

Chemical Evaluation of Oil from Field- and Storage-Damaged Soybeans

J.A. ROBERTSON, W.H. MORRISON, III, and D. BURDICK,
Richard B. Russell Agricultural Research Center,¹ Athens, Georgia 30604

ABSTRACT

In recent years, prolonged wet weather during the harvest season resulted in excessive field- and storage-damaged soybeans, particularly in the Southeast. As the severity of the damage increased, analysis of the oil extracted from these beans showed a corresponding increase in free fatty acids, Lovibond color, and content of oxidative deterioration products which absorb at 270 nm. In general, there was a substantial decrease in total oil content and an almost complete deterioration of phospholipids in severely damaged beans during storage. Initially, the oxidative stability of the oils decreased rapidly. After storage damage became severe, the stability increased substantially, possibly because of the formation of unidentified deterioration products which had high antioxidant properties. The study clearly showed that the processing of field- and storage-damaged soybeans would result in substantial refining losses to processors and that the finished oil would be of inferior quality.

INTRODUCTION

In recent years, prolonged wet weather in the Southeastern and North Central regions of the U.S. during the harvest season has damaged large quantities of soybeans in these areas. When the damaged soybeans were placed in storage at high moisture levels, the damage became progressively severe (1-4). Crude oils extracted from damaged soybeans have been reported to be high in free fatty acids (5) and bleach color and to have poor flavor quality (6-8). It also has been reported that storage-damaged soybeans were lower in carbohydrates and oil but higher in protein

than normal beans (5).

As a result of this damage, oil refining losses have risen from a normal of 1 to 1 1/2% to over 4%, and finished oils prepared from the damaged beans have been turned down by manufacturers because they were of inferior quality (1). Consequently, because this damage to soybeans in the Southeast has resulted in financial losses to both farmers and industry, it was deemed necessary to analyze beans of different degrees of damage to determine the extent of oil quality deterioration.

EXPERIMENTAL PROCEDURES

A field-damaged soybean sample was obtained from Prichard Seed Farm, Louisville, Georgia, and 4 soybean samples of different degrees of storage damage were obtained from Goldkist, Inc., Valdosta, Georgia. The soybeans were analyzed for total oil content, crude protein, and moisture using official AOCS methods (9).

The samples were ground with a high-speed grinder and then extracted with petroleum ether (30-60 C) for 6 hr in a Soxhlet extractor. The solvent was removed from the oil under vacuum with a rotary evaporator. The solvent-free oil was held at -20 C until analyzed.

The crude soybean oils were analyzed for phosphorus content, peroxide value, Lovibond color, per cent free fatty acids, and active oxygen (AOM) by official AOCS methods (9). Gas chromatographic analyses of the fatty acid methyl esters (10) were made using a Tracor MT 220 gas liquid chromatograph equipped with an Infotronic Model CRS-101 digital integrator. A 12 ft. x 1/4 in. stainless steel column with 10% DEGS on AW-DMCS 60/80 mesh chromosorb W was used for the analyses, and the oven was operated at 205 C. Per cent fatty acids were calculated by determining the response factor for the individual methyl esters using standard mixtures of esters purchased from the

¹ARS, USDA

TABLE I

Chemical Composition of Damaged Soybeans

Soybean samples	Degree of damage	Total oil, % dry basis	Protein, % dry basis	Moisture %
Undamaged	0	19.7	40.2	9.5
Field damaged	1	18.1	46.4	9.0
Storage damaged	2	12.1	43.4	12.5
Storage damaged	3	13.7	43.9	11.8
Storage damaged	4	13.9	45.1	11.3
Storage damaged	5	18.3	44.8	14.4

TABLE II

Chemical Characteristics of the Oil Extracted from Damaged Soybeans

Soybean samples	Degree of damage	Phosphorus %	Phospholipid ^a %	FFA % as Oleic	Lovibond color ^b	Peroxide value
Undamaged	0	0.050	1.50	0.4	70Y 3.0R	2.07
Field damaged	1	0.038	1.14	2.5	70Y 3.5R	2.68
Storage damaged	2	0.005	0.15	7.2	70Y 4.0R	1.88
Storage damaged	3	0.005	0.15	11.3	70Y 5.1R	0.92
Storage damaged	4	0.003	0.09	10.1	70Y 5.3R	1.28
Storage damaged	5	0.001	0.03	47.1	70Y 20.5R	1.46

^aEquivalent phospholipid, % = % phosphorus x 30.

^bAOCS Method Cc 13b-45.

