PS1-4 – 6208

Soybean oil quality from grains stored under different conditions

E.R. de Alencar[1,*], L.R.D'A. Faroni[1], L.A. Peternelli[2], M.T.C. da Silva[3], S.I. Moreira[3]

Abstract

The influence of different storage conditions of soybean grains in the quality of the extracted oil was assessed. The soybean grains were harvested with moisture content around 18% and dried until 11.2, 12.8 and 14.8 % moisture content. The grains were subsequently stored at the following conditions of temperature and relative humidity for 11.2 % m.c.: 20 ºC and 61.7 %; 30 ºC and 67.9 %; 40 ºC and 69.4 %; for 12.8 % m.c.: 20 ºC and 73.7 %, 30 ºC and 76.7 % and 40 ºC and 80.8 %; and for grains with 14.8 % m.c.: 20 ºC and 82.7 %, 30 ºC and 83.9 % and 40 ºC and 85.3 %. Sampling was carried out every 45 days until 180 days of storage and the level of lipids and free fatty acids, besides the index of iodine and peroxide were determined. Despite of no change of iodine index taking place, the other parameters assessed in the extracted oil showed significant change during storage. Nonetheless, only the oil extract from soybean grains stored with initial moisture content of 12.8 % at 40 ºC and with 14.8 % at 30 and 40 ºC surpassed the threshold values established for marketing the oil.

Key words: Soybean, storage conditions, crude oil, quality, rancidity.

Introduction

Soybean shows about 20 % of lipid content and is susceptible to qualitative deterioration with the degradation of these substances when inappropriately stored, which can cause serious losses to the food industry. According to Narayan et al. (1988a), physical, chemical and biochemical changes can occur in soybean grains depending on the conditions and length of storage.

Quality changes in soybean grains during storage contribute to loss of oil quality (Orthoefer, 1978). Storage of soybean with high moisture content compromises the quality of crude, refined, bleached and deodorized oil; traditional analyses such as free fatty acid content, iodice and peroxide value, among others, are used to evaluate the quality of the soybean oil (Frankel et al., 1987; Regitanodarce, et al., 1994). Moreover, degumming of crude oil from grains severely damaged is hindered and the refined oil is darker than that obtained from intact grains, besides occurring larger losses in the refinement (List et al., 1977). Soybean grain quality can also influence qualitative parameters of other byproducts, including pH, total solids and color of hydrosoluble extract, hardness and yield of tofu (Narayan et al., 1988b, Liu, 1997, Hou and Chang, 1998).

Lipid degradation can be caused by oxidation,

[1] Department of Agricultural Engineering, Federal University of Viçosa, Viçosa, MG, Brazil
[2] Department of Computer Science, Federal University of Viçosa, Viçosa, MG, Brazil
[3] Department of Food Technology, Federal University of Viçosa, Viçosa, MG, Brazil
[*] Corresponding author: E-mail - eg40942@vicosa.ufv.br

hydrolysis, polymerization, pyrolysis and absorption of strange flavors and aromas (Araújo, 2004). The oxidative reactions are influenced by several factors such as light, heat, ionization and metal , which are associated with the reaction of oxygen with unsaturated lipids through chemical and enzymatic mechanisms, including self-oxidation, photooxidation and lipoxygenase. According to Athié et al. (1998), during storage, lipids are hydrolyzed by the lipases in free fatty acids (FFAs) and glycerol, mainly in high temperatures and moisture contents. This change is accelerated by fungus growth due to the high lipolytic activity of these microorganisms. As stated by Kirk (1984), lipid oxidation in foods can degrade linoleic and linolenic acids, vitamin A, vitamin C, tocoferols and carotenoids.

In view of this, the objective of the present work was to evaluate the quality of the crude oil extracted from soybean grains stored in different conditions.

