Characterization and Processing of Cottonseed Oil Obtained by Extraction with Supercritical Carbon Dioxide[1]

G.R. LIST*, J.P. FRIEDRICH and J. POMINSKI[2], Northern Regional Research Center, Agricultural Research Service, U.S. Department of Agriculture, Peoria, Illinois 61604

ABSTRACT

Extraction of flaked cottonseed with supercritical carbon dioxide at temperatures of 50-80 C and pressures of 8,000-15,000 psi yields an improved crude cottonseed oil compared to those obtained by conventional solvent or expeller processes. Improvements include lighter initial color, less refining loss and lighter refined bleached colors. Crude cottonseed oils obtained by supercritical fluid extraction require less refining lye and show less tendency to undergo color fixation while in storage.

INTRODUCTION

Recently, there has been much interest in the use of supercritical fluid (SCF) for the extraction of oilseeds, and previous reports from this laboratory have described work with soybeans and corn germ (1-3). This report extends the work to cottonseed and details some preliminary observations on the composition, processing and organoleptic properties of oils obtained by extraction of cottonseed flakes with supercritical carbon dioxide (SC-CO_2). Cottonseed oil generally is considered to be more difficult to process than the other common vegetable oils, because it contains somewhat higher levels of free fatty acids and is more intensely colored as the result of the presence of gossypol and related pigments that are carried along during solvent extraction or expeller pressing.

EXPERIMENTAL

The apparatus used for SCF extractions was that described previously (2). Dehulled cottonseed (8.6% moisture) was passed through cracking and flaking rolls to yield flakes 0.007 inches thick. The flaked cottonseed (1,600 g) was charged into an alloy steel autoclave and extracted as described previously (2,3). After removal from the receiving vessel, the crude oil was slurried with Filter-cel®, and the mixture was filtered through a bed of Celite® under vacuum. Analysis for iron, free fatty acids, neutral oil, phosphorus, unsaponifiable matter, gossypol and color were conducted by official AOCS methods as described previously (2). Tocopherol was determined according to AOAC method 43-092 (4).

Refining, bleaching and deodorizing were carried out as described previously (5). Representative samples of commercial crude prepress-solvent and expeller crude cottonseed oils used for comparative studies were obtained from reliable sources. Color fixation was determined by refining the crude oil at 25 C according to the method of Pohle et al. (6) and determining the refined color. Samples (4 oz) of the crude were then placed in wide-mouthed jars and stored at 40 C and 60 C in a forced-draft oven for varying lengths of time, followed by refining and color determination. The increase in red color after refining was taken as the extent of color fixation that occurred during storage. Organoleptic evaluations were carried out as described previously (7).

RESULTS AND DISCUSSION

The effects of temperature and pressure on the solubility of triglycerides have been reported (8). The present report will deal with these parameters only as they related to crude and finished oil quality. Flaked cottonseed was extracted with SC-CO_2 at 8,000-15,000 psi and at temperatures ranging from 50 to 80 C, to yield 30.5% oil ±0.4% with <1% residual oil remaining in the defatted meal. The resulting crude cottonseed oils were characterized, and the results are shown in Table I. Included for comparison are commercial samples extracted by the traditional prepress-solvent and expeller extraction methods.

Free fatty acids (FFA) are quite soluble in SC-CO_2. The FFA content of crude cottonseed oil extracted under the conditions shown is slightly higher than in the commercially processed samples examined. However, the FFA content of crude cottonseed oil is known to vary with the climatic conditions under which the seed is grown (9). Thus, the FFA content of SC-CO_2-extracted cottonseed will depend on the condition of the seed and would be expected to parallel that of hexane or expeller pressed oil from the same seeds.

Phosphatides show very low solubility in SC-CO_2. Compared to the large amounts of phosphorus in expeller- and solvent-processed oil, crude cottonseed oil obtained from seed extracted with SC-CO_2 contains only trace amounts. In preliminary work with a low capacity CO_2 compressor, which required extraction times of up to 16-18 hr, oils contained up to several hundred ppm phosphorus. However, with a high capacity compressor and under the conditions reported in Table I, the extraction times were shorter (7-8 hr) and phosphorus levels of only 1-59 ppm were observed. Phosphorus contents of expeller- and solvent-extracted oils of 386 and 674 ppm equate to about 1 and 1.7% phosphatides (% P × 25.5), respectively. These values are in line with reported literature values (1). The phosphorus levels of SC-CO_2-extracted oils usually are so low (<5 ppm) as to imply that phosphatides are virtually absent.

