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K. Warner did the organoleptic evaluation and J.H. Johnson made the CO_2 extractions.

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Properties and Processing of Corn Oils Obtained by Extraction With Supercritical Carbon Dioxide[1]

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ABSTRACT

Crude oils were extracted from wet- and dry-milled corn germs with supercritical carbon dioxide (SC-CO_2) at 50-90 C and 8,000-12,000 psi and were characterized for color, free fatty acids, phosphorus, refining loss, unsaponifiable matter, tocopherol and iron content. They were compared with commercial products. Extraction of wet-milled germ with SC-CO_2 has some advantages over the conventional prepress solvent method commonly used in the industry. For example, SC-CO_2 extraction of wet-milled germ at 50 C and 8,000 psi yields crude oil with a lower refining loss and a lighter color. After laboratory processing, a light-colored, bland salad oil is obtained. Crude, refined, bleached and deodorized oils from SC-CO_2-extracted dry-milled germ appear equivalent to those obtained by expeller pressing.

INTRODUCTION

Domestic production of corn oil has doubled from 433 million lbs in 1967 to 865 million lbs in 1982 (1,2). The corn kernel contains only 5% oil, so processing it for oil is uneconomical. Both wet and dry millers separate the lipid-containing germ and recover the crude oils by expeller pressing and/or solvent extraction with hexane.

During 1982, about 607 million lbs of crude corn oil was converted to edible products by the traditional oil processing methods of refining (with sodium carbonate and/or caustic soda), bleaching, hydrogenating and deodorizing (1,3). About 272 million lbs were exported.

Previous reports from this laboratory have described the extraction of soybeans and corn germ oil with supercritical carbon dioxide (SC-CO_2) (4-9). The work reported here describes preliminary studies on characterization and processing of crude corn oils obtained by extraction of wet- and dry-milled corn germ with SC-CO_2 at 50-90 C and pressures ranging from 8-12,000 psi.

EXPERIMENTAL

Materials, extraction and analytical methods were described previously (4). Oil processing methods were described by List et al. (6). Wet-milled corn germ was obtained at the commercial wet grinding step in starch processing. The fresh germ was further processed in the laboratory before SC-CO_2 extraction, as follows: Residual SO_2 was removed by rinsing the germ with water until the fresh water reached pH 5. The raw germ was dried in a forced air draft oven at 27 C until a moisture level of 13% was achieved. Organoleptic evaluations were conducted according to Moser et al. (10,11). Representative samples of crude wet- and dry-milled corn oils were obtained from commercial sources.

RESULTS AND DISCUSSION

The properties of crude oils obtained by extraction of wet- and dry-milled corn germ with supercritical carbon dioxide are shown in Table I. Comparative data for commercially extracted oil also are given. Other SC-CO_2 extraction work has shown that triglycerides approach complete miscibility at 12,000 psi pressure and temperatures of 80 C or above (9). The data given in Table I show that crude oil quality is unaffected by extraction conditions, i.e., no increase in free fatty acid (FFA), color, phosphorus refining loss or unsaponifiable matter was observed by increasing extraction pressures and temperatures. The tocopherol content of dry-milled oil appears to decrease with increasing temperature. The reason for this is unclear and is under further study.

Crude wet-milled corn oil averages 2.3% FFA and varies typically from 1.5 to 4%, whereas FFA in oil from dry-milled germ is lower, the average being 1.8%. Neutral oil content ranges from 93-96% (1). The color of crude oil varies considerably and depends on the method of oil recovery and the storage history of the seed or germ. Expelled oils from wet- or dry-milled germ may be so dark that color cannot be measured by the AOCS Lovibond color test. However, there is no clear relationship between crude oil color and the ease with which it can be converted to a commercial light-colored product (1). The expeller- and prepress solvent-extracted wet-milled oils that we acquired for this work appear equal to or better than the typical oils in terms of color, free fatty acids and neutral oil content.

Extraction of dry-milled germ with SC-CO_2 at a pressure

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of 12,000 and temperature of 70-90 C yields a crude corn oil with low FFA content, light color and a neutral oil content of about 98%. Although extensive experiments were not conducted at higher extraction temperatures, wet-milled germ extracted at 50 C and 8,000 psi yielded a good quality crude oil.

The unsaponifiable content of corn oil reportedly is about 1.3%, the majority of it sterols (3). $SC\text{-}CO_2$-extracted and commercial dry- and wet-milled crudes show typical unsaponifiable matter contents of 1.2-1.4%.