Materials and Methods

Soybean (*Glicine max* (L.) Merril) were obtained from the District of Almeida Campos, Ponte Nova County, MG, Brazil. Grains with about 18 % moisture content (w.b.) at harvest were dried in a fixed bed dryer with natural air to moisture contents of 11.2, 12.8 and 14.8 % (w.b.). After drying, the grains were stored in plastic containers of approximately 3.0 L and taken to BOD incubators, at 20, 30 and 40 ºC. To keep the same grain moisture content during storage at different temperatures, the equilibrium relative humidity (ERH), previously calculated by the Chung-Pfost model (Navarro and Noyes, 2001) for each temperature combination and moisture content (Table 1), was controlled inside each BOD. The data acquisition monitoring was performed by a *1-wire*^{TM} system (Martins et al., 2004). Analyses of lipid content, free fatty acids (FFA), peroxide value and iodice value were carried out every 45 days throughout the 180 days of storage period. Determination of lipid content, FFA, peroxide value and iodice value followed the AOCS (1993) norms (Ac 3-44, Ca 5a-40, Cd 8-53 and Cd 1b-87 methods respectively). The experiment was arranged in completely randomized split-plot design with three replicates. The treatments, temperature combinations (20, 30 and 40 ºC) and moisture content (11.2, 12.8 and 14.8 %) were allocated in the main plot, whereas the subplot consisted of the storage periods (0, 45, 90, 135, 180 days), with the treatments arranged into a 3 × 3 × 5 factorial design. Initially, a repeated measures analysis of variance was carried out to determine the best residual covariance structure. Regression analysis was performed for the variables lipid content, FFA and peroxide value.

Table 1. Equilibrium relative humidity (ERH) for each combination of moisture content and temperature.

	Moisture content (%) b.u.		
Temp. (ºC)	11.2	12.8	14.8
20	61.0	72.0	80.0
30	67.0	76.0	83.0
40	71.0	80.0	86.0

Results and Discussion

Lipid content

The analysis of variance ($p < 0.05$) indicated that there was significant variation of lipid content in soybean grains due to the interaction moisture content-temperature-storage period.

The effect of the storage period on the lipid content (expressed on a dry weight basis) of soybean at the three moisture contents and three temperatures is shown in Figure 1. In general, grain lipid content did not change over the storage period, except for grains stored with 14.8 % moisture content at the temperatures 30 and 40 ºC (Figure 1B-C).

