Effects of Soybean Pretreatments on Crude Oil Quality

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ABSTRACT: The effects of soybean pretreatments, including infrared (IR) radiation, oven toasting, microwave heating and live steam treatment on crude oil quality were investigated. Free fatty acid, oxidation value, carbonyl value and tocopherol content were used to monitor crude soybean oil quality. All soybean pretreatments were effective in improving the quality of oils from 15 and 18% moisture beans. Based on the analyses, recommended treatments are 3–4 min for IR at 220 V–250 W; 1 min for microwave heating at 650 W–2450 mHz; 1–1.5 min for steam heating; and 100–120°C, 30 min for oven toasting. Heat treatment of high-moisture soybeans before extraction yielded crude oil with a lower content of phosphatidic acid as compared to that of the untreated beans. *JAOCS 72*, 177–181 (1995).

KEY WORDS: Carbonyl value, free fatty acid, infrared radiation, microwave heating, oil, phosphatidic acid, soybeans, steaming, toasting, tocopherol.

Storage of soybeans at moisture contents higher than 11-12% is known to adversely affect the quality of extracted crude oil (1-4). Oils extracted from high-moisture beans have higher free fatty acids (FFA) and lower tocopherol (TOC) contents than oils from normal-moisture beans. Previous studies showed that the activities of enzymes such as lipase, lipoxygenase and phospholipase D were detrimental to oil quality (5-7). The increase in FFA during seed storage at high moisture was reported to be the result of soybean lipase activity (3). Field-, storage- and transportation-damaged beans have been reported to yield crude oil containing higher amounts of nonhydratable phospholipids (NHP) (4,8). List et al. (7) showed that NHP formation increased with increasing moisture content of beans due to phospholipase D activity. Lai et al. (9) and Chu and Lin (10) showed that the enzyme reaction was responsible for the reduction of γ -TOC content in a color-reverted soybean oil from high-moisture beans. Enzymic activity increases with increasing a_w (water activity) or increased substrate mobility (11). An increase in a, would increase the amounts of free water which, in turn, become available to serve as a vehicle for the enzymic process (12). Our previous study indicated that the occurrence of highly active enzyme reactions during processing (cracking and flaking) resulted in lower TOC content of oil in high-moisture (15 and 18%) untreated control beans as compared to the oil from untreated beans at 12% moisture content (10). The degree of enzyme inactivation of soybeans prior to cracking and flaking becomes an important factor affecting the crude oil quality.

For most of the normal beans at 11-12% moisture content, phospholipids are almost completely removed from crude oil in the degumming process. Phosphatidylcholine (PC), phosphatidylinositol and phosphatidylethanolamine (PE), which are classified as hydratable phospholipids, are usually removed by simple water degumming. However, phosphatidic acid (PA), an NHP which results from the degradation of PC and PE by phospholipase D (13), cannot be easily removed by water degumming. The processing of such beans results in a dark-colored oil, high refining losses and poor quality lecithin (1,4,8,13,14). Because of the deleterious effects of NHP on the quality of soybean oil, treatments including microwave heating and live steam treatment have been proposed to inactivate phospholipase D activity (15). Heat, moisture and enzyme activity are important factors contributing to the formation of NHP in extracted crude oil (15). This paper reports the effects of infrared (IR) radiation, oven toasting, microwave heating and live steam treatment on whole soybeans and the quality of extracted crude oil.

MATERIALS AND METHODS

Materials. Soybeans were Feed Grain Inspection Service (FGIS) Grade No. 2 U.S. soybeans with moisture content of *ca.* 12%. Whole intact soybeans were segregated from splits and foreign matters. Soybeans at various moisture contents were prepared by adding the required amount of water in a closed vessel and equilibrating them for one week. TOC homologues (α , β , γ and δ forms) were purchased from E. Merck (Darmstadt, Germany). All solvents used in the high-performance liquid chromatograph analyses were LC grade, including *n*-hexane, isopropanol, isopropyl ether and alcohol. Commercial grade *n*-hexane was used to extract the flakes.

