Characterization of Soybean Oil Extracted by Supercritical Carbon Dioxide and Hexane

Exhaustive extraction of full-fat soybean flakes with supercritical carbon dioxide (SC-CO$_2$) yields an oil that is comparable to hexane-extracted oil except for significantly lower chromatographic refining loss and phosphorus content. In a long cylindrical batch extractor, the flakes act much like the stationary phase of a chromatography column, which permits the recovery of light-colored, essentially degummed, crude oil fractions.

Essentially all of the oil from the more than one-billion bushels of soybeans crushed annually for use in the United States is extracted with hexane. This solvent is subject to rapidly increasing costs and uncertain availability. It is also highly flammable and explosive when mixed with air. Hexane is not selective for triglycerides, and extracts from soybeans free fatty acids, phospholipids, pigments, and unsaponifiables. Significant refining losses and attendant energy requirements contribute to production costs.

Supercritical fluid (SCF) technology may be a viable alternative to current extraction methods. The phenomenon of SCF extraction was observed over 100 years ago (Hannay and Hogarth, 1879) but has been slow to find commercial applications, due no doubt in part to the sophisticated and expensive high-pressure equipment and technology required. The theory and practice of supercritical gas extraction have been reviewed (Paul and Wise, 1971). A group of German researchers has been active in this field since the early 1960s. Much of the SCF work on food products, and in particular on soybeans, done during the 1960s and early 1970s is in the patent literature (Zosel, 1964, 1967; Vitzthum and Hubert, 1972). There is currently a flurry of interest in SCF technology in the United States, probably stimulated by the first symposium on SCF's (Schneider et al., 1978). Chemical Process Industries applications have been reviewed by Kohn and Savage (1979), and 21 patents related to the extraction of food products are listed by Bott (1980). A recent paper (Stahl et al., 1980) reports the extraction of seed oils with SC-CO$_2$. Although the yields of SC-CO$_2$-extracted oil were referred to as "comparable to those obtained by conventional solvent extraction", yields were in fact more than 17% less for soybean oil. This communication reports efficient extraction of soybean oil with SC-CO$_2$ and provides a more complete analytical characterization of SC-CO$_2$-extracted oil and hexane extracted oil from the same beans.

EXPERIMENTAL SECTION

One kilogram of soybean flakes (certified seed, cracked, dehulled, and flaked at 9.8% moisture) was placed in a 2-L cylinder (Figure 1) and extracted with SC-CO$_2$ at 5000 psi and 50 °C. The CO$_2$ flow rate was maintained at about 2 kg/h. After reaching equilibrium solubility, the oil extraction rate remained at 25.5 g/h until 179 g of oil (18% of flake weight) was obtained. The next 3 h produced 12.2, 7.1, and 0.7 g, respectively. The extraction was terminated after 11 h and use of 20.4 kg of CO$_2$. The overall yield (19.9% based on full-fat flakes) was comparable to that obtained by hot hexane extraction of the same flakes in a Soxhlet extractor for 5 h (Table I). The efficiency of the SC-CO$_2$ extraction is further evidenced by the low residual oil content of the flakes (0.9%). Stahl et al. (1980) reported significantly higher residual oil (3.1%) and lower oil yield (16.4%).

In a separate experiment, a sample of soybean flakes was extracted with SC-CO$_2$ until half of the oil had been re-

Table I. Comparison of SC-CO$_2$- and Hexane-Extracted Soybean Oil

analyses	AOCS method no.[a]	hexane	SC-CO$_2$
yield, %	Ac 3-44	20.0	19.9
residual oil, %	b	c	0.9
chromatographic refining loss, %	Ca 9f-57	1.9	0.5
free fatty acid, %	Ca 5a-40	0.5	0.5
peroxide value, mequiv/kg	Cd 8-53	<0.1	0.2
unsaponifiables, %	Ca 6a-40	0.6	0.5
Fe, ppm	Ca 15-75	1.6	0.3
Cu, ppm	Ca 15-75	<0.1	0.4
phosphorus, ppm	Ca 12-55	630	60
fatty acid analysis (GC), %	Ce 1-62		
palmitic		10.8	11.0
stearic		4.2	3.5
oleic		27.0	27.5
linoleic		51.4	52.0
linolenic		6.6	6.0

[a] American Oil Chemists' Society (1975). [b] Determined according to Black et al. (1967). [c] Hexane-extracted flakes were not further extracted.

moved, and then the flakes were carefully divided into three equal fractions. The first fraction (nearest the introduction port for SC-CO$_2$) was almost white and had an oil content of 2.4%. The top part of the second fraction was like the first but became progressively more yellow and had an oil content of 10.6%. The third fraction was a brighter yellow than the original flakes and had an oil content of 19.8%.