Table 2 shows the adjusted regression equations

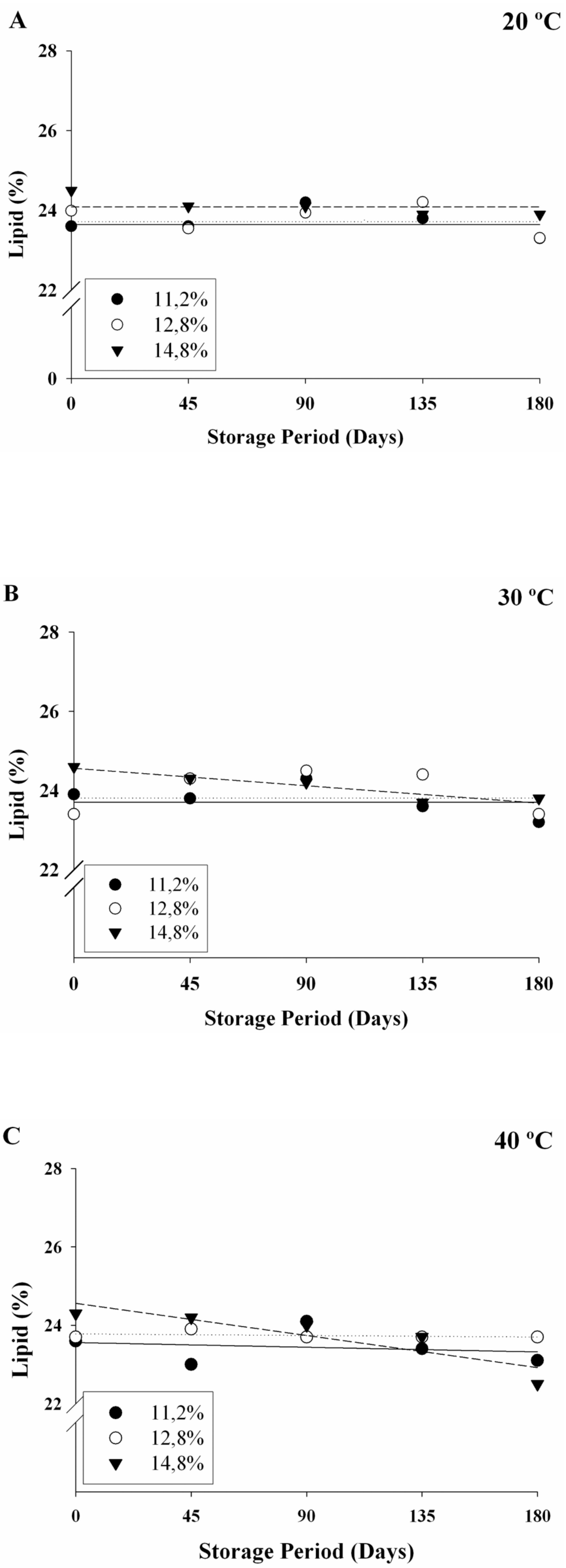

Figure 1. Lipid content of soybean (expressed on a dry weight basis) as function of time of storage for each combination of temperature and moisture content.

and their respective determination coefficients that relate the soybean grain lipid content with storage period. The decrease in lipid content was significant only when the grains were stored with 14.8 % moisture content at the temperatures 30 and 40 ºC.

Hou and Chang (2004), studying the chemical composition of soybean stored in different conditions, found that lipid content increased when the grains were stored at 30 ºC and 84 % relative humidity. However, the authors could not explain this increase. On the other hand, Rupullo et al. (2004) affirmed that lipid degradation during the storage occurs due to biochemical processes, such as respiration or oxidation. The authors found significant decrease in lipid content mainly in oat grains in the first three months of storage. Similar results were reported by Molteberg (1995), when they found decrease in lipid content of oat stored in different conditions. Zhou et al. (2002) showed the influence of temperature and storage period on lipid content of rice grains. While there was a significant decrease in lipid content of grains stored at 35 ºC, there was no decrease in grains at 5 ºC after 12 months of storage.

Free fatty acids

The analysis of variance indicated that there was significant difference in the percentage of free fatty acids (FFA) in the oil extracted from soybean for the interaction moisture content-temperature-storage period.

Figure 2 shows the regression curves for free fatty acid percentage in crude oil of grains stored with moisture contents of 11.2, 12.8 and 14.8 % at the temperatures 20, 30 and 40 ºC. At 20 ºC (Figure 2A) only the oil extracted from soybean grains stored with 14.8% moisture content showed significant increase in free fatty acid percentage over the storage period. Nevertheless, at 30 and 40 ºC (Figure 2B and C), regardless the grain moisture content, there was increase in the free fatty acid percentage of the extracted oil, more remarkably from grains with 14.8 % moisture content. Table 3 shows the adjusted regression equations and their respective determination coefficients, which relate FFA of oil extracted from soybean grains with three moisture contents for each storage temperature.

Table 2. Adjusted regression equations for lipid content from soybean as function of time of storage for each combination of temperature and moisture content and respective determination coefficients.

Temp. (ºC)	Moisture content (%)	Equation	r^2	F	Prob.
	11.2	$\hat{y} = 23.6$		0.23	0.6364
20	12.8	$\hat{y} = 23.7$		3.36	0.0897
	14.8	$\hat{y} = 24.0$		4.39	0.0562
	11.2	$\hat{y} = 23.7$		2.26	0.1571
30	12.8	$\hat{y} = 23.8$		0.27	0.6105
	14.8	$\hat{y} = 24.6 - 0.0049X$	0.56	16.27	0.0014
	11.2	$\hat{y} = 23.6$		1.09	0.3161
40	12.8	$\hat{y} = 23.7$		0.14	0.7117
	14.8	$\hat{y} = 24.6 - 0.0091X$	0.76	40.64	<0.0001