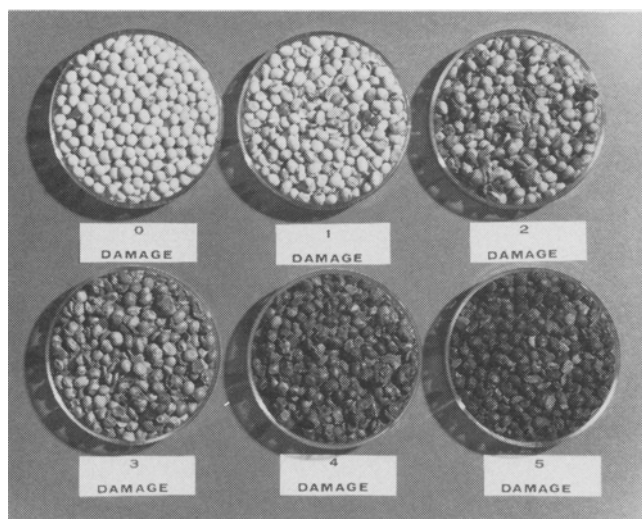


FIG. 1. Soybeans of different degrees of field and storage damage.

Hormel Institute. Spectroscopic examination was conducted using the Cary 15 low-UV recording spectrophotometer. Absorptivities were determined on a 1% solution of the oils (1 cm cell) in cyclohexane.

RESULTS AND DISCUSSION

Because of harvesting in wet weather, some soybeans have been placed in storage at a mean moisture content of 16-18% vs. a normal moisture of 10-11% or lower (1). With an initial moisture content of 12% or lower, soybeans will usually resist changes in grade for 2 years (11). High moisture content promotes fungus growth which will cause deterioration of the beans, impart a moldy odor, and reduce the beans to sample grade. Also, physiological changes occurring in the beans cause a heat build-up. This heating can be great enough to char the beans, as seen in Figure 1. This figure shows soybeans of different degrees of damage which we have visually rated from 0 to 5. The undamaged, control soybeans were rated 0, the field-damaged beans rated 1, and the storage-damaged beans rated 2 to 5.

The chemical composition of the damaged soybeans is shown in Table I. There was a small decrease in total oil content of the field-damaged sample and a substantial decrease for 3 out of 4 of the storage-damaged samples. Although variable, the protein content was higher in the damaged beans than in the undamaged. The moisture content of the storage-damaged soybeans was higher than desired for storage of soybeans.

Table II shows the chemical characteristics of the oil extracted from the damaged soybeans. As the severity of the visual damage increased, the phospholipid content of the oil decreased, and the Lovibond color and per cent free fatty acids increased. The surprising result was the finding that the phosphorus content of the oil extracted from the storage-damaged soybeans was negligible. This indicates

TABLE III

Fatty Acid Composition of the Oil from Damaged Soybeans

Soybean samples	Degree of damage	Fatty acid composition (Area %)				
		16:0	18:0	18:1	18:2	18:3
Undamaged	0	10.5	3.0	21.2	58.3	6.9
Field damaged	1	10.6	4.6	22.6	55.6	6.4
Storage damaged	2	13.3	4.5	23.8	55.5	3.0
Storage damaged	3	12.8	4.4	21.9	56.8	3.9
Storage damaged	4	14.1	4.4	23.6	55.9	2.0
Storage damaged	5	12.0	4.1	23.2	55.3	5.3

TABLE IV

Evaluation of Stability of Oil from Damaged Soybeans

Soybean samples	Degree of damage	Absorptivity ^a		R ^b	AOM ^c 8-hr
		228 nm	270 nm		
Undamaged	0	0.33	0.03	11.0	18.9
Field damaged	1	0.64	0.10	6.4	35.8
Storage damaged	2	0.63	0.20	3.1	143.3
Storage damaged	3	0.77	0.24	3.2	45.9
Storage damaged	4	0.74	0.26	2.8	37.3
Storage damaged	5	0.70	0.49	1.4	4.1

^aAbsorbance divided by the product of sample path length (cm), and the concentration of the oil (g/liter).

$$R = \frac{\text{absorptivity } 228 \text{ nm}}{\text{absorptivity } 270 \text{ nm}}$$

^cIncrease in peroxide value in active oxygen method in 8 hrs.

that the phospholipids are more susceptible to storage deterioration than the triglycerides and that they were almost completely destroyed during storage, probably by enzymatic action (12).

A soybean oil refinery in the Southeast has reported that mildly damaged beans contain nonhydratable phospholipids which are not removed easily by degumming or refining and that the finished salad oil from such beans is inferior in flavor stability. Evidently, the formation of nonhydratable phospholipids is the first stage in the rapid deterioration of phospholipids in damaged soybeans. The oil from the field-damaged soybeans (Table II) may have contained nonhydratable phospholipids; our sample, however, was too small for further investigations of the phospholipids.