RESULTS AND DISCUSSION

Equilibrium solubility conditions are readily established in the extractor as shown by the constant extraction rate (straight-line portion of Figure 2). Higher extraction rates could therefore be achieved by increasing the SC-CO$_2$ flow until equilibrium conditions are exceeded. Likewise, during the final stages of extraction, it would be more efficient to reduce the flow rate to maintain equilibrium solubility. Oil extracted with SC-CO$_2$ showed significantly less phosphorus and correspondingly less chromatographic refining loss than hexane oil (Table I). The accepted method for estimating phosphatide content is to multiply the percent elemental phosphorus by 31.7 (List et al., 1978). The phosphatide content calculated on this basis is 2% for the hexane-extracted oil and 0.19% for the SC-CO$_2$-extracted oil. These values are reflected in the significant difference in chromatographic refining loss between the SC-CO$_2$ and hexane oils. Therefore, the oil obtained by SC-CO$_2$ extraction has the advantage of being essentially equivalent to a degummed, hexane-extracted crude oil. The color intensity of the oil increases rapidly near the end of the extraction (Gardner 10 → 13).

The observations on the partially extracted flakes suggest that the column of flakes acts much like the stationary phase of a chromatography column, with the SC-CO$_2$
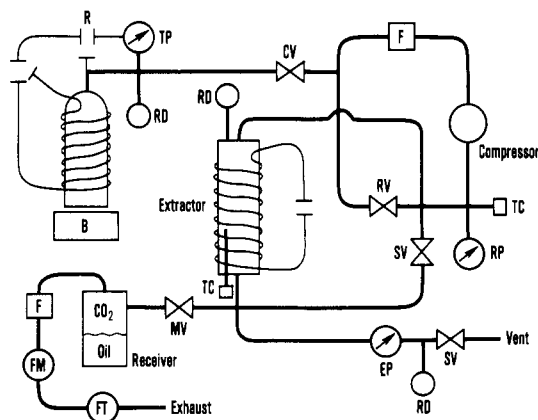
Figure 1. Supercritical CO_2 extraction apparatus: (B) balance, (R) relay, (TP) tank pressure, (RD) rupture disk, (CV) check valve, (F) gas filter, (TC) thermocouple, (RP) regulated pressure, (RV) regulating value, (SV) shutoff valve, (MV) micro metering valve, (FM) instantaneous flow meter, (FT) flow totalizer, and (EP) extractor pressure.
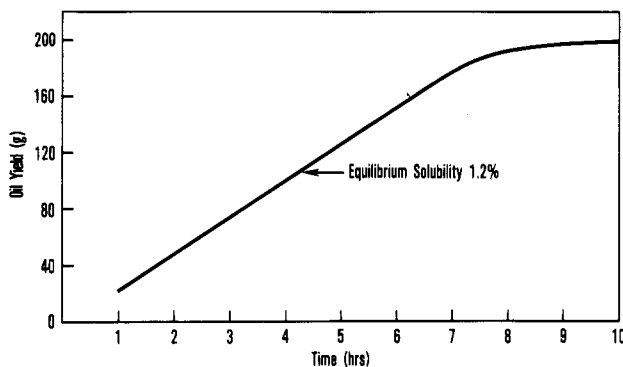

Figure 2. Extraction of soybean oil with supercritical CO_2 at 5000 psi and 50 °C.

eluting the triglyceride to a considerable extent before elution of the pigments and other unsaponifiables. We also found that increasing the extraction pressure in increments of 1000 psi, from 2500 to 9500 psi, and at a constant temperature of 50 °C gave oils of increasing color intensity.

These observations are contrary to those of Stahl et al. (1980), who reported that oil fractions collected at low pressure were dark and turbid whereas those taken at high pressure were clear and lighter colored.

Work is continuing on the extraction and refining of soybean oil by conventional and supercritical methods. Organoleptic studies on both oil and meal will be reported in a future paper. Other edible and nonedible oilseeds, seed oils, and other plant materials also are being examined.

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John P. Friedrich*
Gary R. List

Northern Regional Research Center
Agricultural Research
Science and Education Administration
U.S. Department of Agriculture
Peoria, Illinois 61604

Inhibition of Larval Growth in *Spodoptera frugiperda* by Sublethal Dietary Concentrations of Insecticides

Sublethal concentrations of some insecticides inhibited larval growth of the fall armyworm *Spodoptera frugiperda*. Fenvalerate, permethrin, endosulfan, SD-35651, and CGA-72662 inhibited growth by more than 39% at 12 days, while chlorpyrifos, methyl parathion, sulprofos, precocene, and piperonyl butoxide were less inhibitory. Toxaphene, carbaryl, thiodicarb, methomyl, amitraz, chlordimeform, and imidazole produced only a transitory growth reduction. Aldicarb, profenofos, CGA-19255, diflubenzuron, and SKF-525-A had no sublethal effect while methiocarb and methoprene increased growth. Dose–response relationships were determined for fenvalerate, methyl parathion, SD-35651, and CGA-72662.

There is much interest in chemicals which might be applied to protect crops by deterring insect feeding. This strategy aims to prevent damage to the plant rather than to kill the insect and might have advantages in reduced risks of pest resistance and side effects on beneficial insects. Candidate chemicals for this use include natural products such as warburganal (Nakanishi, 1977) and syn-

thetic chemicals such as tryclazol and other organotins (Ascher, 1980).

Some commercial insecticides might act in part through repellency or other sublethal effects as recently demonstrated with carbaryl (Young and McMillian, 1979) and chlordimeform (Lund et al., 1979). These discoveries have led us to investigate the growth inhibiting effects of sub-