Effects of Processing Steps on the Contents of Minor Compounds and Oxidation of Soybean Oil

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The processes of degumming, alkali refining, bleaching and deodorization removed 99.8% phospholipids, 90.7% iron, 100% chlorophyll, 97.3% free fatty acids and 31.8% tocopherols from crude soybean oil. The correlation coefficient between the removals of phosphorus and iron in soybean oil during processing was r = 0.99. The relative ratios of α-, β-, γ- and δ-tocopherols in crude oil, degummed oil, refined oil, bleached oil and deodorized soybean oil were almost constant. γ- and δ-tocopherols represented more than 94% of tocopherols in soybean oil. The order of oxidation stability of oil is crude > deodorized > degummed > refined > bleached oil.

Crude soybean oil is generally processed by degumming, alkali refining, bleaching and deodorization to obtain an odorless, bland and oxidatively stable oil which is acceptable to consumers (1). Each processing step has specific functions for removing certain minor compounds which can act as prooxidants or antioxidants (1-4). Degumming removes phospholipids and mucilaginous gums. Alkali refining removes free fatty acids, phospholipids, metals and chlorophylls. Bleaching reduces chlorophylls, carotenoids, peroxides and residual fatty acid salts. Deodorization removes volatile compounds, carotenoids, free fatty acids and tocopherols and decomposes peroxides to improve flavor quality and stability of the oil.

Several papers have been published on the oxidation stabilities of vegetable oils during processing. Cowan (5) reported that bleaching increased the flavor stability of refined oil. Going (6) reported that refined and bleached soybean oil was more easily oxidized than crude oil according to peroxide value. Park et al. (7) reported that soybean oil triglycerides obtained by Florisil column chromatography were more susceptible to oxidation than deodorized oil. Kwon et al. (8) reported that crude oil was most stable when oxidation stabilities of crude, degummed, refined, bleached and deodorized oils were compared by weight gain during storage.

Several studies have reported the effects of one or two processing steps such as bleaching or deodorization on the selected few minor compounds and/or oxidation of oil (5, 6). Information on all processing effects on the minor compounds and oil oxidation is not easily available. Therefore, the objectives of this paper were to study the effects of processing steps on phospholipids, iron, chlorophyll, free fatty acids, peroxide value and tocopherol, and the oxidation of soybean oil.

EXPERIMENTAL PROCEDURES

Materials. Fresh crude oil, degummed oil, alkali refined oil, bleached oil and deodorized oil processed from the same soybean batch were obtained from a commercial refinery. No additives were used. The oil bottles were nitrogen flushed and then stored in a dark cooler (4°C) until used. Ferrous ammonium sulfate was purchased from Matheson Coleman & Bell (Norwood, Ohio). D-α-tocopherol was purchased from Sigma Chemical Co. (St. Louis, Missouri).

Determination of minor compounds. Phosphorus, chlorophylls, free fatty acids and peroxide values were determined by AOCS methods Ca 12-55, Cc 13d-55, Ca 5a-40, and Cd 8-53, respectively (9). Iron was measured using a Perkin-Elmer (Norwalk, Connecticut) 360 atomic absorption spectrophotometer according to AOAC method 2.109-2.112 (10). Samples were ashed at 550°C in a muffle furnace overnight and then were mixed with two ml concentrated HCl and heated for five min at 100°C. The sample was diluted to a volume of 10 ml with double distilled demineralized water and then measured at 248.3 nm. The standard iron solutions were prepared with ferrous ammonium sulfate.

Tocopherols in soybean oils were analyzed by normal phase HPLC using UV detector (Waters Associates, Milford, Massachusetts) as described by Carpenter (11). D-α-tocopherol was used for a standard curve as well as an external standard. Tocopherols in soybean oil were expressed as D-α-tocopherol. The samples were analyzed in duplicate for the determination of minor compounds.

Sample preparation for oxidation of soybean oil. To study the effects of degumming, refining, bleaching and deodorization on the oxidation of soybean oil, 15 g oil was transferred into a 30-ml serum bottle. The bottles were sealed air tight with Teflon-coated rubber septa and aluminum caps. All samples were prepared in duplicate, stored in a forced-draft air-oven at 55°C and evaluated for oxidation stability every 24 hr for six days.