Methods: Soybean pretreatments. Soybean pretreatments, including IR, microwave heating, live steam and oven toasting, were performed in duplicate on whole soybeans at 12, 15 and 18% moisture contents before oil extraction. Soybeans at each moisture content without any pretreatments were used as untreated control.

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IR radiation. Forty-five-gram soybeans were spread in a one-bean-thick layer in a flat vessel and subjected to radiation heating at 220 volts (V)-250 watts (W) for 1, 2, 3, 4 and 5 min.

Microwave heating. Microwave heating of soybeans was accomplished with a TATUNG unit (Taipei, Taiwan) equipped with a revolving carousel. One hundred and fifty grams of soybeans were place evenly in a 10×10 cm Pyrex baking dish and treated for 0.5-2 min at 650 W-2450 mHz. Bean temperatures during microwave heating were determined immediately after treatment.

Live steam treatment. Soybean samples (150 g) were heated in a steamer with steam produced from 1.5 L water added into the steamer for 0.5-2 min for each test. After treatment, soybeans were dehulled, cracked and flaked without additional heating.

Toasting. Each 150-g batch of soybeans was oven-toasted at 100, 120 and 140°C for 30 min.

Oil extraction and oil analyses. Treated soybeans were dehulled, cracked and flaked prior to oil extraction. Oil was extracted from flakes in a Soxhlet extractor for 3 h with n-hexane at 70-80°C. The crude oils were analyzed in triplicate for peroxide value (PV) (16), FFA (as % oleic) (16), p-anisidine value (AnV) (16), percentage of PA in total phospholipids (TPL) (16), carbonyl value (COV) (17) and TOC content (9).

Statistical analysis. Pair-wise Student's t-test was used for statistical evaluation by means of the general linear model of SAS (18). Standard deviations were calculated on triplicate analyses for each sample.

RESULTS AND DISCUSSION

Results of FFA, oxidation value (OV) (OV = 2 PV + AnV), COV and TOC content of each soybean oil extracted from untreated beans at each moisture content are shown in Table 1. The FFA, OV and COV for the extracted oils increased significantly (P < 0.05), whereas TOC content significantly decreased (P < 0.05) as bean moisture increased from 12 to 18%.

IR radiation treatment. Crude oils from soybeans at 15 and 18% moisture contents treated with IR radiation before extraction decreased in FFA, OV and COV, and increased in TOC content with increasing heating time of more than 1 min (Fig.

TABLE 1 Analyses of Crude Soybean Oils from Untreated Control Beans at 12, 15 and 18% Moisture Content

