# Industrial Trial to Evaluate the Effect of Oxygen Concentration on Overall Quality of Refined, Bleached, and Deodorized Soybean Oil in PET Bottles

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**ABSTRACT**: Soybean oil, owing to its FA composition, is highly susceptible to deterioration by oxidation. The use of nitrogen gas permits the removal of dissolved oxygen and oxygen in the headspace of tanks and bottles. The objective of this work (an industrial trial) was to evaluate the shelf life of soybean oil packaged in polyethylene terephthalate (PET) bottles with different levels of oxygen in the headspace (<0.3, 5–6.5, 7–9, and >15%). The quality of the oil was evaluated during 6 mon. FFA and moisture increased and the smoke point decreased in all experimental conditions, even though the difference between the experiments was not significant. An increase was observed for peroxide value (PV), anisidine value (AV), and specific extinction, and higher increases in these parameters were observed in higher oxygen concentrations. After 180 d, the difference between the PV and AV was significant. According to sensory analysis, the shelf life of the oil increased from 60 to 90, 120, and 180 d as the initial concentration of oxygen was reduced from >15%, 7–9%, 5–6.5%, and 0–3%, respectively. The results demonstrated that shelf life of soybean oil packaged in PET bottles can be significantly increased by using nitrogen to reduce available oxygen in the headspace.

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**KEY WORDS:** Oxidation, oxygen in headspace, PET, soybean oil, stability.

Because of its quality and low cost, soybean oil is the most important vegetable oil produced worldwide. Brazil produced more than 4.4 million tons and consumed approximately 2.4 million tons in 2005, the latter tonnage representing 95% of the total vegetable oils consumed (1). Because of its high content of PUFA, soybean oil is susceptible to oxidative rancidity, which can be caused by the reaction of atmospheric oxygen and/or the oxygen in the headspace of the plastic containers and/or the oxygen dissolved in the product with the unsaturated portion of the FA present in the oils and fats. The reaction is favored by high temperatures, the incidence of light, and the presence of pro-oxidant metals (2).

Soybean oil processing includes several stages, such as refining and packaging, that are designed to provide high-quality refined oil to the consumer. The package has a fundamental role in the control of interactions between the oil and the environment, protecting against oxidation and preserving product quality until the end of its useful life. Plastic, mainly PET (polyethylene terephthalate), has been dominating the Brazilian market in the last two decades. Although PET forms a good barrier to oxygen, its permeability to water vapor is relatively high, and the product contained therein is more exposed to light, which can affect the oxidative stability of oil (3). Because the oxygen concentration in the package affects the speed of the oxidation reaction, industries use nitrogen to fill the internal space of the tanks during storage and the plastic bottles during filling to reduce the amount of oxygen in contact with the oil, delaying oxidation reactions and increasing the shelf life of the oil.

The importance of investigating the oxidative stability of oil lies in the complexity of the oxidation reactions; besides, many oxidation products (particularly of low M.W.) can have odors that consumers can perceive even at low levels. A small fraction of oil oxidation can result in development of undesirable odors, leading to rejection of the product, considering that odor and flavor are the most important characteristics of quality in edible oils (4). Therefore, in this industrial trial research work, the effect of different levels of oxygen in the headspace of PET bottles and their relation to soybean oil quality and shelf life were evaluated for a period of 6 mon.

## MATERIALS AND METHODS

*Soybean oil*. Four lots of 45 tons each of refined, bleached, and deodorized (RBD) soybean oil, with 30 ppm of TBHQ and 45 ppm of citric acid, were produced and packaged in PET bottles at ADM (Archer Daniels Midland) in Campo Grande, MS, Brazil. Lot numbers 1, 2, 3, and 4 were produced according to the conditions described in Table 1, with headspace oxygen concentrations of <3, 5–6.5, 7–9, and >15%, respectively.

*Packaging material.* The RBD soybean oil was packaged in PET bottles with plastic caps made of HDPE (high-density polyethylene), but without internal seals, and packaged in cardboard boxes with 20 units in each, as done for the Brazilian market. The boxes were stacked seven high and kept at room temperature. The temperature and relative humidity of the air were measured daily during the entire period of the experiment (mean ± SD: T = 30.7 ± 2.3°C; RH = 71.2 ± 3.0%).