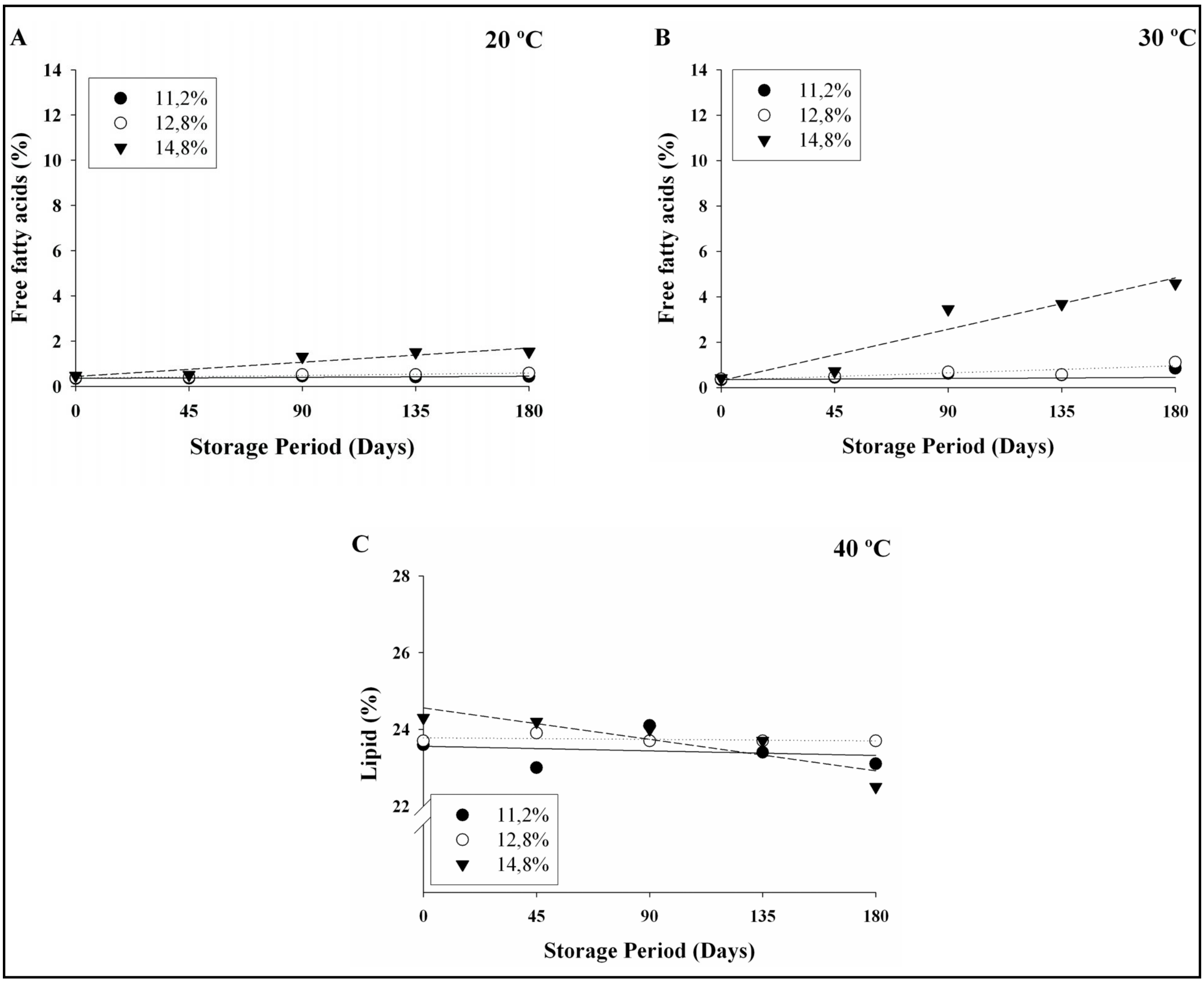

Figure 2. Fat free acids (expressed as % oleic acid) in crude oils from soybeans as function of time of storage for each combination of temperature and moisture content.

Table 3. Adjusted regression equations for fat free acids in crude oils from soybeans as function of time of storage for each combination of temperature and moisture content and respective determination coefficients.

