as there is now no longer a Florida State restraint on the percentage of juice that can be extracted. The state does, however, prohibit any use of pulp wash solids in orange juice products.

The concentration of the orange juice is generally performed today on the TASTE Evaporator (Gulf Machinery Co., Clearwater, Fla.) This highly efficient, multi-effect falling film plant incorporates a tubular stabilizing unit that inactivates the pectinesterase enzymes in the juice. It is important that these evaporators are operated within design capacity, with no vacuum leaks or inadequate cooling of barometric condenser water. All of the aforementioned will increase the temperatures in the vapor separators, resulting in increased thermal load on the concentrated juice. The thermal or heat load of processed citrus juices seems to be positively correlated to the browning potential of the product (Ekasari, 1987).

Vacuum concentration of the fruit juice removes essentially all of the volatile flavor components. Aroma, cold-press oil, or essence oil must be added back to

The authors are from Tetra Pak, Inc., 889 Bridgeport Ave., Shelton, CT 06484