presently exists in the separation of individual molecular species, these chromatographic rules might be invariant until a complete separation of the individual molecular species can be accomplished. Then, a matrix model would be the most convenient way to distinguish the positional isomers.

ACKNOWLEDGMENT

M. Hatano and K. Takama provided considerable assistance. H. Ebina and M. Egi contributed experimental skills to the program.

REFERENCES

1. Hitchcock, C., and E.W. Hammond, in Developments in Food Analysis Techniques 2, edited by R.D. King, Applied Science Publishing, Ltd., London, 1980, pp. 199-201.
2. El-Hamdy, A.H., and E.G. Perkins, JAOCS 58:49 (1981).
3. Petersson, B., O. Podlaha and B. Toregard, JAOCS 58:1005 (1981).
4. El-Hamdy, A.H., and E.G. Perkins, JAOCS 58:867 (1981).
5. Plattner, R.D., G.F. Spencer and R. Kleiman, JAOCS 54:511 (1977).
6. Plattner, R.D., JAOCS 58:638 (1981).
7. Wada, S., C. Koizumi and J. Nonaka, Yukagaku 26:11 (1977).
8. Wada, S., C. Koizumi, A. Takiguchi and J. Nonaka, JAOCS 27:21 (1978).
9. Wada, S., Jasco Report 18:18 (1983).
10. Dong, M.W., and J.L. Dicesare, JAOCS 60:788 (1983).
11. Takahashi, K., T. Hirano and K. Zama, Bull. Japan. Soc. Sci. Fish. 49:1301 (1983).
12. Takahashi, K., T. Hirano, K. Takama and K. Zama, Bull. Japan. Soc. Sci. Fish. 48:1803 (1982).
13. Martin, A.J.P., Biochem. Soc. Symposia (Cambridge, England) 3:4 (1950).

[Received October 26, 1983]

Adiabatic Reactor for Simulating Storage-Damaged Soybeans

E. DUANE BITNER, J.M. SNYDER, J.P. FRIEDRICH, and **T.L. MOUNTS,** Northern Regional Research Center, Agriculture Research Service, USDA, Peoria, IL 61604

ABSTRACT

An adiabatic reactor was constructed to simulate conditions that lead to storage-damaged soybeans. The heart of the system is an electronic temperature controller that causes the reactor temperature to closely follow intrinsic heating of the soybeans. Using moisture concentrations between 17% and 20%, we observed intrinsic heating ranging from 47 C to 52 C after 3-13 weeks. Quality of the extracted oil was determined by analyses for triglyceride (TG) composition, total phosphorus (P), peroxide value and free fatty acid (FFA). Higher FFA and lower P and linolenic acid concentrations in the damaged beans compared with undamaged beans agree with the literature and indicate reliability of the adiabatic reactor for further studies, e.g., the effect of enzymatic activity on the quality of resulting soybean oil.

INTRODUCTION

Oilseeds and cereals are subject to damage by pests, weather, harvesting, handling and storing (1-7). Especially after extreme wet harvest and storage conditions, grain can be affected adversely (8). Breakdown of monitoring and control equipment also can cause grain to be damaged, even during ideal storage conditions. Damage to soybeans has a deleterious effect on the extracted oil (9-11), which affects its processing requirements (12,13). The primary purpose for designing an adiabatic reactor was to better understand storage damage and its effects on grain and extracted oil. Normally, the site of maximum storage damage is the center of large volumes of grain. Adiabatic conditions prevail because the central location is the most thermally insulated. An adiabatic system loses very little, if any, heat generated, and an exothermic reaction, even though extremely slow, can cause a positive thermal feedback resulting in accelerated spoilage or even fire. Spoilage can be simulated in an adiabatic reactor by placing moist grain in an environment that favors the activity of microorganisms with accompanying increase in temperature (14-16). This paper presents a detailed description of the apparatus and data demonstrating its satisfactory operation.

[1]Presented at the Great Lakes Regional ACS Meeting, Normal, IL, June 1982.

APPARATUS AND PROCEDURE

The adiabatic reactor, Figure 1, was designed to incorporate a 500 mL Dewar flask, which holds ca. 165 g of soybeans. Holes were drilled in the flask skirt-base to permit air circulation. Aluminum foil and a large rubber stopper were used for a seal. A squirrel-cage type fan blower circulated the temperature-controlled air within the box containing the Dewar. The motor for driving the fan was mounted ca. 1 ft from the top of the box to minimize the effect of motor heat. A flexible electric heating cord, 140 watts, 6 ft long for 115 volts AC was used as the heating element (Cole-Parmer Instr. Co., Chicago, IL). The complete box, except for the top panel, was placed in a large plastic sack for additional heat and humidity retention. Other details of the reactor are shown in the diagram.