Temp. (°C)	Moisture content (%)	Adjusted regression	r^2	F	Prob.
	11.2	$\hat{y} = 0.41$		7.11	0.0194
20	12.8	$\hat{y} = 0.370 + 0.0012X$	0.85	76.02	<0.0001
	14.8	$\hat{y} = 0.438 + 0.0069X$	0.80	51.17	<0.0001
	11.2	$\hat{y} = 0.352 + 0.025X$	0.82	51.12	<0.0001
30	12.8	$\hat{y} = 0.332 + 0.035X$	0.72	33.69	<0.0001
	14.8	$\hat{y} = 0.307 + 0.0251X$	0.86	77.93	<0.0001
	11.2	$\hat{y} = 0.277 + 0.0066X$	0.96	314.00	<0.0001
40	12.8	$\hat{y} = 0.440 + 0.0121X$	0.87	83.43	<0.0001
	14.8	$\hat{y} = -0.294 + 0.0692X$	0.84	72.04	<0.0001

The maximum limit of FFA established by the Brazilian legislation for crude soybean oil commercialization is 2 %. In this context, it was found that oil extracted from grains stored with 14.8 % moisture content at the temperatures 30 and 40 ºC and from grains stored with 12.8 % at 40 ºC presented percentage of FFA above the established limit after 90 and 135 days of storage respectively.

According to O'Brien (2004), the hydrolytic rancidity results in release of FFA from glycerol, which can affect flavor, aroma and other oil characteristics. The author reports that vegetable oils can show relatively high levels of free fatty acids when the grains was field damaged or inappropriately stored, and high values of FFA can cause significant losses during refinement. Wilson et al. (1995) reported that losses in refinement between 1 and 1.5 % are considered normal; however, such losses can reach up to 4% or more with higher values of FFA.

Several authors relate the increase of free fatty acid percentage to storage conditions. Yanagi et al. (1985) confirmed the influence of storage time, when soybean was stored at 30 ºC and 80 % relative humidity, on the free fatty acid percentage of crude oil. The variation in percentage of FFA in crude oil extracted from soybean grains stored with different moisture contents was studied by Frankel et al. (1987). Grains stored with 13 % m.c. had smaller increase in free fatty acid percentage than grains stored with 16 and 20 % m.c.. In the crude oil extracted from grains stored with 13 % m.c., the free fatty acid percentage raised from 0.2 to 1.25 % after 49 days of storage, whereas for the crude oil obtained from grains stored with 16 and 20 % m.c. the rise was from 0.5 to 2.0 %, after 27 days, and from 0.6 to 2.3 %, after 28 days of storage. Narayan et al. (1988a) verified increase in free fatty acid percentage in soybean stored at different temperatures (between 16 and 40 ºC) and relative humidity (between 50 and 90 %), obtaining mean values of 0.69, 4.31, 5.37 and 9.85 % after 12, 24, 36 and 108 months of storage. The free fatty acid percentage from crude oil extracted from stored soybean increased significantly, according to Dhingra et al. (1998), due to the interaction of grain moisture content and storage period. These authors also discuss that the increase in free fatty acid percentage represents economic losses during oil processing.

The increase in FFA is the action of the enzymes lipases, peroxidases and phospholipases present in the grains or produced by the associated microflora that contributes to the break down of triglyceride ester bonds (Zadernowski et al., 1999).

Peroxide value

The analysis of variance ($p < 0.05$) indicated that there was significant difference in the peroxide value of oil extracted from soybean grains for the interaction moisture content, temperature and storage period.

Figure 3 shows the regression curves for peroxide value of the crude extracted oil from soybean grains stored with 11.2, 12.8 and 14.8 % m.c. at three temperature levels (20, 30 and 40 ºC).

There was rise in peroxide value in all temperatures, although less significantly for grains with 11.2 and 12.8 % m.c., at 20 and 30 ºC (Figure 3A-B). At 40 ºC (Figure 3C), the increase in the peroxide value of crude oil extracted from soybean grains was more significant regardless of the grain moisture content. Similar results were obtained by Narayan et al. (1988a) studying the increase of peroxide value for crude oil extracted from grains stored at different temperatures and relative humidity. They found mean peroxide values of 18, 40, 65 and 98 meq kg^{-1}, after 12, 24, 36 and 108 months of storage respectively.