The tocopherol content of $SC\text{-}CO_2$-extracted wet-milled oil appears to be somewhat lower than commercial prepress hexane-extracted oil. Similarly, the tocopherol content of $SC\text{-}CO_2$-extracted dry-milled oil appears comparable to expeller oil, but the values for both oil types are higher than those reported in the literature (12). Milling is known to have a pronounced effect on the recovery of tocopherol from corn germ. Grams (12) et al. found that only 18% of the tocopherol present in whole grain was found in the oil after wet milling, and 73% was recovered after dry milling.

As reported previously (5), phospholipids show little if any solubility in $SC\text{-}CO_2$. The phosphorus contents of $SC\text{-}CO_2$-extracted wet- and dry-milled oils are exceedingly low (1-5 ppm) compared to 120 ppm phosphorus for expelled and 670 ppm for hexane prepress commercial products, respectively. Since phospholipids are essentially absent in $SC\text{-}CO_2$-extracted oils, this process yields more neutral oil than that produced with other commercial processes. For example, commercial wet-milled oil showed a neutral oil content of 95.8% compared to 98.4% for the $SC\text{-}CO_2$-extracted sample. The differences in refining loss or neutral oil for expeller and $SC\text{-}CO_2$-extracted dry-milled oil are not as great because both are low in phosphorus. $SC\text{-}CO_2$-extracted dry-milled oils varied from 98.4-99.0% neutral oil compared to 97.2% for the expeller oil. Thus, more yield in neutral oil would be expected from $SC\text{-}CO_2$ extraction of wet-milled germ than from dry-milled germ.

Processing of Corn Oils

Little processing data for corn oil have been reported. Reiners and Gooding (1) state that refining of corn oil does not present problems over those encountered with oils of similar composition, with the exception that more intense treatment may be required to produce a light-colored and bland-flavored oil when the crude oil is dark. Corn oil is processed according to the following guidelines: Lye requirements, according to the official AOCS methods, calls for 16 Be′ lye at excesses of 0.25-0.36% (1). According to Carr (13), commercial refining of corn oil is carried out with 18 Be′ lye at an excess of 0.13%. Production of a light colored salad oil usually requires bleaching with 1-2% activated clay, whereas dark colored oil often requires 4% (1). Deodorization of well-refined corn oil can be achieved easily by conventional vacuum steam processes at 227-238 C (1).

Processing data and properties of finished corn oils are given in Table II. Lye requirements for $SC\text{-}CO_2$-extracted and expeller dry-milled oils are slightly more than theoretical. Oils refined with 0.05-1% excess of 10% lye yielded finished oils with acceptable color, initial flavor and storage stability. A red color of 3.5 for a refined-bleached oil prior to deodorization indicates acceptable refining efficiency (1). With one exception all oils shown in Table II meet this

TABLE I

Properties of Hexane Prepress, Expeller and $SC\text{-}CO_2$ Extracted Corn Oils

Milling method	Extraction method	Oil yield, %	Oil color[a] Y	R	FFA, %	Phosphorus, ppm	Neutral oil loss, %	Unsaponifiables, %	Tocopherol, μg/g	Iron, ppm
Wet	Hexane prepress	–	70	16	1.2	661	4.2	1.26	1,000	0.5
Wet	$SC\text{-}CO_2$, 50 C, 8,000 psi	43.3	70	8	1.15	1	1.1	1.26	890	0.3
Dry	Expeller	–	70	12	0.7	119	1.6	1.34	1,690	0.3
Dry	$SC\text{-}CO_2$, 70 C, 12,000	22.9	70	10	0.5	3	1.4	1.20	1,840	0
Dry	$SC\text{-}CO_2$, 80 C, 12,000	23.1	70	11	0.5	> 1	1.4	1.20	1,650	0
Dry	$SC\text{-}CO_2$, 90 C, 12,000	21.6	70	11	0.6	> 1	1.0	1.20	1,180	0

[a]Lovibond color, 5¼″ depth; Y = yellow; R = red.

TABLE II

Processing and Properties of Refined, Bleached and Deodorized Corn Oils[a]

