Prediction of Crude Sunflower Oil Deterioration After Seed Drying and Storage Processes

M.M. Bax, M.C. Gely, and E.M. Santalla*

Seeds Technology Program (TECSE), Chemical Engineering Department, Facultad de Ingeniería, Universidad Nacional del Centro de la Provincia de Buenos Aires (UNCPBA), Argentina

ABSTRACT: The effects of air-drying temperature and storage time on several characteristics of crude sunflower oil were evaluated in terms of FFA and PV. Long storage affected oil content to a greater extent than air-drying temperature. FFA and PV varied between 0.53 and 1.22% and between 10.7 and 23.3. meq O_2/kg, respectively, when samples of uniform initial moisture content (approximately 28%) were dried at various temperatures between 25 and 90°C to approximately 7% moisture content, stored for 8 mon, and then analyzed. Both oil quality characteristics increased exponentially with air-drying temperature (*T*) and linearly with storage time (*t*). Mathematical functions of the form $A \cdot \exp(B \cdot T) + C \cdot t$ (where *A*, *B*, and *C* are parameters adjusted from experimental data) most closely predicted the experimental loss of quality of sunflower oil in terms of FFA and PV with variations in *T* and *t*. Statistical analysis showed SE of the estimated parameters of 0.08 and 1.19 and coefficients of determination, R^2, of 0.922 and 0.939 for FFA and PV, respectively, which were significant at 95% confidence. High-oleic seeds from a similar experiment were used to validate the proposed equation. The results of applying the mathematical function proposed above showed a reasonable ability to predict the experimental values with SE of 0.037 and 0.808 and R^2 of 0.983 and 0.972 for FFA and PV, respectively, which were significant at 95% confidence. Plots of residuals showed random distribution. The results obtained suggested that the equation proposed could be used as a quality-loss model in sunflower drying simulations.

Paper no. J10720 in *JAOCS 81*, 511–515 (May 2004).

KEY WORDS: Deterioration models, drying, free fatty acids, oil content, peroxide value, storage, sunflower.

Drying and storage constitute two fundamental steps in sunflower production because they influence the quality of both the seed and the oil. Seed losses caused by jostling of the sunflower head or attack by birds or insects can be avoided when harvest is carried out in advance of complete dryness; therefore, artificial drying is required to reach a safe moisture content. This moisture value varies between 8 and 10%, depending on the seed storage period. For long storage (more than a year), this value should be about 8% dry basis (d.b.), whereas for 6-mon storage a maximum value of 10% d.b. is allowable (1).

Both harvest (unloading, cleaning, transport) and postharvest processes (drying, storage) affect grain quality; undoubtedly, artificial drying is the step that causes the most damage (2). Stress cracks or fissures are often created in grains by artificial drying (3). In Argentina, sunflower seeds are conventionally dried at around 90°C (4), followed by cooling with ambient air, in spite of recommendations about the benefits of drying sunflower seeds at lower temperatures (5,6). Sunflower seeds tend to shrink during drying owing to the moisture difference between the hull and the kernel. Seeds with high moisture content are susceptible to quality deterioration at high temperature because of hydrolysis of the oil and phospholipids and an increase in acidity (5). Inadequate storage conditions cause degradation of the grain components, mainly in its oil; decrease the yield; and increase hydrolysis, oxidization, and accumulation of FA (7). The effect of temperature and O_2 concentration during storage of crude sunflower oil extracted by pressing and solvent extraction has been investigated (8). However, there is a lack of information about the combined effect of drying temperature and storage time on oil quality before the industrial process. FFA content reflects the degree of hydrolysis of the TG, and PV represents the amount of oxygen associated with rancidity, or oil oxidation, due to the first products of these transformations, which are peroxides or hydroperoxides. These indexes, together with the *p*-anisidine value, the oxidative stability index, and levels of FA esters and polar compounds, are usually used to evaluate oil quality.

For the design of an optimal grain drying system, it is essential that potential deterioration can be quantified through quality-loss models (2). Simple equations that can predict the behavior of crude sunflower oil would be a useful tool to determine the potential loss of quality during the postharvest processing.

The objective of the present work was to analyze the effects of the air-drying temperature and storage duration on deterioration of oil from sunflower seeds, having a uniform initial moisture content, in terms of the increase of FFA and PV contents when seeds are dried to 8 or 10% moisture (d.b.).