Table 4 shows the adjusted regression equations and their respective determination coefficients

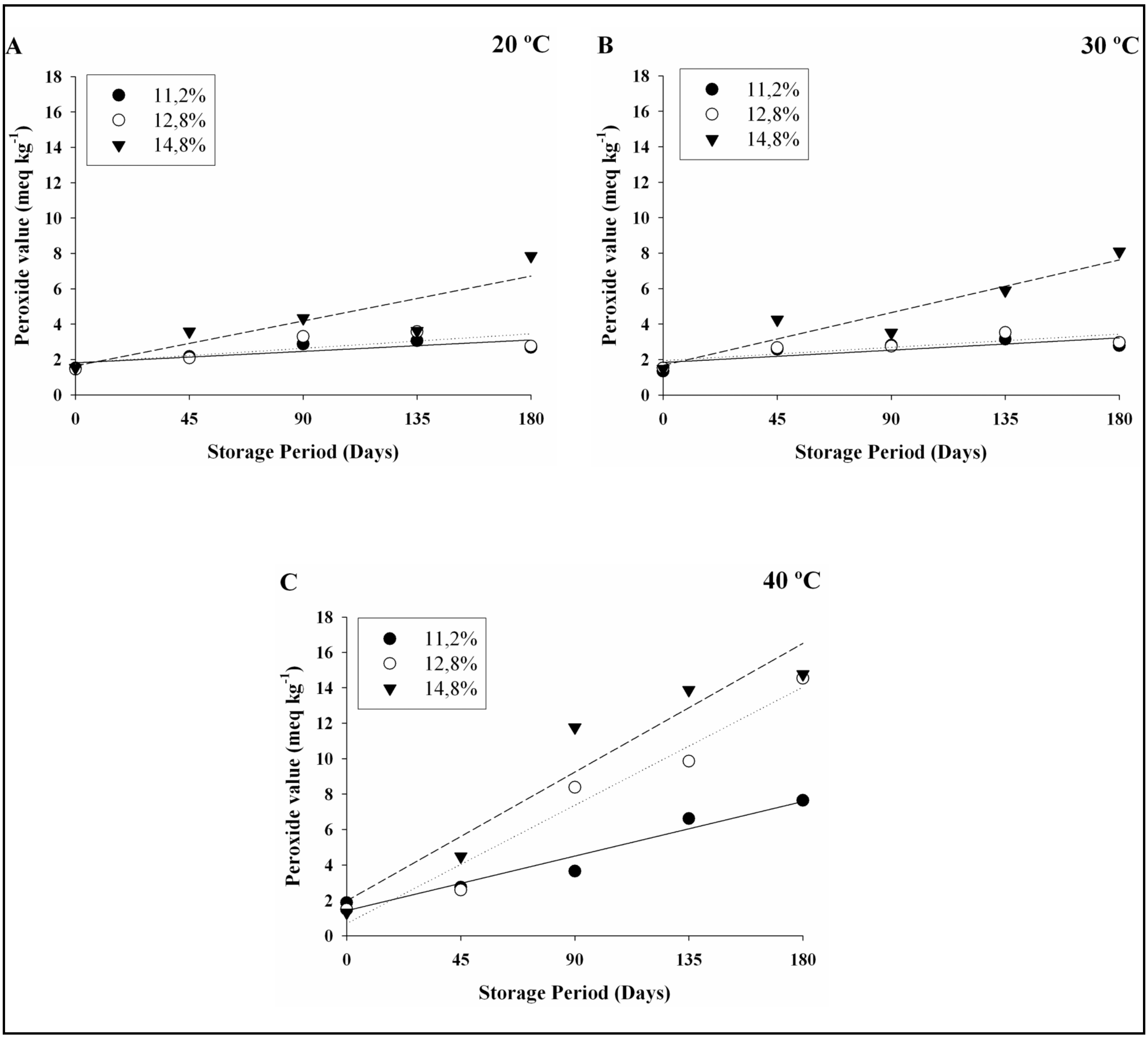

Figure 3. Peroxide value in crude oil from soybeans as function of time of storage for each combination of temperature and moisture content.

relating peroxide value of oil extracted from soybean grains at three moisture contents with each storage temperature.

