

Supercritical CO₂ Degumming and Physical Refining of Soybean Oil

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A hexane-extracted crude soybean oil was degummed in a reactor by counter-currently contacting the oil with supercritical CO₂ at 55 MPa at 70°C. The phosphorus content of the crude oil was reduced from 620 ppm to less than 5 ppm. Degummed feedstocks were fed (without further processing, *i.e.*, bleaching) directly to a batch physical refining step consisting of simultaneous deacidification/deodorization (1 h @ 260°C and 1–3 mm Hg) with and without 100 ppm citric acid. Flavor and oxidative stability of the oils was evaluated on freshly deodorized oils both after accelerated storage at 60°C and after exposure to fluorescent light at 7500 lux. Supercritical CO₂-processed oils were compared with a commercially refined/bleached soybean oil that was deodorized under the same conditions.

Flavor evaluations made on noncitricated oils showed that uncomplexed iron lowered initial flavor scores of both the unaged commercial control and the CO₂-processed oils. Oils treated with .01% (100 ppm) citric acid had an initial flavor score about 1 unit higher and were more stable in accelerated storage tests than their uncitricated counterparts. Supercritical CO₂-processed oil had equivalent flavor scores, both initially and after 60°C aging and light exposure as compared to the control soybean oil. Results showed that bleaching with absorbent clays may be eliminated by the supercritical CO₂ counter-current processing step because considerable heat bleaching was observed during deacidification/deodorization. Colors of salad oils produced under above conditions typically ran 3Y 0.7R.

KEY WORDS: Counter-current refining, crude oil processing, degumming, deodorization, flavor and oxidative stability, hexane-extracted, soybean oil, steam-refining, supercritical fluid extraction.

A number of factors have rekindled interest in physical refining of fats and oils, including economics, the influx of palm oil into the world market, the need for pollution control, environmental concerns and the needs of emerging third world countries (1). Generally, physical refining is most advantageous when high-acid, low-phosphatide fats and oils, such as coconut or palm oil, are considered (2).

Soybean oil contains appreciable amounts of gums that must be completely removed prior to deodorization, because residual phospholipids will cause the oil to darken when heated (3). Experience has shown that simple water degumming will not remove gums or prooxidant metals to levels where color and oxidative stability are not impaired (4–6). A number of processing adjuncts have been proposed to aid the removal of phospholipids during degumming including acetic anhydride, phosphoric acid and organic acids (7–9). Unfortunately, these additives have disadvantages, including corrosion of stainless steel processing equipment, destruction of the gums which lowers their value as by-products and pollution of water from inorganic phosphates.

In the past decade the use of supercritical fluid to extract oilseeds has received considerable attention (10–20), and the method has been shown to possess certain advantages over

conventional solvent extraction or expeller methods. Among these are the absence of phosphatides in crude oils, lighter color and less tendency to undergo color fixation (15,16).

Results from a previous study suggested that crude supercritical CO₂ (SC-CO₂)-extracted soybean oil could be fed to a continuous laboratory deodorizer and that degumming, caustic refining and bleaching could be eliminated, resulting in good quality, flavor stable and light colored oils (21).

A new supercritical fluid-based process has been developed which permits the counter-current refining (treatment) of extracted soybean oil to produce a refined feedstock suitable for direct deodorization. The process makes use of a packed vessel that facilitates interfacial contact between the high-pressure CO₂ and a liquid soybean oil in a counter-current mode. A new high-pressure liquid-delivery pump was also developed to aid in the introduction of the soybean oil against the high CO₂ back pressure in the refining vessel.

EXPERIMENTAL PROCEDURES

Materials. Welding grade carbon dioxide was obtained in 132-kg cylinders from National Welding Co. (Bloomington, IL). Crude soybean oil (Quality Plus Grade) and refined/bleached soybean oil were obtained from Central Soya (Decatur, IN).

Apparatus. The counter-current refining experiments were performed by using a modification of the semi-continuous pilot plant constructed in our high-pressure laboratory (22). A schematic of the unit is given in Figure 1. The following components were used in the unit: main compressor, Haskel gas booster Model 14 AGT-125/315 (Haskel Inc., Burbank, CA); auxiliary compressor, Haskel gas booster AGT-62/152; back pressure relief valve adjustable from 17.2–172 MPa, Haskel Model 5700-26; in-line high-pressure mass flow meter, Model D12 (Micro Motion, Inc., Boulder, CO); high-pressure parts and gauges (Autoclave Engineers, Erie, PA).