EXPERIMENTAL PROCEDURES

Sunflower seed. Two sunflower seed (*Helianthus annuus* L.) cultivars were used to carried out the experiments: Paraíso 20 (56% oil and 0.35 hull/kernel ratio) was used to generate the experimental data for selecting the prediction model, and a high-oleic type, Trisum 568 (Mycogen-Morgan Co.; 43.6%

*To whom correspondence should be addressed at Facultad de Ingeniería, UNCPBA, Av. Del Valle 5737, B7400JWI Olavarría, Argentina.
E-mail: esantall@fio.unicen.edu.ar

oil and 0.53 hull/kernel ratio), was used for the validation of the model. Seeds from both varieties were obtained from the 1999/2000 harvest and were grown at 37°45′ S and 58°18′ W, Argentina. Seeds were manually cleaned and separated from impurities. For the thin-layer drying experiments, subsamples of 200 g of seeds were conditioned by spraying them with an amount of distilled water calculated to achieve a moisture content of approximately 28% (d.b.). The wet seeds were sealed and stored at 5°C until use.

Drying. A thin-layer dryer was used for carrying out the experiment (9). A fan drove the air through a heating unit toward the drying chamber in which the seeds were spread on a 0.0232 m^2 removable tray. The hot air flowed uniformly across the sample at constant velocities from 0.28 to 0.31 m/s, controlled by a damper and measured on a calibrated orifice plate. The thin-layer drying rate of grains is independent of air velocity above 0.2 m/s (10). Before each experiment, the air was heated to the desired dry bulb temperature through electrical resistance. RH was measured by using an aspirated psychrometer (Type 8550 VW; Papst, St. Georgen, Germany). The air-drying conditions are shown in Table 1. To stabilize the conditions before each test, the equipment was run for 1 h beforehand. Drying runs were carried out in duplicate at 25, 40, 60, 75, and 90 ± 1°C, and the moisture loss was registered with time until the desired moisture content was reached. SD for duplicate drying runs were less than 0.5% for all temperatures (Fig. 1).

Storage. After being dried, approximately 250-g samples were stored in five (one for each drying temperature) laboratory-scale silos of galvanized iron with a perforated base, a conic lid of the same metal, and a diameter/height ratio of 0.55. Seeds were held under environmental conditions for 8 mon from June 2000 to February 2001. Maximum, minimum, and noon temperatures and RH were registered daily during this period, and average values are presented in Figure 2. Mean daily temperature varied between 1.3 and 32.9°C with an average of 15.5°C and an SD of 7.5°C. RH varied between 30 and 99% during the same period, and the average value was 71.8% with an SD of 15.1%.

During the storage period, samples of seeds were periodically removed from the central sector of the silos to determine moisture, oil, FFA content, and PV value. Two simultaneous storage experiments were carried out, one with traditional sunflower seeds and the second one with high-oleic sunflower seeds.

TABLE 1
Conditions for Air-Drying

Dry bulb temperature (°C)	RH of ambient air (%)	RH of drying air (%)	Air velocity (m/s)	Moisture content achieved (% d.b.)[a]
25 ± 1	51.0–60.4	23.5–23.9	0.285	7.5 ± 0.082
40 ± 1	59.1–69.3	9.5–11.0	0.292	7.6 ± 0.287
60 ± 1	53.3–65.9	3.5–4.8	0.300	7.3 ± 0.434
75 ± 1	50.5–65.9	1.9–3.6	0.308	7.4 ± 0.608
90 ± 1	54.8–65.8	1.1–1.6	0.314	7.6 ± 0.263

[a]d.b., dry basis.