*Experimental procedures. (i) Oil characterization and quality evaluation*. Procedures for RBD soybean oil characterization

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**TABLE 1**
**Filling Conditions for RBD Soybean Oil in PET Bottles for Different Oxygen Headspace Concentration**.

| Experimental lots | Filling speed (bottles/min) | Pressure of nitrogen ($kg/cm^2$) | Flow of nitrogen in the stripping ($m^3/h$) | Flow of nitrogen in the blow system ($m^3/h$) | Headspace oxygen concentration (%) |
|---|---|---|---|---|---|
| 1 | 190 | 5.2 | 0.5 | 10 | <3 |
| 2 | 190 | 5.2 | 0.4 | 7 | 5–6.5 |
| 3 | 220 | 4.2 | 0.3 | 7 | 7–9 |
| 4 | 220 | —[a] | —[a] | —[a] | >15 |

[a]Without nitrogen added. RBD, refined, bleached, deodorized; PET, polyethylene terephthalate.

were performed according to the American Oil Chemists' Society official methodology (5) by the following analyses: FFA (Ca 5a-40), moisture and volatile matter (Ca 2c-25), peroxide value (PV) (Cd 8-53), saponification value (Cd 3-25), iodine value (Cd 1-25), color (Cc 13b-45), specific extinction at 232 nm (Ch 5-91), smoke point (Cc 9a-48), anisidine value (AV) (Cd 18-90), unsaponifiable matter (Ca 6a-40), chlorophyll (13d–55), refractive index (Cc 7-25), oxidative stability index (Cd 12b-92), FA composition (Ce 1-91), and metals determination (Ca 20-99). RBD soybean oil quality was evaluated for a period of 6 mon, on days 0, 30, 60, 90, 120, and 180 after packaging by the determination of FFA, moisture, smoke point, color, PV, AV, specific extinction at 232 nm, and sensorial analysis (Cg 2-83).

*(ii) Oxygen concentration in the headspace and dissolved oxygen in the oil.* The amount of oxygen in the headspace of the packages was determined according to Alves *et al*. (6) as the percentage of the gas volume, using a Pac Check 450; (MOCON< Minneapolis, MN) oxygen analyzer. An aliquot of 5 mL of the free headspace gas was collected from each bottle with a gas-tight syringe, through a septum pasted in the package, and immediately injected into the analyzer. The content of oxygen dissolved in the oil was determined using an Orbisphere (Geneva, Switzerland) analyzer, model 3600, with a device for penetrating the package, model 29971,29972 and 2952A membrane.

*(iii) Sensorial analysis.* The sensory analysis was carried out according to recommended AOCS practice Cg 2–83 (5). The Descriptive Quantitative Analysis method was used, in which samples were presented to the 10 members of the trained panel, sitting in individual booths. The trained analysts identified the attribute and the respective intensity.

*(iv) Statistical analysis*: The statistical analyses were done according to the Statistica program (Statistica, 1995; Statsoft, Tulsa, OK). For each experimental condition, a linear regression analysis was performed. To compare the behavior of the parameters during the storage period, the following analyses were used: ANOVA, Tukey test of multiple comparisons, linear correlation analyses, and Pearson's. These statistical tools were used to verify the significance among all the variables and the time period studied.

## RESULTS AND DISCUSSION

*Characteristics of RBD soybean oil.* The results related to the identity, quality characteristics, and composition of the RBD soybean oil used in this study are presented in the Table 2. The results obtained indicate an adequate refining process, according to Brazilian legislation (7,8). Soybean oil FA composition was 83.7% unsaturated and 15.6% saturated FA, indicating a high susceptibility to oxidation.

*Oxygen concentration in headspace and dissolved in oil during storage.* Oxygen concentrations in the headspace and dissolved in the oil during the storage period of 180 d are presented in Table 3.