Determination of oil oxidation. Oxidation of oil samples was determined by molecular oxygen disappearance in the headspace of sample bottles. Oxygen contents in the headspace of sample bottles were measured using a Hewlett-Packard (Avondale, Pennsylvania) 5880A gas chromatograph equipped with an electronic integrator as previously described by Min and Schweizer (12) and Mistry and Min (13). The gas chromatographic peak area of molecular oxygen in one ml of headspace gas was expressed in electronic counts. Electronic counts of O_2/ml of headspace gas were converted to μmoles O_2/ml headspace gas by the following methods. One ml of air contains 0.20946 ml of oxygen (14), and 22,400 ml of oxygen is equal to 10^6 μmol, according to Avogadro's Law. Therefore, 0.20946 ml of oxygen is equal to 9.35 μmol O_2. The gas chromatographic peak area of 9.35 μmol of oxygen was measured in electronic counts by injecting one ml of air into the gas chromatograph. Elecronic counts for one μmol O_2 were calculated. The electronic counts for O_2 in one ml headspace were converted into μmol O_2 using the formula, μmol of O_2 in one ml of headspace gas = electronic counts of O_2 in one ml sample of headspace gas $\times$ one μmol O_2/electronic counts of one μmol of O_2.

RESULTS AND DISCUSSION

Effects of processing steps on the contents of minor compounds in soybean oil. The contents of phospholipids, iron, chlorophyll, free fatty acids, peroxides and tocopherols in soybean oil at different processing steps are shown in Table 1.

TABLE 1

Effects of Processing Steps on the Contents of Minor Compounds in Soybean Oil

Oil samples	Phosphorus (ppm)	Iron (ppm)	Chlorophyll (ppm)	FFA (%)	PV (meq/kg)	Tocopherol (ppm)
Crude	510.0	2.90	0.30	0.74	2.4	1,670
Degummed	120.0	0.78	na	0.36	10.5	1,579
Refined	5.0	0.55	0.23	0.02	8.8	1,546
Bleached	1.4	0.30	0.08	0.03	16.5	1,467
Deodorized	1.0	0.27	0	0.02	0	1,138

FFA, free fatty acid; PV, peroxide value; na, not available.

Oil processing by degumming, alkali refining, bleaching and deodorization removed 99.8% of the phospholipids in crude soybean oil. Crude oil contained 510 ppm phosphorus. Degumming removed 76% of the phospholipids of crude oil. Mounts et al. (15) stated that phospholipids remaining after water degumming might be nonhydratable phospholipids. Racicot and Handel (16) reported that the phosphorus in 19 different degummed soybean oils ranged from 9 to 163 ppm. We found alkali refining, bleaching and deodorization processes reduced the phosphorus content from 120 ppm in degummed oil to 5, 1.4 and 1 ppm, respectively.

Oil processing removed 90.7% of the iron in crude soybean oil. Degumming reduced iron content from 2.9 to 0.78 ppm. Alkali refining, bleaching and deodorization further reduced the iron content to 0.55, 0.30 and 0.27 ppm, respectively. Degumming was the most important process in reducing iron content in soybean oil.

Linear regression of phosphorus removal and iron removal from soybean oil by degumming, refining, bleaching and deodorization was determined from the data in Table 1. The regression equation was $Y = 197.74 \times -62.35$, where Y and X are phosphorus and iron contents in ppm in the oils, respectively, and the correlation coefficient was $r = 0.99$. This good correlation might be due to the chelating properties of phospholipids for iron (17). This result suggests that the removal of iron is closely related to the removal of phospholipids. It also has been reported that distribution and concentration of metal ions are dependent on the phospholipid content in the oil (4, 18).

Oil processing removed most of the chlorophyll in crude soybean oil (Table 1). The chlorophyll contents of crude oil and refined oil were 0.30 and 0.23 ppm, respectively. Bleaching reduced the chlorophyll from 0.23 ppm in refined oil to 0.08 ppm. Deodorized oil did not contain measurable amounts of chlorophyll. Bleaching was primarily responsible for removing the chlorophyll from soybean oil.

Complete oil processing removed 97.3% of free fatty acids in crude oil (Table 1). Degumming reduced the free fatty acids from 0.74% in the crude oil to 0.36%. Alkali refining reduced free fatty acids content in soybean oil to 0.02%. Bleaching increased the contents of free fatty acids to 0.03%. This probably was due to the hydrolysis of triglycerides by the use of acid activated clay at high bleaching temperature (19). Deodorization decreased the content of free fatty acids to 0.02%. Sarkadi (20) reported that free fatty acids are formed by the hydrolysis of triglycerides and removed simultaneously during deodorization. Degumming and caustic refining are the most important steps for removing free fatty acids in processing our oils.

The effects of processing steps on the peroxide value of oil are shown in Table 1. Peroxide value increased from 2.4 in crude oil to 10.7 in degummed oil. The high peroxide value of degummed oil might be due to oxidation caused by moisture (1-3%) and temperature (70-80°C) during the degumming process. Peroxide value decreased to 8.8 during alkali refining. Bleaching increased peroxide value to 16.5. The increase or decrease of peroxide value during bleaching depends upon the type and amount of clay used (21). King and Wharton (21) reported that usually at low concentration of bleaching clay there is an increase in peroxide value, while at high concentration there is a reduction in peroxide value. Deodorization completely decomposed peroxides, as would be expected and as is shown in Table 1.