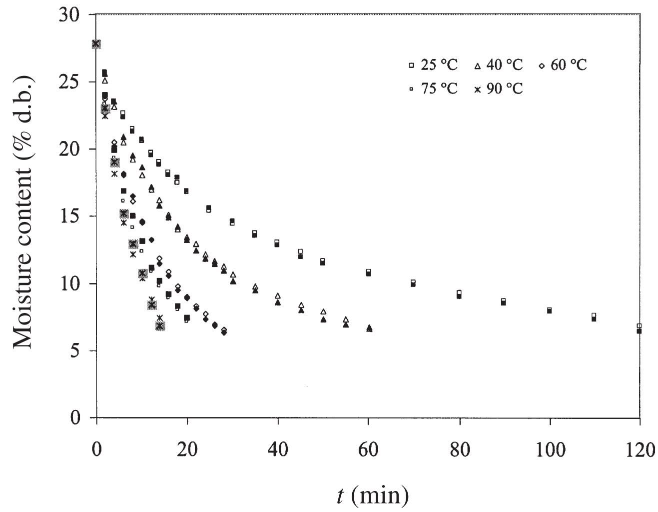

FIG. 1. Thin-layer drying of Paraíso 20 sunflower seeds at air temperatures between 25 and 90°C. Runs are represented by open (sample) and solid (duplicate) symbols, except for 90°C, where asterisks (*) represent the sample and shaded asterisks represent duplicates.

Analyses. Moisture content was determined in a forced-air oven according to American Society of Agricultural Engineers Method S352.1 (11). Oil content was determined by solvent extraction according to AOCS Method Ai 3-75 (12) with the following modifications: *n*-hexane (b.p. 69°C) instead of petroleum ether (b.p. 37–65°C) was used, and the solvent was removed under reduced pressure by means a rotatory evaporator. FFA as the percentage of oleic acid and PV as meq oxygen/kg oil were determined according to AOCS Methods Ca 5a-4D and Cd 8-53 (12), respectively. Triplicate determinations were carried out, and the results we obtained were not significantly different from their respective standards.

ANOVA was used to estimate the effects of air temperature and drying time on FFA and PV. Correlation analysis of the data was performed using Systat Statistical Software (13), and Student's *t*-test was used to determine the significance of

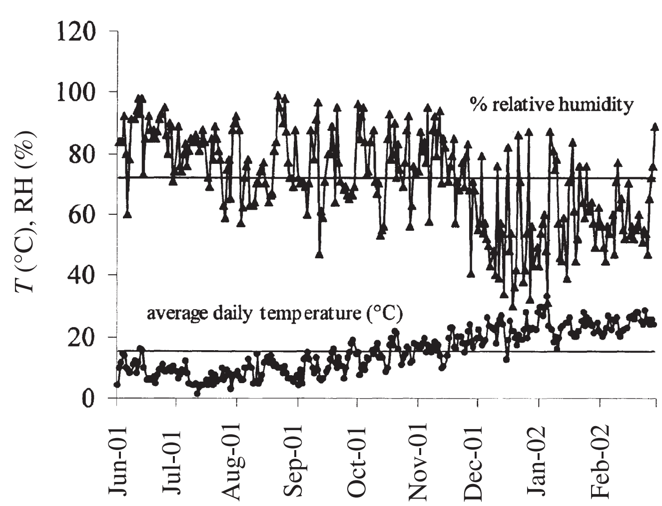

FIG. 2. Ambient air temperature and RH during the storage period.

the coefficient of determination (R^2) at the 95 and 99% confidence levels.

RESULTS AND DISCUSSION

Drying and storage. Air-drying characteristics and moisture content achieved after drying runs are shown in Table 1. The final moisture contents obtained after each drying run varied from 7.3 to 7.6% d.b.

FFA of dried unstored seeds increased from 0.53 to 1.22% owing to the effect of air temperature. An increase in FFA content of 37.6% occurred when seeds dried at 40°C were compared with those dried at 25°C, whereas the FFA of seeds dried at 90°C increased 128.4% compared with those dried at 25°C. According to the ANOVA results the air temperature significantly affected FFA ($F = 162$ for $F_{0.01;4;10} = 5.99$).

PV varied from 10.7 to 23.3 meq/kg oil. An increase of 1.12% was detected when seeds dried at 40°C were compared with seeds dried at 25°C, whereas there was an increase of 118.3% when seeds dried at 90°C were checked against those dried at 25°C. The effect of air temperature on PV increase turned out to be more marked at 40°C and above (Fig. 3). ANOVA results showed that the air temperature also significantly affected this characteristic ($F = 302$ for $F_{0.01;4;10} = 5.99$).

Oil content of dried unstored seeds varied between 56.4 and 54.9% when drying air temperature increased from 25 to 90°C. According to ANOVA results air-drying temperature did not significantly affect oil content at $P < 0.01$ ($F = 0.47$ for $F_{0.01;4;10} = 5.99$).