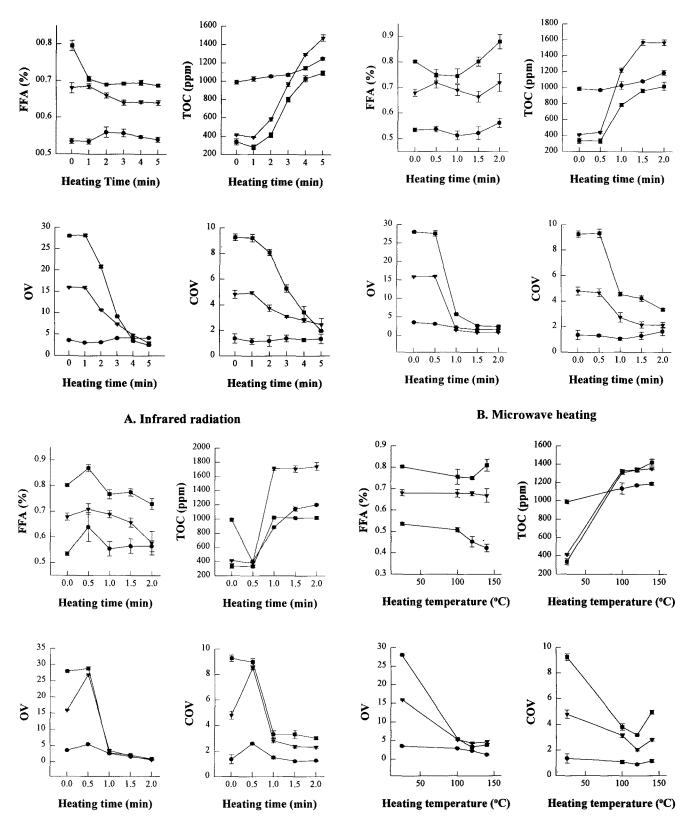
Analysis ^a	Moisture content (%)		
	12	15	18
FFA (%)	0.57 ± 0.01^{b}	$0.68 \pm 0.02^{\circ}$	0.81 ± 0.01^{d}
OV	3.55 ± 0.14^{b}	$15.95 \pm 0.14^{\circ}$	28.04 ± 0.13^{d}
COV	1.36 ± 0.36^{b}	$4.81 \pm 0.31^{\circ}$	9.26 ± 0.26^{d}
TOC (ppm)	989.62 ± 21.90^{b}	$415.34 \pm 8.24^{\circ}$	$337.38 \pm 33.11^{\circ}$

^aMean ± SD; FFA (% oleic), free fatty acid; OV, oxidation value; COV, carbonyl value; TOC, tocopherol. Means in the same row bearing different letters differ significantly at a level of P < 0.05.

1A). However, IR treatment of 12% moisture soybeans for 3-4 min showed adverse effects on the oils with significant (P <0.05) increases in FFA and OV, but no significant difference (P > 0.05) in COV as compared to those for untreated beans. Bean temperature ranged from 82 to 94°C during 3-4 min radiation. The effect of 3-4 min radiation of sovbeans on TOC content of the extracted oil showed 8-16% increase for 12% moisture-treated beans and 1.3-2-fold increases for 15 and 18% moisture-treated beans over the corresponding untreated beans (Fig. 1A). Increasing exposure to IR radiation of 15 and 18% moisture beans resulted in higher retention of TOC content in the crude oil. However, these 15-18% moisture soybeans were burned and pulverized after exposure to IR radiation for 5 min, and were therefore unsuitable for oil extraction. Short exposure time of 1 min for 12% moisture soybeans gave crude oil with no significant differences (P > 0.05) in the COV, FFA and TOC content over untreated beans. Oils from 15 and 18% moisture soybeans treated for 1 min had no significant change (P > 0.05) in OV, COV and TOC content over the corresponding untreated beans. Oils from $\leq 2 \text{ min IR-treated}$ beans at 15 and 18% moistures gave significantly (P < 0.05) lower TOC content and higher OV and COV than oils from 3-4 min IR-treated beans at 15 and 18% moistures. Hence, an exposure time of moist soybeans to IR radiation of 220 V-250 W for 3–4 min is suggested.

Microwave heating. Microwave heating of soybeans at 12, 15 and 18% moisture content for 0.5 min showed no significant differences (P > 0.05) in the OV, COV and TOC content over the corresponding untreated beans (Fig. 1B). For 12% moisture soybeans, there was no significant difference in COV between all microwave-treated and untreated beans. Increasing the microwave heating of 15 and 18% moisture beans to 1.0 min resulted in oils with significant differences (P < 0.05) in OV, COV and TOC content as compared to the oils from untreated beans. Significant differences were found in the OV and TOC of oils from ≥1.5 min microwave-treated beans over untreated beans. As microwave heating time increased beyond 1.5 to 2 min, all soybeans were dried, burned, and unsuitable for oils extraction. The effect of microwave heating of 12 and 15% moisture beans for 0.5 min on the FFA of extracted oils showed a significant (P < 0.05) increase in the FFA for 15% moisture-treated beans and no significant (P > 0.05) difference for 12% moisture-treated beans over the corresponding untreated beans. Oils from 1 min-treated beans at 12 and 18% moisture contents showed significant decreases (P < 0.05) in the FFA over the corresponding untreated beans. As heating time increased to 2 min, the FFA of the oils from all moisture beans significantly (P < 0.05) increased compared to those from untreated beans.