The heart of the system is an in-house constructed temperature controller, which is shown schematically in Figure 2. Most components are mounted on a 3″ × 5″ printed circuit board, which is positioned directly on top of the commercial power supply (Polytron Devics Inc., Paterson, NJ). The sensors used are 2 type J thermocouples wired

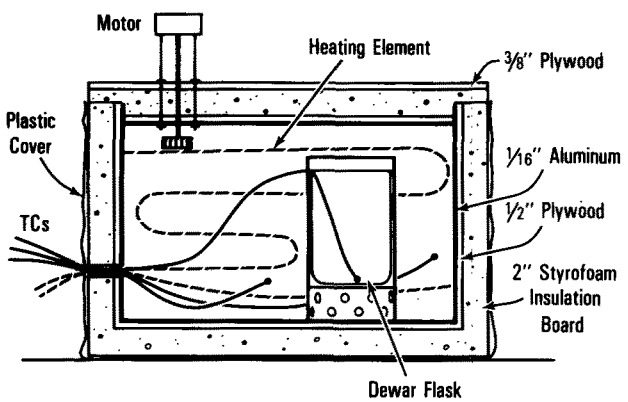

FIG. 1. Diagram of adiabatic reactor. TC—thermocouples and thermistors. Outside dimensions—18 in (length) × 12 in. (width) × 18 in. (height). Grain placed in Dewar flask. See text for details.

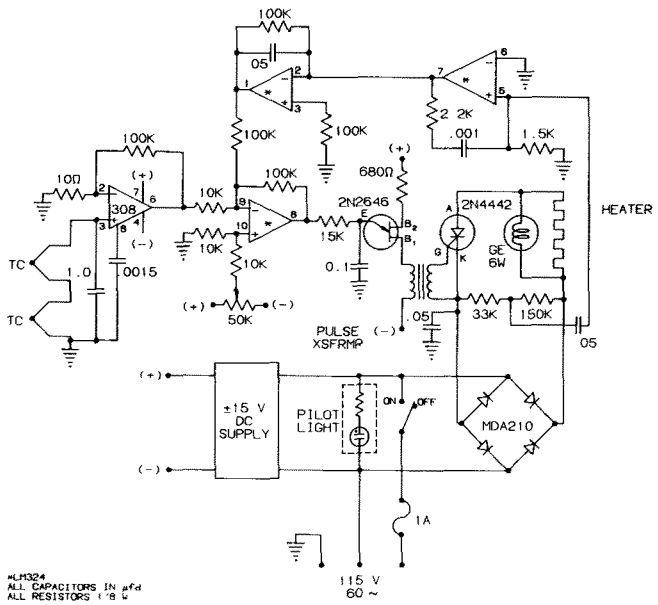

FIG. 2. Schematic diagram of temperature controller. LM308—instrument operational amplifier. *LM324N—quad general purpose operational amplifier. Resistors are 1/8 W unless otherwise noted. Capacitors are in microfarads (μfd) unless otherwise noted. TC—iron constantan thermocopules. See text for details.

back to back. Thus, when temperatures are identical, the thermocouple voltage will cancel each other and their total output will be zero. The first amplifier, LM308, is a typical instrument op-amp with high gain and low noise used to increase the very small voltage difference of the sensors to a usable signal for control. This difference signal then goes to a second amplifier (general purpose op-amp LM324N), where it is mixed with a feedback pulse, nulled for zero control and amplified. The combined signal then switches a unijunction transistor (2N2646), forming a gate trigger for the silicon-controlled rectivier (SCR-2N4442). Current flow through the SCR activates the heater and increases the temperature of the reactor chamber. Feeding back a pulse from the heater circuit ensures operation of the unijunction transistor and forms a type of proportional control; the greater the signal, the more pulses are formed for triggering. Greater detail of the required circuitry is readily available (17-19).

Temperatures within the reactor box and flask were followed automatically with a scanning telethermometer (Yellow Spring Instruments Co., Inc., Yellow Springs, OH) and recorder. In addition, manual measurements, including room temperature, were recorded 3 times a day, when possible. The temperature difference between box and flask was essentially constant at ca. 0.1 C (limit of instrument capability), with the box purposely being held at a temperature slightly under the beans so that no external heating of the beans would occur. No significant induction peroid was observed.