With respect to the combined effect of the air-drying temperature and storage time, oil content decreased 21.5% during 8 mon of storage (Fig. 4). The effect of air-drying temperature was comparatively lower since a decrease of 2.6% was detected. The results of the ANOVA showed that the effect of the air-drying temperature was not significant ($F = 5.22$) at $P < 0.01$ ($F_{0.01;4;12} = 5.41$) but was significant at $P < 0.05$ ($F_{0.05;4;12} = 3.26$), whereas the effect of storage time was significant at $P < 0.01$ ($F = 217$).

FFA content of sunflower oil varied between 0.53 and 1.51% during the 8 mon storage. This variation represented an increase of 128.3% due to air temperature and an increment of 28.5% at 75°C due to storage time (Fig. 5). ANOVA results showed that both effects were relevant at $P < 0.01$, obtaining $F = 150.5$ and 16.1 for the effect of temperature and storage time ($F_{0.01;4;12} = 5.41$), respectively. In all cases, the degree of deterioration of oil TG by hydrolysis was higher due to the effect of air temperature than to the effect of storage time. FFA did not exceed the limit value of 3%, that is, the acceptable limit for commercialized crops after August 31 in Argentina (7), and it hardly reached 1.5% (maximum drying temperature and extended storage), the value used in Argentina for commercialized crops from the moment of harvest up to the next August 31. In all cases, the oil of the seeds that were dried but not stored showed lower signs of deterioration in terms of FFA and PV than the ones stored under environmental conditions. Values of FFA between 0.67 and 0.90% and 1.07% for crude sunflower oils obtained by pressing and solvent extraction, respectively, have been reported (8). The same authors demonstrated that oil acidity increased with time of storage of the extracted oils.

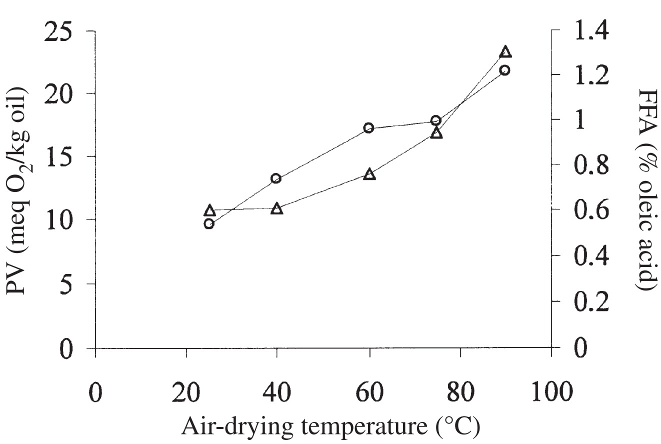

FIG. 3. FFA (○) and PV (△) of sunflower seed oil dried at air temperatures between 25 and 90°C.

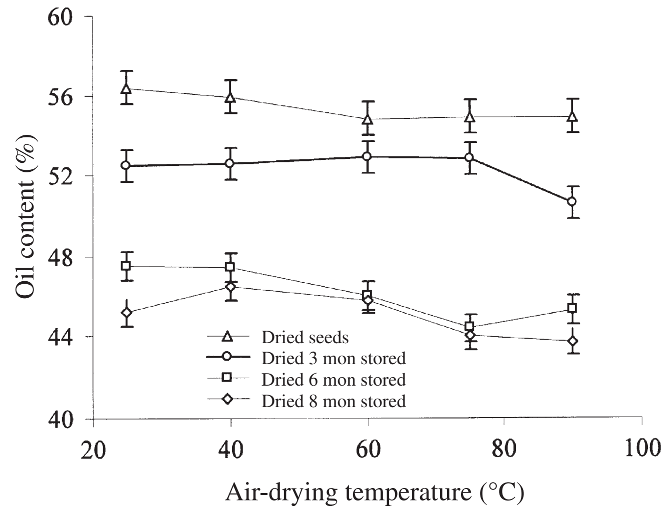

FIG. 4. Variation of oil content during storage time.