Live steam treatment. Steam treatment of 12% moisture beans for 1-1.5 min gave the oil with 15% (maximum) increase in TOC content and 23-53% decrease in OV but no significant differences in COV and FFA (P > 0.05) over the untreated beans (Fig. 1C). However, for soybeans at 15 and 18% moisture contents, the COV, OV and TOC contents of extracted oils were significantly (P < 0.05) improved by steam



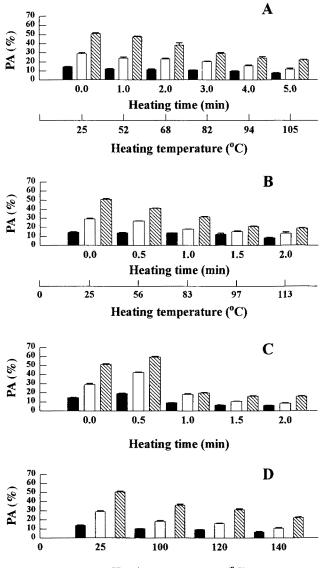
C. Steaming

D. Toasting for 30 min

FIG. 1. Effects of various soybean pretreatments: A, infrared radiation; B, microwave heating; C, steaming; and D, toasting on free fatty acid value (FFA), oxidation value (OV), carbonyl value (COV) and tocopherol (TOC) content of crude oils from 12 (\bullet), 15 (∇) and 18% (\blacksquare) moisture content soybeans. Data points are means of triplicates; error bars represent the SD of the means. Data points without error bars indicate SD less than 2% of means.

treating these beans for 1-1.5 min (Fig. 1C). Oil from these beans had lower OV (at least 77% decrease) and COV (at least 43% decrease) and higher TOC content (at least twofold increase) (P < 0.05) as compared to the oils from untreated beans. Significant decreases (P < 0.05) in FFA were found for the oils from 15 and 18% moisture beans steamed for 2 min over the corresponding untreated beans. Short steam treatment of beans at 0.5 min adversely affected the oil quality. The oils from all 0.5 min steam-treated beans at 12, 15, and 18% moisture contents had lower TOC content, and higher FFA, OV and COV (except 18% moisture beans for COV) than the oils from untreated beans. Incomplete heat penetration of the beans and water condensation on the surface of beans due to inadequate steam treatment might have caused these some deleterious effects on the oil quality. As the length of steam treatment time increased, the TOC content, OV and COV of the oils from beans at 15 and 18% moisture contents were significantly (P <0.05) improved, as mentioned previously. The TOC content of the oils from 15% moisture beans steam treated for 1-1.5 min was more than 1700 ppm compared to 415 ppm for oil from untreated beans. Among all soybeans steamed for 1-1.5 min, 15% moisture-steamed beans produced oil with the highest TOC content, indicating that these conditions were optimum for high TOC retention. Steaming of 12% moisture beans at 1.5 min gave only a 15% increase in the TOC content of extracted oil as compared to the untreated beans. The presence of water in a food increases the rate of heat penetration into the center of food due to high heat transfer coefficient of water $(60 \text{ to } 3000 \text{ W/m}^2\text{K})$ (19), as compared to that of air (0.6 to 60) W/m^2K (19) or food without water. The rate of heat transfer was probably affected by the bean moisture content in these samples. The water content of low-moisture beans during steam treatment was probably insufficient for heat penetration into the center of beans to inhibit enzyme activity. As bean moisture was increased to 18%, the TOC content of extracted oil was increased from 337 ppm for untreated beans to 1022 ppm for beans steamed for 1 min. The increase of TOC content in the extracted oil from soybeans at 18% moisture content was less than that from soybeans at 15% moisture content. Accordingly, to obtain oil with higher TOC content and lower FFA, OV and COV, soybeans should be conditioned to 15% moisture content and treated with at least 1 min of steaming prior to oil extraction.