Counter-current refining vessel. An alloy steel 4-L vessel, rated at 207 MPa, having an internal bore of 91.4 cm length and 7.6 cm width (Autoclave Engineers, Erie, PA) and outfitted with self-sealing closures, was used for the counter-current refining process. The inside of the vessel was packed with six sections of 15.2 cm × 7.6 cm type 779 Goodloe packing (Otto York Co., Inc., Parsippany, NJ) by inserting the sections one on top of the other in the refining vessel. High-pressure carbon dioxide was fed into the packed vessel from a 0.635-cm portal located 5.08 cm above the bottom-sealing closure, and the liquid soybean oil entered the vessel 5.08 cm below the top-sealing closure. Temperature control on the extraction vessel was maintained with a fiberglass-insulated heating mantle (Glas-Col, Terre Haute, IN), 112 cm in length, 15.2 cm i.d. with a nominal thickness of 2.54 cm. Power to the mantle was supplied by two 1200-watt, 115-volt circuits controlled by a Barber Coleman Model 560 controller (Carlen Automation, Inc., Rock Island, IL). Temperature control of the vessel was accomplished with a Durakool mercury relay (American Electronic Components, Elkhart, IN) and a contact thermocouple mounted on the outside of the vessel.

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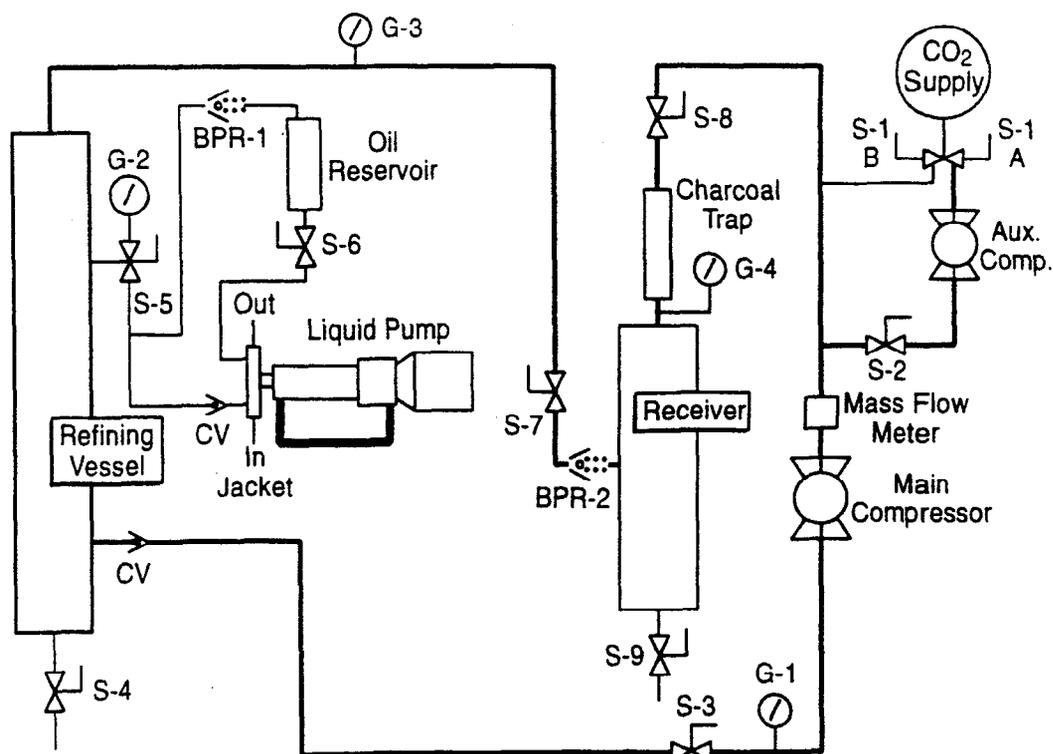


FIG. 1. Schematic of continuous supercritical CO₂ degumming equipment. Legend: G, pressure gauge; BPR, back pressure regulator; CV, check valve; S, on/off valve.

Receiver vessel. A 316 SS 2-L vessel, rated at 70 MPa for 22°C, was used as a receiver. The vessel, which was 7.6 cm i.d. × 45.7 cm in length, incorporated O-ring closures at both ends to seal the vessel. The receiver was placed downstream from the back pressure relief valve and was typically held at 17.2 MPa and 60°C to precipitate the extracted oil coming from the refining vessel through the back pressure relief valve. This condition removed most of the oil from the SC-CO₂ without having to substantially recompress the CO₂.