Taking into account the results of the effects of air temperature and storage time, a regression analysis was carried out to find a model that could represent the behavior of the FFA content with these two variables. A three-parameter equation of the form $\mathrm{FFA} = A\cdot\exp(B\cdot T) + C\cdot t$ resulted in the best expression to explain the experimental data. The values of A, B, and C, the coefficient of determination, the SE of each parameter, and the mean relative error of the regression model were estimated from the experimental data and are shown in Table 2. Figure 5A shows the experimental data (symbols) and the trend of the proposed equation (lines). The second experiment, to evaluate the goodness of fit, was carried out using high-oleic sunflower seeds (Fig. 5B). Experimental values for FFA content of high-oleic sunflower oil showed a similar trend to a more standard sunflower cultivar. The coefficients of determination of the regression analysis between the experimental data and the values predicted by the proposed equation were

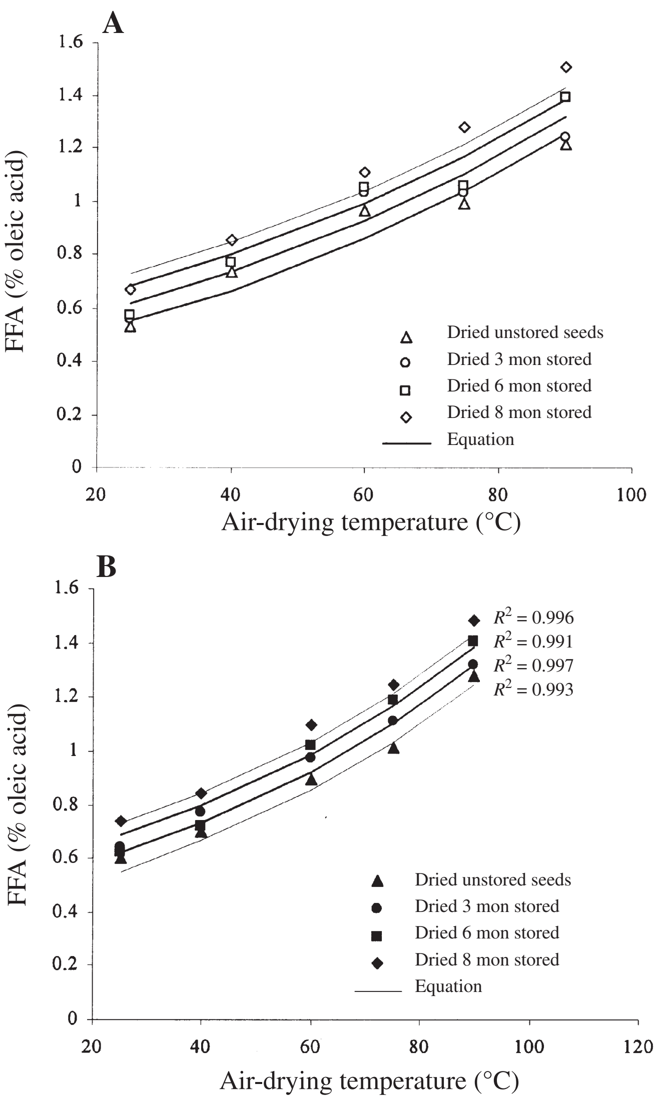

FIG. 5. Variation of FFA with storage time when seeds were dried at temperatures between 25 and 90°C. (A) Studies with Paraíso 20 seed; (B) studies with Trisum 568 (high-oleic type) seed.

0.993, 0.997, 0.991, and 0.996 for unstored seeds at 3-, 6-, and 8-mon storage times, respectively. All these values were significant at the 95% confidence level (Fig. 5B). The maximum relative error between the predicted and experimental data was 9.8%, the SE of the estimated value was 0.037, and the residual plot showed random distribution.

The PV, expressed as meq O_2/kg oil, accepted for commercial oil is 10 meq O_2/kg (14). The values obtained for seeds that had been dried but not stored varied between 10.7 (25°C) and 23.3 meq O_2/kg (90°C). Samples dried at 60°C showed higher signs of deterioration (above 13.6 meq O_2/kg). The increase in PV due to increases in air temperature was 118.3%, whereas the maximum increment due to the storage time was 63.6%, detected at 40°C (Fig. 6A). ANOVA showed significant effects ($P < 0.01$) when temperature ($F = 120.5$) and storage time ($F = 41.4$) effects were both analyzed ($F_{0.01;4;12}$ = 5.41). An increase of PV with air-drying temperature was detected in a previous work (15) when seeds of an oil sunflower hybrid were dried at different air temperatures. PV between 2.45 and 3.92 meq/kg oil and 3.36 meq/kg for different crude sunflower oils obtained by pressing and solvent extraction, respectively, have also been reported (8). The same authors demonstrated that the formation of peroxides increases with oil storage time and with temperature.