Probably of greater concern to processors than the nonhydratable phospholipids is the high free fatty acids content of the damaged soybeans. The refining loss of the oil from such beans has been so great that some processors are diluting southeastern beans with midwestern beans to overcome the high refinery losses (1).

The effects of field- and storage-damage on the fatty acid composition of the oil from the soybeans are shown in Table III. There was a substantial decrease in the linolenic acid content of the oil extracted from all storage-damaged soybeans except from those damaged most severely (degree damage 5); whereas, there was only a small decrease in the linoleic acid content and no apparent change in the oleic acid content. The decrease in the polyunsaturated fatty acids indicates that oxidative deterioration took place during storage and is reflected in the lower total oil content of the storage-damaged beans (Table I). The fatty acid composition of the oil extracted from the degree damage 5 soybeans indicated little oxidative deterioration; however, there was substantial hydrolysis of the extracted oil. The degree damage 5 soybeans contained 47% free fatty acids (Table II).

Additional evidence of oxidative changes in the oils extracted from the field- and storage-damaged soybeans was obtained by UV spectrophotometry and the active oxygen method (AOM). Initially absorptivity(a) sharply increased at 228 nm with increase in degree of damage (Table IV). This absorption then leveled off and began to decrease. Also, as the degree of damage increased, absorptivity at 270 nm increased and the R value (the ratio of the absorptivity at 228 nm vs. 270 nm) decreased. When oils, such as soybean oil, which contain linoleate and linolenate, are oxidized, the diene conjugation, measured by UV absorption at 228-234 nm, increases proportionately to the uptake of oxygen with the subsequent formation of peroxides in the early stages of oxidation. These peroxides increase rapidly, reaching high values. Then they decompose giving rise to a series of compounds such as α , β -unsaturated aldehydes and ketones which absorb in the regions

260-280 nm. The more oxidized the oil, the stronger is the absorption ca. 270 nm (13,14). Therefore, as oxidation of an oil progresses, a_{228} nm increases, reaches a maximum, and later decreases; whereas, a_{270} nm steadily increases as oxidation advances, presenting higher and higher values, while the R value decreases (14).

The AOM data in Table IV suggest that as the severity of the damage increased, the stability of the crude extracted oils first decreased then gradually increased. Results were similar with the oxygen bomb method. The AOM data are misleading because damage to soybeans lowers the flavor and keeping quality of the refined and deodorized oils (15). Apparently small concentrations of materials which have strong antioxidant properties are present and make the crude oils very stable. The presence of the high concentration of liberated free fatty acids in the oil from the storage-damaged beans might have a small antioxidant effect.

Further work is needed to assess the importance of storage damage on the content of nonhydratable phospholipids in the extracted oil and on the quality and stability of the finished oil.

ACKNOWLEDGMENT

J.K. Thomas provided analytical assistance.

REFERENCES

1. *The Feed Bulletin*, The Jacobsen Publishing Co., Chicago, Ill., May 5, 1972, p.1.
2. *Soybean Digest*. 32:7 (1971).
3. *Ibid.* 33:26 (1972).
4. *Agribusiness Report*, Vol. 5, No. 10, March 6, 1972.
5. Krober, O.A. and F.I. Collins, *JAOCS* 25:296 (1948).
6. Evans, C.D., P.M. Cooney, H.A. Moser, J.E. Hawley and E.H. Melvin. *Ibid.* 29:61 (1952).
7. Hutchins, R.P., *Oil and Soap* 22:165 (1945).
8. Sanders, J.H., *Ibid.* 21:357 (1944).
9. "Official and Tentative Methods of the American Oil Chemists' Society," Vol. I, Third edition, AOCS, Champaign, Ill., 1964 (revised to 1971).
10. Metcalfe, L.D., A.A. Schmitz and J.R. Pelka, *Anal. Chem.* 38:14 (1966).
11. Wolf, W.J., and J.C. Cowan, "Soybeans as a Food Source," CRS Press, Cleveland, Ohio, 1971, p. 17.
12. Lehninger, A.L. "Biochemistry," Worth Publishers, Inc., New York, 1970, p. 198.
13. Markley, K.S., "Fatty Acids. Their Chemistry, Properties, Production, and Uses," Part 2, Interscience Publishers, Inc., New York, 1961, p. 1399.
14. Boekennoogen, H.A., "Analysis and Characterization of Oils, Fats, and Fat Product," Vol. 2, Interscience Publishers, London, England, 1968, p. 353.
15. Evans, C.D., E.N. Frankel, P.M. Cooney and H.A. Moser. *JAOCS* 37:452 (1960).

[Received July 27, 1973]