Decreasing the quantities of nitrogen (0.5, 0.4, 0.3, and 0.0 $m^3/h$; experimental tests 1, 2, 3, and 4, respectively) used in the stripping process resulted in significantly higher oxygen removal from the headspace, achieving increasing contents of residual oxygen (2.7, 5.7, 7.9, and 16.7%).

The use of 0.5 $m^3/h$ of nitrogen in the stripping process plus 10 $m^3/h$ of nitrogen in the blowing process, just before filling (Experimental test 1 with <3% of oxygen in the headspace) reduced the oxygen concentration 87.2% compared with the atmospheric oxygen concentration (21%) and reduced the residual oxygen concentration in the headspace 65.7% compared with the packaging condition, which used 0.3 $m^3/h$ of nitrogen in the stripping process and 7 $m^3/h$ of nitrogen in the blowing process, just before filling (Experimental test 3 with 7–9% of oxygen in the headspace).

After 30 d, a decrease in oxygen concentration in the headspace was observed in all experiments. This reduction corresponds to 70, 60, 60, and 66% of the initial oxygen content in the headspace for treatments 1, 2, 3, and 4, respectively. There was no significant difference after 30 d of storage when comparing Experimental tests 1 and 2 (0–3 and 5–6.5% oxygen content, respectively).

After 60 d of storage, there was an increase in oxygen concentration in the headspace that may have been a consequence of the entrance of oxygen through the package walls and the capping system. The content of oxygen in the headspace for the first three packaging conditions (0–3, 5–6.5, and 7–9%) presented no significant difference.

In the final storage period, the oxygen content in the headspace under all packaging conditions was less than 3.1%. Thus, oxygen disappearance/reduction was greater when the initial concentration of oxygen in the headspace was higher. The packaged samples with oxygen contents above 15% in the headspace collapsed after 180 d of storage, probably because of very low oxygen concentrations in the headspace at the end of the shelf life period, indicating that, during the storage period, a great amount of oxygen had been consumed in the oxidation reaction.

**TABLE 2**
**Physical and Chemical Characteristics, Metals Content, and FA Profile of the RBD Soybean Oil Packed in PET Bottles**

| Parameter/ unit | Value | Brazil (8) | Brazil (7) |
|---|---|---|---|
| FFA/ % (w/w) | 0.01 | 0.03 | 0.3 |
| Moisture/ % (w/w) | 0.01 | 0.03 | — |
| Peroxide value/ mequiv $O_2$/ kg of oil | 0.00 | 2.5 | — |
| Saponification value/ mg KOH/g | 190 | 189–198 | 189-195 |
| Iodine value (Wijs) | 133.0 | 120–143 | 120-143 |
| Lovibond color (cell 5 ¼″)/ Y/R[a] | 9.0/1.0 | 15/1.5 | — |
| Specific extinction 232nm | 1.80 | — | — |
| Smoke point / ºC | 230 | 230 | — |
| Anisidine value | 1.05 | — | — |
| Unsaponifiable matter/ % (w/w) | 0.78 | 1.5 | 1.5 |
| Chlorophyll concentration/ µg/kg | 10 | — | — |
| Refraction index (30ºC) | 1.4728 | 1.470–1.476 | 1.466–1.470 |
| Insoluble in petroleum ether/ % (w/w) | 0.016 | 0.03 | 0.05 |
| Oxidative stability index (OSI)/ h | 7.6 | — | — |
| Metals (mg/kg) | | | |
| Calcium | 0.3650 | — | — |
| Sodium | <0.1860 | — | — |
| Magnesium | 0.1379 | — | — |
| Copper | <0.0072 | — | — |
| Nickel | <0.0511 | — | — |
| Iron | 0.5080 | — | — |
| Phosphorus | 1.6420 | — | — |
| FA composition (%) | | | |
| Palmitic (C16:0) | 11.24 | 7–14 | — |
| Stearic (C18:0) | 3.47 | 1.4–5.5 | — |
| Oleic (C18:1) | 25.16 | 19–30 | — |
| Linoleic (C18:2) | 55.63 | 44–62 | — |
| Linolenic (C18:3) | 2.87 | 4–11 | — |
| Arachidonic (C20:0) | 0.89 | <1.0 | — |
| Others | 0.74 | — | — |

[a]Y= Yellow; R= Red. For other abbreviations see Table 1

In the initial 30 d of storage, the level of oxygen dissolved in the oil increased rapidly as the oxygen in the headspace decreased, indicating a balance of liquid (oil) and gas (air in headspace) phases. After 30 d, and up to 150 d, the level of oxygen dissolved in the oil was practically constant and at the same levels in all conditions. In the last 30 d of storage (150–180 d), with the exception of Experimental test 1, a reduction in dissolved oxygen that corresponds to the reduction in the level of oxygen in the headspace in the same period was observed.