TABLE 2
Parameters of the Regression Models for FFA (% oleic acid) and PV (meq O_2/kg oil) with the Air Temperature (°C) and Storage Time (d) for the Range 0–90°C and 0–240 d Storage

	FFA		PV	
Parameter	Value	SE	Value	SE
A	0.402074	0.02489	7.437986	0.39690
B	0.012462	0.00071	0.011727	0.00062
C	0.000739	0.00014	0.022923	0.00209
P^a	0.084		1.19	
$R^{2,b}$	0.922		0.939	

[a]Mean relative error calculated as the squared root of (residual/degree of freedom).
[b]Corrected coefficient of determination of the adjusted model, significant at a level of 95%.

The same method used to evaluate the FFA dependence of crude sunflower oil with air temperature and storage time was developed with respect to the PV. According to the regression analysis, an exponential temperature and linear time dependence were the best fits for the experimental data (Fig. 6A). The statistical analysis (Table 2) indicated that this model could be a preliminary and simple tool to describe the grade of oxidation of sunflower oil during drying and storage processes. The loss of quality of high-oleic sunflower oil after similar treatment was analyzed. Experimental values of the PV of high-oleic sunflower oil showed a trend similar to a more standard sunflower cultivar (Fig. 6B). The coefficients of determination of the regression analysis between the experimental data and the values predicted by the proposed equation were 0.975, 0.963, 0.993, and 0.978 for unstored seeds, and for seeds held for 3-, 6-, and 8-mon, respectively; all were significant at 95% confidence. The maximal relative error between the predicted and experimental data was 13.9%, the SE of the estimated value was 0.808, and the residual plot showed random distribution.

In conclusion, the storage period affected the oil content of sunflower seeds significantly, decreasing up to 21.5% in 8 mon. By comparison, air-drying temperature affected the oil content to a lesser degree. ANOVA results demonstrated that the increase in air-drying temperature significantly increased FFA and PV contents. Simple equations based on exponential temperature and linear time dependences were proposed as a loss-of-quality model that could be used for sunflower drying simulations:

$$\text{FFA (\% oleic)} = 0.402\, e^{(0.012\, T)} + 0.00074\, t \ (R^2 = 0.922) \qquad [1]$$

$$\text{PV (meq } O_2\text{/kg oil)} = 7.44\, e^{(0.011\, T)} + 0.023\, t \ (R^2 = 0.939) \qquad [2]$$

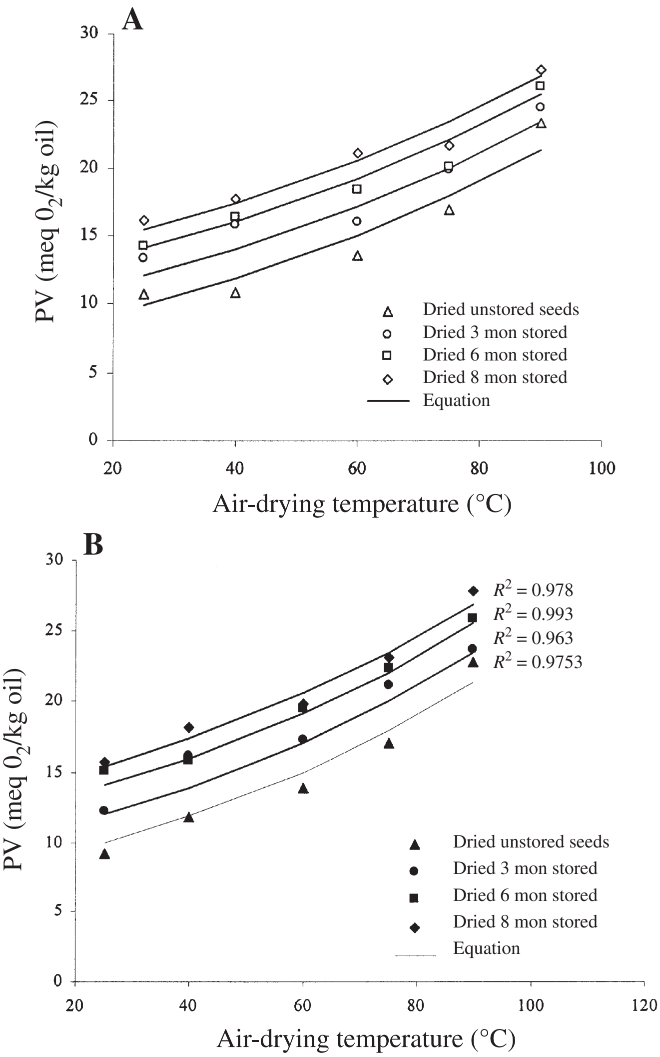

FIG. 6. Variation of PV with storage time when (A) Paraíso seeds were dried at temperatures between 25 and 90°C and (B) high-oleic seeds were dried at similar temperatures.