The absence of phosphatide in SC-CO_2-extracted crude cottonseed oil accounted for the lower neutral oil losses compared to expeller- and solvent-processed oils.

Total unsaponifiable matter in SC-CO_2-extracted crude cottonseed oil is slightly lower but comparable to expeller and prepress-solvent crudes. Total unsaponifiables for cottonseed oil reportedly range from 0.5-7% (9). Tocopherol contents of CO_2-extracted crude are somewhat lower than of commercially extracted oils.

Commercially extracted crude cottonseed oils are extremely dark because of their gossypol and related pigment content. Typically these oils are so dark that color cannot be measured at the standard height of 5¼ inches in the Lovibond color test because they exceed 20 red units and must be measured for color at a 1-inch depth. Crude CO_2-extracted cottonseed oils are markedly lighter in color than solvent or expeller oils and may be analyzed at the full depth in the Lovibond sample tubes.

Crude cottonseed oil contains up to 0.21% gossypol, depending on the extent of heat treatment of the seed prior to extracting or expelling (1). The solvent-prepress and expeller oils (Table I) contained 0.18 and .085% gossypol, respectively. The gossypol content of CO_2-extracted oils typically is about .02% under the most stringent extraction conditions, i.e., 80 C and 15,000.

The effects of processing on the color of hexane-extracted

*To whom correspondence should be addressed.

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

[2]Present address: Southern Regional Research Center, ARS, USDA, New Orleans, Louisiana 70179.

TABLE I

Effect of CO_2 Extraction Conditions on Crude Cottonseed Oil Quality and Minor Constituents

Oil	CO_2 extraction Temp. C	CO_2 extraction Press. psi	Lovibond color Y	Lovibond color R[a]	FFA %	Phos. ppm	Ref. loss[b] %	Excess Alkali, %	Neutral oil, % loss	Iron ppm	Unsaps %	Tocopherol %	Gossypol %
Prepress solvent	–	–	70	20(1")	1.15	664	6.7	0.5	3.4	1.8	0.87	0.092	0.18
Expeller	–	–	70	20(1")	0.92	386	3.6	0.5	3.6	1.9	0.76	0.095	0.085
CO_2	50	8,000	70	8(5¼")	1.3	1	1.8	0.2	1.8	0.2	0.51	0.072	0.015
CO_2	50	15,000	70	12(5¼")	1.3	1	1.8	0.2	1.8	0.2	0.53	0.046	0.016
CO_2	80	8,000	70	7(5¼")	1.7	1	1.7	0.2	1.7	0.2	0.52	0.053	0.019
CO_2	80	15,000	70	>20(5¼")	1.4	59	1.7	0.2	1.7	0.6	0.52	0.053	0.021

[a]Value in parentheses is the cell depth.
[b]Refined with 10% NaOH—Pohle et al. (6). Losses are centrifugal losses, % excess alkali is that over amount needed to neutralize FFA.

TABLE II

Effects of Processing on Cottonseed Oil Color[a]

Oil type	Lovibond color[b] Crude Y	Crude R	Refined, % Excess alkali	Refined Y	Refined R	Bleached Y	Bleached R	Deodorized Y	Deodorized R	Flavor score[c] O, Time	Flavor score[c] 4-Day, 60 C
Hexane (Prepress solvent)	70	20	0.5	70	8	70	4	20	2.5	7.9	7.7
Hexane (Prepress solvent)	70	20	0.3	70	16	20	9	20	5.0	8.2	6.4
Hexane (Prepress solvent)	70	20	0.2	70	20	20	16	20	6.0	8.1	7.4
CO_2[d]	70	7.6	0.1	70	3.5	30	2	20	1.0	7.6	7.1

[a]Refining steps ref.: 10% lye; bleached with 0.5% activated clay, 80 C; vac. 15 min; deodorized, 3 hr at 210 C.
[b]Prepress solvent (hexane) crude oils at 1", all others 5¼".
[c]10 Point scale; 10 = bland, 1 = extreme.
[d]Composite oil extracted 40-80 C, 8,000-15,000 psi.

cottonseed oil at various stages of processing are shown in Table II. Included are typical comparative data for CO_2-extracted cottonseed oil. According to the literature, cottonseed oil is refined with a sufficient excess of caustic to give the desired color consistent with a low refining loss (6). Refined, bleached and deodorized cottonseed oils typically range from 4 to 7 red units in color compared to 1.0-2.5 red units for shortening stocks (9). In order to achieve acceptable color (2.5-6 R) in refined, bleached and deodorized products, hexane-extracted oil required 0.2 to 0.5% excess of 10% lye, whereas the CO_2 oil required only 0.1-0.2% excess of the same lye.