Oil delivery pump. The delivery of soybean oil to the counter-current refining vessel required the development of a modified liquid pump. A Chemtrol Simplex Model CP1.A04646 (Clark Cooper Co., Cinnaminson, NJ) was used for this purpose with a discharge pressure rating of 70 MPa. Special packing consisting of glass-filled Teflon and stainless steel was used to hold the high-pressure seal. The pump was equipped with a fully adjustable eccentric and jacketed delivery end. Heating of the soybean oil at the delivery head was accomplished by a Polysciences Model 9500 constant-temperature circulator (Polysciences, Inc., Niles, IL). Soybean oil was fed to the pump from a 2-L graduated cylinder under nitrogen sparge.

Calibration of the oil delivery pump was made against a 55 MPa, 70°C SC-CO₂ back pressure. Plots of delivery rate (3–25 mL/min) vs. % speed control at two different stroke adjustment settings were linear. The pump output remained constant during each refining run at 55 MPa back pressure.

Refining procedure. The refining apparatus (Fig. 1) was operated as follows: (i) valves S-1A, S-2, and S-8 were opened; (ii) heating of the receiver vessel was started; (iii) the

auxiliary compressor was turned on; (iv) the receiver was pressurized to 17.2 MPa and 60°C; (v) valves S-8 and S-2 were closed and valves S-1B and S-3 opened; (vi) the main compressor was started; (vii) heating of the extractor vessel was started; (viii) the extraction vessel was pressurized to 55 MPa and 70°C; (ix) valve S-1B was closed and valves S-7 and S-8 were opened; (x) BPR-2 was adjusted to give 55 MPa on the refining column; (xi) with the system recycling the CO₂, the compressor air-drive cycling rate was adjusted to maintain the desired CO₂ flow rate; (xii) at the same time that the system was being equilibrated, the liquid pump was initiated as follows: (a) pump head was heated to 60°C; (b) valve S-6 was opened to pass crude soybean oil to the heated pump head; (c) BPR-1 was adjusted to give a pressure of 70 MPa as read on gauge G-2; then, (xiii) after the refining apparatus was equilibrated as detailed above, valve S-5 was opened; (xiv) the mass flow meter was zeroed; and (xv) counter-current refining of the crude oil was initiated.

Initial pressurization of the system required 17.2 kg of CO₂. A column filled with charcoal was placed in-line after the receiver vessel in order to remove odoriferous components from the recycled CO₂. Refined samples were stored under nitrogen until steam deodorization/deacidification was performed.

Deodorization/deacidification. The deodorization equipment was that described by Schwab and Dutton (23) and modified according to Moulton (24). Steam-refining was conducted for 1 h at a temperature of 260°C under a vacuum of 1 mm Hg. Citric acid (.01%) was added as a 20% aqueous solution on the cooling side of deodorization at above 100°C.

ANALYTICAL METHODS

Peroxide values (Cd 8-53), color (Cc 13b-45), free fatty acid (Ca 5a-40), contents of iron (Ca 15-75) and phosphorus (Ca 12-55) were determined according to official AOCS methods (25). Sensory evaluations were performed as described previously by Warner *et al.* (26-28). A 14-member, trained, experienced panel evaluated the oils on a 10 point intensity scoring scale (10 = bland, 1 = strong) as: (i) freshly deodorized samples, (ii) after storage under Schall 60°C oven-storage conditions and (iii) after 2-, 4- and 8-h exposure to 7500 lux fluorescent light (29).

RESULTS AND DISCUSSION

Production of SC-CO₂ refined oil. A number of preliminary refining runs were performed prior to the production of 4-kg lots of soybean oil for deodorization and storage stability or taste panel studies. Initial trials with an unpacked refining column at 55 MPa showed that 97% of the soybean oil could be extracted by the described procedure. Use of the counter-current refining option yielded an oil with a phosphorus content below 2 ppm. The lecithin-rich sludge that formed in the bottom of the refining column was partially removed by depressurizing the refining column or completely removed by solvent extraction with acetone.

The resultant refined oils were considerably improved in color and turbidity. Typically, the supercritical-refined oils had a Lovibond color rating of 70Y/10R, a phosphorus content below 5 ppm, peroxide values of 0.5 and a free fatty acid content below 0.1%. Good material balances were obtained for the refining trials, with each 2.2 kg of processed oil yielding between 6-7 g of insoluble residue in the refining vessel.

Based on the above data, several extended runs were performed to prepare larger quantities of the refined oil. Refining was conducted at 55 MPa and 70°C and took approximately 4 h/run for completion. Approximately 3 kg of oil was collected over this period after passage of 4 kg of oil through the refining vessel. Average oil solubility in the SC-CO₂ ranged between 3.5-4.1 wt%. This was consistent with oil solubility in SC-CO₂ as reported previously (30,31). Four lots of oil were prepared for further evaluation in this manner.