The processing removed 31.8% of tocopherols in crude soybean oil (Table 1). This result is similar to the result of Gutfinger and Letan (22) which reported that 31-47% of tocopherols in crude soybean oil were removed during oil processing. Deodorization was mainly responsible for decreasing the tocopherol content in oil during processing (Table 1).

The tocopherol compositions of soybean oil at different processing steps are shown in Table 2. Even though total tocopherol content decreased during processing, the relative compositions of tocopherols in soybean oils were constant during processing. Gutfinger and Letan (22) also reported that no significant differences were observed in the composition of tocopherol fractions in crude and deodorized soybean oils. γ- and δ-tocopherols were major components which constituted more than 94% of total tocopherol (Table 2). The relative compositions of α-, β-, γ- and δ-tocopherols in deodorized soybean oil were 4.0, 1.1, 66.1 and 28.8%, respectively.

TABLE 2

Effects of Processing Steps on the Composition of Tocopherols in Soybean Oil

Samples	Tocopherol composition (%)			
	α-	β-	γ-	δ-
Crude oil	4.6	0.7	63.6	31.1
Degummed oil	5.3	0.7	67.2	26.8
Refined oil	4.3	0.8	65.4	29.5
Bleached oil	4.6	1.0	64.7	29.7
Deodorized oil	4.0	1.1	66.1	28.8

Effects of processing steps on the oxidation of soybean oil. The effects of oil processing steps on drop in headspace oxygen content of soybean oil during storage are shown in Figure 1. Headspace oxygen disappearance is directly related to oxidation of soybean oil because oxygen reacts with oils to produce peroxy radicals and hydroperoxides (7) to form volatile compounds (23). The headspace oxygen content of crude oil decreased from 9.25 to 3.72 (μmol O_2/ml headspace gas) during six days of storage. The headspace oxygen content of bleached oil decreased from 9.25 to 0.92 (μmol O_2/ml headspace gas) during six days of storage. The headspace oxygen contents in the crude oil and the bleached oil decreased by 60% and 90%, respectively, during six

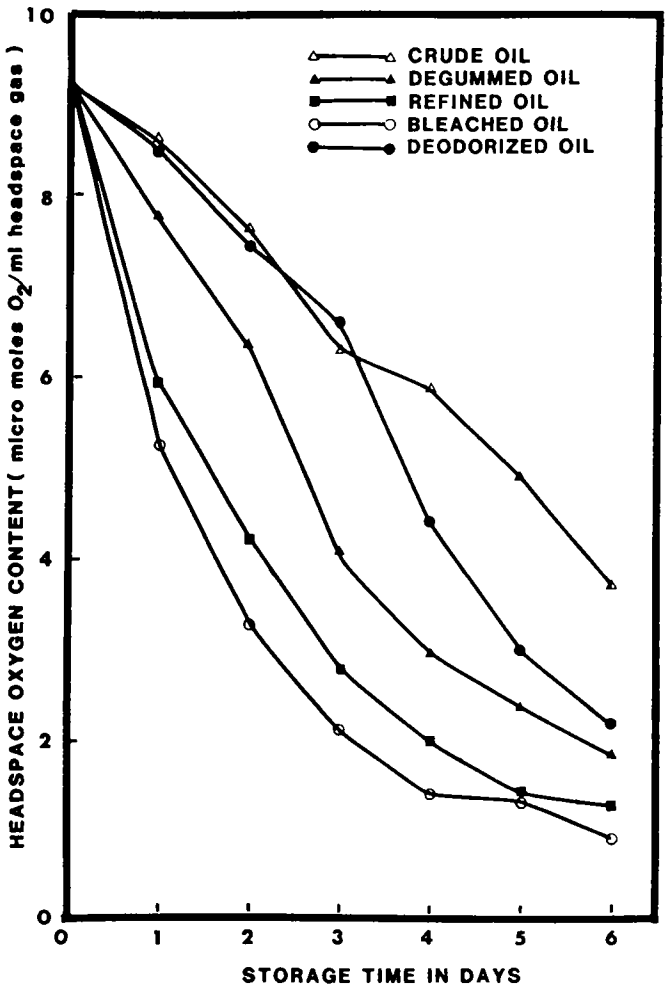

FIG. 1. Effects of processing steps on the oxygen content in the headspace of soybean oil during storage at 55° C.

days storage. That is, the oxygen in the headspace reacted more slowly with crude oil than with bleached oil. The order of oxidation stability of oil is crude > deodorized > degummed > refined > bleached oil (Fig. 1).

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