Processing of crude cottonseed oil presents a problem known as color fixation (9,10). Solvent-extracted and expeller-pressed oils contain appreciable amounts of pigments that, upon heating, become difficult or impossible to remove by refining and/or bleaching. The low solubility of cottonseed pigment in SC-CO_2 suggested that oils extracted in this way would show less tendency to undergo color fixation than conventionally extracted oils. Preliminary experiments (Fig. 1) indeed showed that oils extracted with CO_2 at low temperatures and pressures, i.e., 50 C and 8,000 psi, showed no tendency to undergo color fixation when stored at 40 C. At 60 C the rate of color fixation was about half that of an expeller crude oil. Thus, extraction of cottonseed with SC-CO_2 at low temperatures and pressures

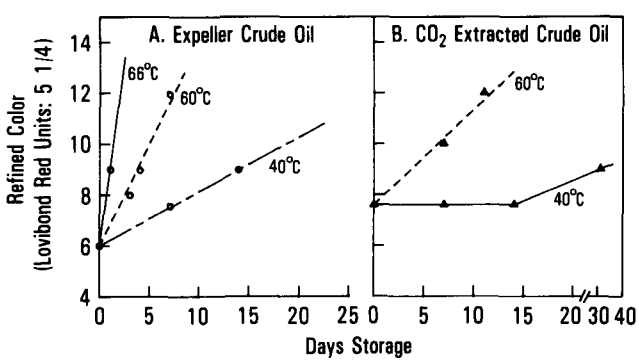

FIG. 1. Color fixation in expeller- and CO_2-extracted cottonseed oils: (A) expeller oil refined with 10% lye, 0.5% excess; (B) CO_2-extracted oils (extracted 70-80 C, 12,000 psi) refined with 10% lye, 0.2% excess.

obviates the problem of color fixation. Further work is in progress and will be reported later.

Preliminary work reported here indicates that extraction of cottonseed with SC-CO_2 yields crude oil that is lighter in color, shows low refining losses, requires less caustic soda for color reduction and is resistant to color fixation.

ACKNOWLEDGMENTS

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

REFERENCES

1. Friedrich, J.P., and G.R. List, J. Agric. Food Chem. 30:192 (1982).
2. Friedrich, J.P.; G.R. List and A.J. Heakin, JAOCS 59:288 (1982).
3. Christianson, D.D.; J.P. Friedrich, G.R. List, K. Warner, A.C. Stringfellow, E.B. Bagley and G.E. Inglett, J. Food Sci. 49:229 (1984).
4. Official Methods of Analysis, (1980), 13th edn., p. 754. AOAC, Arlington, VA.
5. List, G.R.; T.L. Mounts, K. Warner and A.J. Heakin, JAOCS 55:277 (1978).
6. Pohle, W.D.; R.L. Gregory and S.E. Tierney, JAOCS 40:703 (1963).
7. Moser, H.A.; H.J. Dutton, C.D. Evans and J. Cowan, Food Technol. 4:105 (1950).
8. Friedrich, J.P., U.S. Patent Application 06/364,240.
9. Bailey, A.E., Cottonseed and Cottonseed Products. Their Chemistry and Chemical Technology, Interscience Publishers, Inc., New York (1948).
10. Vix, H.L.E.; E.F. Pollard, J.J. Spadaro and A. Gastrock, Ind. Eng. Chem. 38:635 (1946).

[Received August 24, 1984]

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

G.R. LIST, J.P. FRIEDRICH and **D.D. CHRISTIANSON,** Northern Regional Research Center, Agricultural Research Service, U.S. Department of Agriculture, Peoria, IL 61604

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

[1]Presented in part at AOCS meeting, Toronto, Ontario, Canada, May 1982.