Analysis and characterization of oils. Color, free fatty acid, iron and phosphorus contents of crude, partially processed and fully processed soybean oils are shown in Table

1. Results show that the crude hexane-extracted oil used as a feedstock for the degumming studies was typical of good quality crude with respect to color, free fatty acid, phosphorus, iron and peroxide levels. Phosphorus contents of oil obtained by SC-CO₂ degumming typically averaged less than 5 ppm, and, based on the phosphorus content of the crude oil, 99.2% of the gums were removed by SC-CO₂ degumming. Typically, conventional water degumming removes 80-95% of the gums from crude oils. It is interesting to note that SC-CO₂ degumming was quite effective in removing iron to levels considered adequate for optimum flavor and oxidative stability, *i.e.*, 0.1-0.2 ppm. Water degumming often gives erratic removal of trace iron (4).

A further advantage of SC-CO₂ processing was illustrated by the color data. Caustic refining and bleaching typically reduces red color several units over the crude, with substantial amounts of red color removed by heat-bleaching in the deodorizer. Invariably, virtually all the red color is removed from the SC-CO₂-degummed feed stock after deodorization at 260°C, thereby eliminating the need for treatment of the oil with absorbent clays, as is normally done in both caustic refining and conventional physical refining processes. Peroxide determination shows that the crude oil feed stock (peroxide value, 0.5 meq/kg) can be continuously SC-CO₂-degummed without substantial further oxidation (peroxide value, 0.6 meq/kg).

Sensory evaluation of SC-CO₂ degummed oil. Sensory evaluation of SC-CO₂-degummed, physically refined oils is shown in Table 2. The experimental design included comparison of replicate samples of SC-CO₂-degummed oils with a commercially prepared refined/bleached soybean oil, deodorized under the same conditions. To determine the effects of unchelated iron on flavor and oxidative stability, samples were evaluated both in the presence and in the absence of added citric acid. As has been demonstrated previously, the importance of chelating trace amounts of iron cannot be overstressed. Even where the bulk of the iron has been removed, either by caustic or SC-CO₂ degumming, enough iron remains to impair the quality of freshly deodorized oil if not properly treated with citric acid. This is shown by the one flavor score unit increase of citrated oils over those not treated in order to inactivate traces of iron. Initially, flavor scores of both the citrated commercial control and the SC-CO₂-degummed oils are in the range of 7-8, typical of good quality soybean salad oils. After accelerated storage for 4 d at 60°C, the SC-CO₂-processed oils were scored not significantly

TABLE 1

Characterization of Crude, Partially Processed and Fully Processed Oils

Oil type	Color ^a		Free fatty acids (%)	Phosphorus (ppm)	Iron (ppm)	Peroxide value (meq/kg)
Crude	69.0Y	12.8R	0.39	620.0	1.57	0.5
Refined/bleached	69.0Y	7.2R	0.13	0.5	0.23	1.5
Refined/bleached/deodorized	2.4Y	0.0R	0.09	0.4	0.03	0.0
SC-CO ₂ -degummed ^b	67.0Y	10.0R	0.75 ± .09	4.0 ± 1.0	0.5 ± 0.1	0.50 ± 0.06
SC-CO ₂ steam-refined ^b	2.8 ± 0.3Y	0.7 ± .2R	0.10 ± .02	2.2 ± 0.6	0.13 ± .07	0.0

^aColor by Lovibond 5-1/4".

^bMean of four samples. SC = supercritical.

TABLE 2

Flavor^a and Oxidative^b Stability of Fully Processed Soybean Oils

Storage	Flavor scores ^c		
	Commercial Refined bleached	SC-CO ₂ Degummed I	SC-CO ₂ Degummed II
0 d at 60°C	6.3 a (0.5)	6.6 a (0.0)	7.1 a (0.0)
2 d at 60°C	5.7 a b (1.4)	5.3 a (1.0)	6.3 b (0.9)
4 d at 60°C	5.4 a (2.3)	5.6 a (1.5)	5.8 a (1.7)
2 h, 7500 lux	5.0 a (1.4)	6.7 b (1.0)	5.9 b (1.3)
4 h, 7500 lux	5.2 a (7.0)	6.7 b (1.6)	6.1 b (1.8)
	Citrated		
0 d at 60°C	7.1 a (0.4)	7.4 a (0.0)	7.8 a (0.0)
4 d at 60°C	5.6 a (2.1)	6.3 a (1.2)	6.4 a (1.4)
8 d at 60°C	5.1 a (9.7)	6.0 b (9.1)	6.2 b (8.2)
4 h, 7500 lux	5.7 a (2.1)	6.4 a (1.2)	6.2 a (1.6)
8 h, 7500 lux	5.5 a (2.7)	5.6 a (2.1)	5.6 a (2.5)