Lipid oxidation is a major cause of oil and fat degradation, and hydroperoxides are the primary products from the reaction of oxygen and unsaturated fatty acids. Although these compounds neither present flavor nor aroma, they are quickly decomposed, even at room temperature, into aldehydes, ketones, alcohols, hydrocarbons, esters, furanes and lactones, causing unpleasant flavor and aroma in oils and fats (Eys, 2004, O'Brien, 2004).

According to O'Brien (2004), the peroxide value is one of the most used analyses to characterize oils and fat; products that show peroxide values between 1 and 5 meq kg^{-1} are classified as low oxidation state; values between 5 and 10 meq kg^{-1} are characterized as average oxidation state, and those presenting values between 10 and 20 meq kg^{-1} are classified as high oxidation state. When comparing the peroxide values obtained in crude oil (Table 5) with the values suggested by O'Brien (2004), it was verified that the oil obtained from the grains stored with 11.2 and 12.8 at 20 and 30 ºC can be characterized as low oxidation state. On the other hand, the oil extracted from grains stored with 12.8 and 14.8 % m.c. at 40 ºC was in high oxidation state at 180 and 90 days, respectively. It is worth emphasizing that the maximum limit for peroxide value established by the Brazilian legislation for commercialization of soybean crude oil is 10 meq kg^{-1}.

Iodice value

The analysis of variance ($p < 0.05$) indicated that there was no significant variation in the iodice value for the triple interaction among moisture content, temperature and storage period. Significant variation was found only for the storage period. Dhingra et al. (1998), studying the quality of the oil obtained from soybean grains stored with different moisture contents at 25 ºC and infected with *Aspergillus ruber*, also found no significant variation in the iodice value for the crude oil.

The results led to the following conclusions:

- Storage of soybean grains with moisture content up to 14.8 % (w.b.), at 20 ºC, does not affect the quality of the crude oil.
- Crude oil obtained from soybean grains stored with moisture content up to 12.8 % (w.b.), at 30 ºC, maintains satisfactory quality up to 180 days.
- It is not possible to obtain crude oil, within the quality standards demanded for commercialization, from soybean grains stored with moisture content above 11 % (w.b.) at the temperature of 40 ºC.

Table 4. Adjusted regression equations for peroxide value in crude oils from soybeans as function of time of storage for each combination of temperature and moisture content and respective determination coefficients.

Temp. (ºC)	Moisture content (%)	Adjusted regression	r^2	F	Prob.
	11.2	$\hat{y} = 1.812 + 0.0072X$	0.42	9.51	0.0087
20	12.8	$\hat{y} = 1.810 + 0.0091X$	0.45	10.61	0.0062
	14.8	$\hat{y} = 1.640 + 0.0282X$	0.74	37.88	<0.0001
	11.2	$\hat{y} = 1.835+ 0.0077X$	0.56	6.37	0.0014
30	12.8	$\hat{y} = 1.939+ 0.0083X$	0.47	11.46	0.0049
	14.8	$\hat{y} = 1.672+ 0.0330X$	0.75	40.08	<0.0001
	11.2	$\hat{y} = 1.417+ 0.0342X$	0.78	45.77	<0.0001
40	12.8	$\hat{y} = 0.686+ 0.0742X$	0.94	193.98	<0.0001
	14.8	$\hat{y} = 1.968+ 0.0808X$	0.90	115.06	<0.0001

Table 5. Peroxide value in crude oils from soybeans stored for 180 days for each combination of temperature and moisture content.

Temp. (ºC)	Moisture content (%)	Storage Period (Days) 0	45	90	135	180
	11.2	1.51	2.17	2.87	2.81	2.68
20	12.8	1.45	2.09	3.29	3.57	2.76
	14.8	1.52	3.58	4.33	3.62	7.84
	11.2	1.34	2.57	2.80	3.14	2.79
30	12.8	1.52	2.66	2.75	3.52	2.96
	14.8	1.48	4.25	3.51	5.89	8.09
	11.2	1.87	2.73	3.64	6.60	7.64
40	12.8	1.48	2.58	8.37	9.85	14.54
	14.8	1.30	4.47	11.77	13.88	14.76

References

AOCS, 1993. Official methods and recommended practices. Champaign: AOCS.

Araújo, J.M.A., 2004. Química de Alimentos: Teoria e Prática. Viçosa: Editora UFV.