Soybeans of seed quality from the same "lot" were used throughout the experiments. They were tempered to varying moisture content by placing them in a plastic sack, adding water, turning the sack occasionally for 3 or 4 days or until the desired moisture was reached. Moisture measurements were made with a Steinlite moisture meter (electronic capacitive-type measurement). The beans were then loaded into the reactor chamber, sealed and permitted to heat spontaneously. After reaching their maximum intrinsic heating temperature, they were allowed to cool to ca. 30 C within the reactor and then were placed in a closed plastic sack to attain finalized moisture equilibrium (ca. 2 days). The beans then were cracked, dehulled, flaked and extracted with hexane in a glass apparatus. The extracted oil was analyzed and the results were compared with those of oil from undamaged beans.

RESULTS AND DISCUSSION

The adiabatic reactor should produce the worst case of storage damaged soybeans, because we purposely sealed the beans to eliminate moisture loss. Thus, the system should simulate large bulk storage or tightly closed containers.

Results of 5 different runs are shown in Table I. The first 3 runs were made with the sensor probe at the center of the beans, and the last 2 runs with the probe at the bottom of the container. A higher maximum intrinsic temperature rise occurs with the probe at the bottom of the beans and indicates this position to be optimum, because greatest damage appears to occur at the highest temperature (12). The time required to reach equilibrium in elevated temperatures varied in the first 3 experiments, probably because of an insufficient top seal rather than the small differences in moisture content. After the top seal problem was corrected, the difference in moisture concentration (between trials 4 and 5) had a significant effect on the time to reach equilibrium. Despite a peroxide value of zero for the extracted oil, sample 5 indicates that the heat developed at a slightly lower moisture concentration also has a deleterious effect on beans, as indicated by the low phosphorus (P) and high free fatty acid (FFA) content. Although both the linolenic acid concentration and peroxide values show some significant differences between damaged and undamaged beans, the concentration of linolenic acid appears to be a more consistent indicator of the degree of storage damage than the peroxide value.

The appearance and odor of the beans removed from the reactor indicated the presence of molds and other micro-

TABLE I

Adiabatic Soybean Conditions and Extracted Oil Analyses

Sample number	Moisture (%)	Max intrinsic temperature (C)	Time[a] (weeks)	Peroxide value (meq/kg)	FFA (%)	P (ppm)	FFA composition				
							Palmitic	Stearic	Oleic	Linoleic	Linolenic
Control	9.64	—	—	0.00	0.33	724	11.4	3.8	23.4	54.3	6.8
1	18.45	47.9	4	0.99	2.49	59	11.2	3.8	23.4	54.6	6.7
2	19.50	46.8	6	0.00	2.93	17	11.6	3.9	23.8	54.1	6.1
3	19.24	48.2	6	2.10	2.65	7	11.5	3.9	23.8	54.4	6.2
4	18.97	51.9	3	0.75	1.82	82	11.6	3.8	23.5	54.1	6.3
5	17.50	51.8	13	0.00	2.98	4	11.9	3.9	23.9	54.4	5.3

[a]Rounded off to nearest week. Time to reach maximum temperature.

flora, which were also observed by colleagues during previous experiments (see Acknowledgments). Microflora has been reported to cause intrinsic heating in grains to a range of 50-55 C (20) and was the probable source of heat in our experiments. Thus, aside from moisture content, the primary reason for our slightly lower temperature maxima was small sample size.

Oil from simulated storage-damaged beans differs from that of undamaged (control) soybeans in 3 significant respects: (a) higher FFA concentration; (b) much lower P concentration; (c) lower linolenic acid concentration. These trends concur with the literature (9,11,12) on the studies of actual bulk storage damage and field-damaged soybeans, and thus support the reliability of the adiabatic reactor.

Based on the data obtained from the apparatus described, a larger reactor is being constructed. This reactor will permit us to collect additional data, e.g., taste-panel evaluations, headspace analyses, enzyme effects, combustion temperatures, microflora composition and content, and to evaluate various oil extraction and refining methods, storage effects on unripe grains and aeration techniques.

ACKNOWLEDGMENTS

Analyses by Allen Heakin, consultation with G.R. List, E.B. Lancaster, R.J. Bothast, L.T. Black and J.E. McGhee concerning their earlier work on a similar reactor and the assistance of our in-house carpentry, instrument, machine and photography shops are gratefully acknowledged.