Milling method	Extraction	Refining NaOh, %	Refining % Excess	Color - Lovibond 5¼″ Refined Y	Refined R	Bleached Y	Bleached R	Deodorized Y	Deodorized R	Flavor scores and significance[b] 0 Time	4 days 60 C
Wet	$SC\text{-}CO_2$, 50 C, 8,000 psi	10	0.2	40	6	35	4.0	6	0.6	7.3 +	6.3 +
Wet	$SC\text{-}CO_2$, 50 C, 8,000 psi	10	0.5	35	5	35	3.5	6	0.6	7.3	6.4
Dry	$SC\text{-}CO_2$, 80 C, 11,000 psi	10	0.05	30	8	30	4.0	6	0.8	6.5 +	5.5 +
Dry	$SC\text{-}CO_2$, 80 C, 11,000 psi	10	0.10	30	8	30	3.5	6	0.7	6.8	5.0
Wet	Hexane prepress	10	0.2	40	7.6	20	2.5	15	2.0	6.0 +	5.7 +
Wet	Hexane prepress	10	0.5	40	7.6	20	3.0	15	2.0	6.1	5.6
Dry	Expeller	10	0.05	70	8	35	3.5	7	0.6	7.9 +	7.0 +
Dry	Expeller	10	0.10	70	8	35	3.5	7	0.6	7.3	7.0

[a]Refined at 60 C, washed 2X distilled water. Bleached 15 min at 105 C, 1 mm Hg Vac, ½% super filtrol clay, deodorized 3 hr at 210 C, 1 mm Hg. 0.01% citric acid added on cooling side of deodorization.
[b]+ denotes no statistical significance; 10 point scoring system: 10 = bland; 1 = extreme.

requirement.

The results shown for SC-CO_2-extracted wet-milled oil should be considered preliminary because subsequent research has shown that 50 C and 8,000 psi are not optimum conditions for the best extraction of triglycerides. Furthermore, the amount of excess of lye used was not necessarily optimum for all wet-milled oils. However, the results are interesting from the standpoint of the flavor of the deodorized oils. Commercial refined, bleached, deodorized wet-milled corn oil is difficult to obtain in a bland state because of burnt flavors that carry over from the steeping of the corn germ with SO_2 prior to wet-milling. As a result, wet-milled corn oil received lower flavor scores than soy or cottonseed oils. SC-CO_2-extracted, wet-milled crude oil yielded a refined, bleached, deodorized oil that was substantially free of the burnt flavors prevalent in conventionally extracted oil.

The low solubility of phospholipids in SC-CO_2 yields more neutral oil and is an advantage from a processing standpoint. However, phosphatides protect the oil from autoxidation (14). Thus, if SC-CO_2-extracted oil is to be stored for any length of time, it should be handled carefully, and perhaps should even be stored in nitrogen-blanketed tanks. The mechanism by which SC-CO_2-extracted oils undergo oxidative deterioration is under investigation and will be reported later.

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Effect of Moisture and Particle Size on the Extractability of Oils from Seeds with Supercritical CO_2[1]

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ABSTRACT

Moisture level and particle size of soybeans, peanuts and cottonseed were correlated with the extraction rate and yield of oil when extracted with supercritical carbon dioxide (SC-CO_2) at a constant temperature (50 C) and pressure (8000 psig). The rate of extraction and ultimate oil yields were quite low with cracked soybeans. However, good extraction rates and nearly theoretical oil yields were obtained from ground or thinly flaked (<0.010") seeds. Moisture levels between 3% and 12% had little effect on extractability. Oil composition was not influenced by either parameter. Scanning electron microscopy was used to study seed structure before and after extraction with SC-CO_2. Micrographs of SC-CO_2-extracted seeds were similar to hexane-extracted seeds.

INTRODUCTION

German scientists have investigated the extraction of natural products using supercritical fluids since the early 1960's and have demonstrated that carbon dioxide above its critical temperature and pressure is a suitable solvent for the extraction of oil (1-4). Subsequently, Friedrich and co-workers have reported high soybean oil recovery with supercritical carbon dioxide (SC-CO_2). Phosphorus and iron contents of the SC-CO_2-extracted oil were lower and the oil color was lighter than characteristic of hexane-extracted crude oil. Flavor scores of the refined soybean oil extracted by SC-CO_2 were not different from refined hexane-extracted oils (5). Stahl et al. showed that oil yield was dependent on particle size and structure of the oilseed (6). The present study shows the effect of particle size and moisture content of the seed on the extractability of oil with SC-CO_2. The scanning electron microscope (SEM) was used to determine how the native structures of the oilseeds change during extraction and to ascertain the best configuation of the seed for efficient oil extraction with SC-CO_2.

EXPERIMENTAL

Whole soybeans were dried or tempered to 3.5%, 6% and 12% moisture levels which were determined gravimetrically using a Brabender oven; the soybeans were then cracked and dehulled. One-third of the cracked beans were flaked to a thickness of 0.25 mm, another third were ground to a fine flour (over 94% of the flour passed through a 100 mesh screen, which corresponds to 150 microns) by an Alpine Mill, and a final third were used without flaking or grinding. The cracked, ground or flaked soybeans (950 g) were

[1]Presented at the AOCS Meeting, May 1983, Chicago.