^aFlavor scores based on a 1-10 scale where 1 = strong and 10 = bland.^bValues in parentheses are peroxide values determined at the time of tasting.^cScores with common, lower case letters in each row are not significantly different. SC = supercritical.

different from the commercial caustic-refined/bleached oil. After 8 d at 60°C, the SC-CO₂-processed oils had significantly higher scores than the commercial caustic-refined/bleached oil. Oils exposed to fluorescent light showed that SC-CO₂-processed oils have keeping properties equivalent to the commercial caustic-refined/bleached oil. In general, SC-CO₂-processed oils have flavor stability equal to or better than the commercial refined/bleached oil.

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REFERENCES

- Tandy, D.C., and W.J. McPherson, *J. Am. Oil Chem. Soc.* 61:1253 (1984).
- Sullivan, F.E., *Ibid.* 53:358 (1976).
- Beal, R.E., E.B. Lancaster and O.L. Brekke, *Ibid.* 33:619 (1956).
- List, G.R., C.D. Evans, L.T. Black and T.L. Mounts, *Ibid.* 55:275 (1978).
- List, G.R., T.L. Mounts, K. Warner and A.J. Heakin, *Ibid.* 55:277 (1978).
- List, G.R., T.L. Mounts and A.J. Heakin, *Ibid.* 55:280 (1978).
- Hayes, L., and H. Wolff, *Ibid.* 33:440 (1956).
- Brafie, B., *Chem. Ind.*:1152 (1958).
- Ohlsen, R., and C. Svensson, *J. Am. Oil Chem. Soc.* 53:8 (1976).
- Stahl, E., *Fette Seifen. Anstrichm.* 84:444 (1982).
- List, G.R., and J.A. Friedrich, *J. Am. Oil Chem. Soc.* 62:82 (1985).
- Taniguchi, M., T. Tsuji, M. Shibata and T. Kobayashi, *Agric. Biol. Chem.* 49:2367 (1985).
- Goodrum, J.W., and M.B. Kilgo, *Enger. Agric.* 6:265 (1987).
- Eggers, R., and U. Sievers, *J. Chem. Eng. Japan* 22:641 (1989).
- List, G.R., and J.P. Friedrich, *J. Am. Oil Chem. Soc.* 66:98 (1989).
- List, G.R., J.P. Friedrich and J.W. King, *Oil Mill Gazetteer* 95:28 (1989).
- Dakovic, S., J. Turkulov and E. Dimic, *Fat Sci. Technol.* 91:116 (1989).
- Fors, S.M., and C.E. Eriksson, *Lebensm. Wiss. Technol.* 23:390 (1990).
- Favati, F., J.W. King and M. Mazzanti, *J. Am. Oil Chem. Soc.* 68:422 (1991).
- Eggers, R., and V.C. Wilp, *Fat. Sci. Technol.* 93:348 (1991).
- Bitner, E.D., J.P. Friedrich and T.L. Mounts, *J. Am. Oil Chem. Soc.* 63:338 (1986).
- Friedrich, J.P., G.R. List and G.F. Spencer, in *Seventh International Conference on Jojoba and Its Uses*, edited by A.R. Baldwin, American Oil Chemists' Society, Champaign, 1989, pp. 165-173.
- Schwab, A.W., and H.J. Dutton, *Ibid.* 25:57 (1948).
- Moulton, K.J., *Ibid.* 66:302 (1989).
- Official Methods and Recommended Practices of the American Oil Chemists' Society*, edited by D. Firestone, American Oil Chemists' Society, Champaign, 1989.
- Warner, K., E.N. Frankel and T.L. Mounts, *J. Am. Oil Chem. Soc.* 66:558 (1989).
- Warner, K., in *Flavor Chemistry of Fats and Oils*, edited by D. Min and T. Smouse, American Oil Chemists' Society, Champaign, 1985, pp. 207-222.
- Warner, K., *Assessment of Fat and Oil Quality in Analysis of Fats, Oils and Lipoproteins*, American Oil Chemists' Society, Champaign, 1991, pp. 344-386.
- Moser, H.A., C.D. Evans, J.C. Cowan and W.F. Kwolek, *J. Am. Oil Chem. Soc.* 42:30 (1965).
- Friedrich, J.P., U.S. Patent 4,466,923 (1984).
- Friedrich, J.P., G.R. List and A.J. Heakin, *J. Am. Oil Chem. Soc.* 50:288 (1982).

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