Toasting. The oils from 12, 15 and 18% moisture soybeans toasted at 100–120°C for 30 min had significant (P < 0.05) decreases in OV and COV, and an increase in TOC content over the oils from corresponding untreated beans (Fig. 1D). The FFA of oils from 12 and 18% moisture toasted beans at 100–120°C significantly decreased over the corresponding untreated beans. There was no significant difference (P >0.05) in the FFA of the oils between toasted and untoasted beans at 15% moisture content (Fig. 1D). As temperature increased to 140°C, the COV for 15 and 18% moisture beans increased significantly (P < 0.05) as compared to toasted beans at 120°C. Beans with 12% moisture toasted at 100–120°C gave oil with a 15–19% increase in the TOC con-



Heating temperature (°C)

FIG. 2. Effects of various soybean pretreatments: A, infrared radiation; B, microwave heating; C, steaming; and D, toasting on the percentage of phosphatidic acid (PA) in crude oils from soybeans with different moisture contents. black bar, 12% Moisture soybeans; white bar, 15% moisture soybeans; ruled bar, 18% moisture soybeans. Values are given as mean \pm SD of duplicate analyses.

tent compared to untreated beans. However, the TOC content of oils from 15 to 18% moisture beans toasted at 100–120°C increased 2–3 times over that of untreated beans.

Oil from 18% moisture beans toasted at 100–140°C had significantly higher amounts of TOC (\geq 1300 ppm) than the oils from the other heat-treated beans (Fig. 1A, B and C) at the same moisture content. However, toasting at 140°C produced dried and burned beans, unsuitable for extraction. Toasting beans at 100–120°C for 30 min produced crude oils with more than 1140 ppm of TOC and with FFA, OV and COV less than 1.5%, 6 and 4 mg/kg, respectively, and thus was suggested as optimum condition of bean toasting in this study. Oil quality was improved by toasting under these conditions with similar results as for the other methods tested.

Effects on phospholipid composition. The PA in TPL degummed from crude soybean oils from different moisture beans with different treatments are shown in Figure 2. The PA (%) increased with the increase of bean moisture content. The four heat treatments of 18% moisture soybeans (one-week equilibration) prior to oil extraction significantly (P < 0.05) decreased the PA (%) compared to untreated beans, except at the 0.5-min steam treatment. No significant differences (P >0.05) in the PA at 12% moisture soybeans were noted between treatments by IR for 3 min (10.9% PA) or toasting at 100°C (10.4% PA), respectively. Soybeans at 15 and 18% moistures treated by 3-min IR, 100°C toasting, 1-min steaming or microwave heating produced the oils with a 30-40% decrease in PA over the corresponding untreated beans. This agrees with work by List and Mounts (20) showing steam treatment of soybeans stored for one week at high moisture content to markedly decrease the NHP (%). Steam treatment of soybeans for ≥ 1 min reduced PA from 15% for untreated beans at 12% moisture content to below 10% for treated beans at the same moisture content. In beans with either 15 or 18% moisture content, ≥1-min steam treatment reduced the PA from 30 and 50%, respectively, for the corresponding untreated beans to 20% or less. As steaming time increased to 1.5 min, the PA content was significantly (P < 0.05) lowered by more than 55% compared to untreated beans at all moisture contents. Our results corresponded to previous studies which showed that heat treatment of soybeans prior to oil extraction inhibited NHP formation by inactivating the phospholipase D activity (7). The inactivation of phospholipase D in soybeans by heating helps lower PA formation and causes less degradation of PC and PE than in beans without any treatment.

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