Athié, I., Castro, M.F.P.M., Gomes, R.A.R., Valentini, S.R.T., 1998. Conservação de grãos. Campinas: Fundação Cargill.

Dhingra, O.D., Jham, G., Napoleão, I.T., 1998. Ergosterol accumulation and oil quality changes in stored soybean invaded by *Aspergillus ruber* (*A. glaucus* group). Mycopathologia 143, 85–91.

Eys, J.E., A.Offner, Bach, A., 2004. Manual of quality analyses for soybean products in the feed industry. Fourqueux .

Frankel, E.N., Nash, A.M., Snyder, J.M., 1987. A methodology study to evaluate quality of soybeans stored at different moisture levels. Journal of the American Oil Chemists' Society 64, 987-992.

Hou, H.J., Chang, K.C., 1998. Yield and quality of soft tofu as affected by soybean physical damage and storage. Journal of Agricultural and Food Chemistry 46, 4798-4805.

Kirk, J.R., 1984. Biological availability of nutrients in processed foods. Journal of Chemical Education 61, 364-367.

List, G.R., Evans, C.D., Warner, K., Beal, R.E., Kwolek, W.F., Black, L.T., Moulton, K.J., 1977. Quality of oil from damaged soybeans. Journal of the American Oil Chemists' Society 54, 8-14.

Liu, K., 1997. Soybeans: chemistry, technology and utilization. New York: Chapman & Hall.

Molteberg, G.L., Vogt, G., Nilsson, A., Frolich, W., 1995. Effects of storage and heat processing on the content and composition of free fatty acids in oats. Cereal Chemistry 72, 88-93.

Martins, J. H.; Monteiro, P. M. B.; Mota, A. M. N.; Fonseca, J. A. G., 2004. The *1-wire™* system – an application for agricultural processes. In: Portuguese Conference on Automatic Control. Proceedings of 6th Portuguese Conference on Automatic Control, Faro, Portugal, pp. 602-607.

Narayan, R., Chauhan, G..S., Verma, N.S., 1988a. Changes in the quality of soybean during storage. Part 1 – Effect of storage on some physico-chemical properties of soybean. Food Chemistry 27, 12-23.

Narayan, R., Chauhan, G.S., Verma, N.S., 1988b. Changes in the quality of soybean during storage. Part 2 – Effect of soybean storage on the sensory qualities of the products made therefrom. Food Chemistry 30, 181-190.

Navarro, S., Noyes, S.T., 2001. The Mechanics and Physics of Modern Grain Aeration Management. Boca Raton: CRC Press.

O'Brien, R.D., 2004. Fats and Oils Formulating and Processing for Applications. Boca Raton: CRC Press.

Orthoefer, F.T., 1978. Processing and utilization. In: Norman, A.G. (Ed.), Soybean: physiology, agronomy and utilization. New York, pp. 219-246.

Regitanodarce, M.A.B., Rauenmiguel, A.M.O., Casagrande, J.R.R., Marcos, E.A., Plonis, G., 1994. Time of harvesting and storage of soybeans - influence on oil quality. Grasas Y Aceites 45, 237-240.

Rupollo, G., Gutkoski, L.C., Marini, L.J., Elias, M.C., 2004. Hermetic and conventional storage systems in oat grains conservation. Ciência Rural 34, 1715-1722.

Wilson, R.F., Novitzky, W.P., Fenner, G.P., 1995. Effect of fungal damage on seed composition and quality of soybeans. Journal of the American Oil Chemists' Society 72, 1425-1429.

Yanagi, S.O., Galeazzi, M.A.M., Saio, K., 1985. Properties of soybean in model storage studies. Agricultural and Biological Chemistry 49, 525-528.

Zadernowski, R., Nowak-Polakowska, H., Rashed, A.A., 1999. The influence of heat treatament on the activity of lipo and hydrophilic components of oat grain. Journal of Food Processing and Preservation 33, 177-191.

Zhou, Z., Robards, K., Helliwell, S., Blanchard, C., 2002. Ageing of Stored Rice: Changes in Chemical and Physical Attributes. Journal of Cereal Science 35, 65-78.