REFERENCES

1. Krober, O.A., and F.I. Collins, JAOCS 25:296 (1948).
2. Gustafson, E.H., Ibid. 55:751 (1978).
3. Mounts, T.L., G.R. List and A.J. Heakin, Ibid. 56:883 (1979).
4. Hill, L.D., M.R. Paulsen, T.L. Mounts, A.J. Heakin and G.R. List, Special Publication #63, Agricultural Experiment Station, College of Agriculture, University of Illionis, Urbana, IL, 1981.
5. Milner, Max, and W.F. Geddes, Cereal Chem. 23:449 (1946).
6. Seitz, L.M., D.B. Sauer, H.E. Mohr and D.F. Aldis, Ibid. 59:9 (1982).
7. Perez, R.A., J. Tuite and K. Baker, Ibid. 59:205 (1982).
8. Anonymous, Soybean Dig. 31:7 (1971).
9. Evans, C.D., G.R. List, R.E. Beal and L.T. Black, JAOCS 51:444 (1974).
10. List, G.R., C.D. Evans, K. Warner, R.E. Beal, W.F. Kwolek, L.T. Black and K.J. Moulton, Ibid. 54:8 (1977).
11. Robertson, J.A., W.H. Morrison, III and D. Burdick, Ibid. 50: 443 (1973).
12. Handbook of Soy Oil Processing and Utilization, ASA and AOCS, 1980, chapter 17.
13. Sleeter, R.T., JAOCS 58:239 (1981).
14. Chapman, G.W., Jr., and J.A. Robertson, Ibid. 57:339 (1980).
15. Ramstad, Paul E., and W.F. Geddes, University of Minnesota, Agricultural Experiment Station, Minnesota Technical Bulletin #156, June 19, 1942.
16. Christensen, C.M., and C.E. Dorworth, Phytopathology 56:412 (1966).
17. Linear Applications Handbook #2, National Semiconductor Corp., LB 24, 26, 27 and 32 (1976).
18. Silicon Controlled Rectifier Manual, 3rd edn., General Electric Corp., 1964, p. 104.
19. Jung, Walter G., IC Op-Amp. Cookbook, 1st Edition, Howard W. Sams and Co., Inc., 1974, p. 235 .
20. James, Lawrence H., J. Bacteriol. 15:117 (1928).

[Received January 16, 1984]

⁂High Performance Liquid Chromatography of the Tocols in Corn Grain[1]

EVELYN J. WEBER, Agricultural Research Service, U.S. Department of Agriculture, S-320 Turner Hall, Agronomy Department, University of Illinois, Urbana, IL 61801

ABSTRACT

A sensitive and selective method was developed for analyzing the tocol isomers in corn grain by high performance liquid chromatography (HPLC) with fluorescence detection. The relative proportions and the total amounts of the tocol isomers (α-tocopherol, α-tocotrienol, γ-tocopherol and γ-tocotrienol) varied greatly among the 15 corn inbreds that were examined. Although γ-tocopherol has traditionally been considered to be the predominant vitamin E isomer in corn, inbreds with equal or higher levels of α-tocopherol have been discovered. No tocotrienols were found in corn germ oil, only α- and γ-tocopherols. Analysis of the tocopherols of the germ oils of inbreds and their reciprocal crosses indicated that the proportions of the α- and γ-isomers and the total amount of the tocopherols are heritable.

INTRODUCTION

The increased use of vegetable oils has modified the fatty acid composition of American diets. The amount of linoleic acid (18:2) in the diet increased from 20.2 g per capita per day in 1969 to 25.2 in 1979, a 25% gain (1). The daily requirement of vitamin E is markedly influenced by the polyunsaturated fatty acid content of the diet, and the adequacy of vitamin E in American diets is still being debated (2). Animal feed is being supplemented with α-tocopherol (α-T), because vitamin E deficiency can lead to muscle degeneration, central nervous disorders and lack of fertility in animals (3,4). The vitamin E biological activities of β-, γ-, and δ-tocopherols and the tocotrienols in animals are generally less than 15-25% of that of α-T (5). The functions of tocols (tocopherols and tocotrienols) in plants are little known, but one role may be as antioxidants to protect the unsaturated lipids. As an antioxidant, γ-tocopherol (γ-T) may be superior to α-T (6-8). This study was made to determine the variability for total tocol content and the proportions of the tocol isomers that might exist in various cultivars of corn.

Very few studies of the vitamin E isomers in corn grain have been done previously. Quackenbush et al. (9) determined the total tocols in inbreds well-known to corn breeders in 1963. These workers used the colorimetric Emmerie-Engel procedure (10). Karaiwanow et al. (11) also used a colorimetric method to determine the total tocol content of Russian and German hybrids with different endosperm colors. Grams et al. (12) analyzed the distribution of tocols within the germ, endosperm and pericarp fractions of 4 hybrids by thin layer chromatography (TLC). Yoshida and Kajimoto (13) used TLC to follow the tocopherol composition of corn grain during development. Slover (14) analyzed the tocols of one sample of dry, yellow corn by gas chromatography (GC). All of these procedures, colorimetric, TLC and GC, are time-consuming and, during the many required manipulations, the risk of losing the tocols by oxidation is

[1] Presented at the 74th AOCS annual meeting, Chicago, 1983.