ACKNOWLEDGMENTS

This work was supported by research grants from TECSE (Seeds Technology) Program from Secretaría de Ciencia y Técnica UNCPBA to M.M. Box for pursuit of her chemical engineering degree.

REFERENCES

1. Robertson, J.A., G.W. Chapman, and R.L. Wilson, Jr., Effect of Moisture Content of Oil Type Sunflower Seed on Fungal Growth and Seed Quality During Storage, *J. Am. Oil Chem. Soc. 61*:768–771 (1984).
2. Brooker, D.B., F.W. Bakker-Arkema, and C.W. Hall, Grain Production, Preservation, and Trade, in *Drying and Storage of Grains and Oilseeds*, Van Nostrand Reinhold, Chapman & Hall, London, 1992, pp. 2–16.
3. Litchfield, J.B., and M.R. Okos, Prediction of Corn Kernel Stress and Breakage Induced by Drying, Tempering and Cooling, *Trans. ASAE 31*:585–594 (1988).
4. Pagano, A.M., I. Riccobene, A. Latreite, S. Nolasco, N. Apro, and S. Resnik, *Diagnóstico del almacenamiento de granos en los partidos de Olavaria y 9 de Julio de la Provincia de Buenos Aires*, Facultad de Ingeniería UNCPBA, Instituto Superior Experimental de Tecnología Alimentaria ISETA, 1990.
5. de Dios C.A., Secado de Diversos Granos, in *Secado de Granos y Secadoras*, edited by Organización de las Naciones Unidas para la Agricultura y la Alimentación, Oficina Regional para América Latina y el Caribe, Chile, 1996, pp. 243–255.
6. Morrison, W.H., III, and J.A. Robertson, Effects of Drying on Sunflower Seed Oil Quality and Germination, *J. Am. Oil Chem. Soc. 55*:272–274 (1978).
7. Aguirrezábal, L.A.N., and F.H. Andrade, Girasol, in *Calidad de productos agrícolas. Bases ecofisiológicas, genéticas y de manejo agronómico*, Instituto Nacional de Tecnología Agropecuaria, Facultad de Ciencias Agrarias, Unidad Integrada Balcarce, Argentina, 1998, pp. 139–192.
8. Crapiste, G.H., I.V. Brevedan, and A. Carelli, Oxidation of Sunflower Oil During Storage, *J. Am. Oil Chem. Soc. 76*:1437–1443 (1999).
9. Gely, M.C., and E.M. Santalla, Effect of Some Physical and Chemical Properties of Oilseeds on Drying Kinetics Parameters, *Drying Technol. 18*:2155–2166 (2000).
10. Hutchinson, D., and L. Otten, Thin-Layer Air Drying of Soybeans and White Beans, *J. Food Technol. 18*:507–522 (1983).
11. *ASAE Standards*, Standards Engineering Practices Data, American Society of Agricultural Engineers, St. Joseph, MI, 1999.
12. *Official Methods and Recommended Practices of the AOCS*, 5th edn., edited by D. Firestone, AOCS Press, Champaign, 1997.
13. Wilkinson, L., 1990, *SYSTAT: The System for Statistics*, SYSTAT, Inc., Evanston, IL, 1990.
14. Madrid Vicente, A., I. Cenzano Del Castillo, and J. Madrid Cenzano, *Manual de Aceites y Grasas Comestibles*, ed. A. Madrid Vicente, Almansas, 94, 28040 Madrid (1997).
15. Santalla, E.M., O.E. Quiroga, and M.C. Gely, Effect of Sunflower Seed Drying on Some Quality Parameters of the Seed and Oil, *Proceedings of the 15th International Sunflower Conference*, 12–15 June, Toulouse, France, 2000, A97–A102 (2000).

[Received August 19, 2003; accepted January 16, 2004]