The concentration of dissolved oxygen after 180 d of storage was significantly different ($P < 0.001$) for the three levels of initial oxygen in the headspace (0–3, 5–6.5, 7–9%). Experimental test 4, with oxygen level above 15% in the headspace, did not present a difference in relation to the samples with 7–9% (Experimental test 3). Min and Wen (9) studied the reduction of oxygen dissolved in soybean oil and observed a faster reduction in the level of dissolved oxygen in the samples with higher amounts of initial oxygen. These results agree with the present study, once the samples with less initial oxygen presented greater contents of dissolved oxygen during storage.

Andersson and Lingnert (10) studied the influence of different oxygen concentrations in the headspace (0.03; 0.3; 1.0, and 1.8%) in the oxidation of safflower oil stored at 35 and 50°C. The PV and the oxygen consumption were significantly reduced in samples with oxygen concentrations below 0.5% at 50°C, indicating the importance of minimizing the availability of oxygen in delaying the oxidation reaction.

*Evaluation of RBD soybean oil quality.* Parameters (PV and AV) related to oil oxidative stability are presented in Table 3. Correlated with time, the PV increased for all the conditions studied ($R^2$ = 0.91; 0.92; 0.94; and 0.94, for Experimental tests 1, 2, 3, and 4, respectively). During storage, a significant difference ($P < 0.05$) in PV was observed for the four experimental tests. The difference among the experimental conditions was significant for the tests with 0–3% oxygen in the headspace when compared with the conditions with 7–9 and >15%. This difference becomes significantly higher ($P < 0.001$) after 120 d of storage.

For the experiments with oxygen at <3% and between 5 and 6.5%, a significant difference was not observed, indicating that the oxygen availability in these concentrations was not enough to increase the oxidation reaction during the storage for 6 mon, or there was a greater oxygen permeability effect for the initial oxygen level of <3%, equaling the total available oxygen inside of the bottles. After 120 d of storage, the increase in PV for Experimental test 4 (initial level of >15% of $O_2$ in the headspace) became pronounced.

Tawfik and Huyghebaert (3) reported a significant increase

**TABLE 3**
**Headspace and Dissolved Oxygen[a] in RBD Soybean Oil and Oxidative Stability Parameters**

| Time (d) | $O_2$ in the headspace (%) | | | | $O_2$ dissolved in oil (%) | | | | Peroxide value (mequiv/kg) | | | | Anisidine value | | | | Specific extinction $K_{232}$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Test | | | | Test | | | | Test | | | | Test | | | | Test | | | |
| | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 |
| 0 | 2.7 | 5.7 | 7.9 | 16.7 | 0.02 | 0.0 | 0.03 | 0.02 | 0.0 | 0.0 | 0.0 | 0.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.8 | 1.8 | 1.8 | 1.8 |
| 30 | 1.9 | 2..3 | 3.1 | 5.7 | 1.4 | 1.3 | 1.5 | 1.6 | 0.4 | 0.6 | 0.7 | 0.7 | 1.0 | 1.2 | 1.2 | 1.3 | 2.1 | 2.0 | 2.5 | 2.3 |
| 60 | 2.9 | 3.1 | 4.8 | 6.1 | 1.6 | 1.4 | 1.5 | 1.6 | 0.3 | 0.5 | 0.7 | 0.9 | 1.3 | 1.1 | 1.3 | 1.5 | 2.0 | 2.0 | 2.5 | 2.4 |
| 90 | 2.9 | 3.0 | 3.3 | 5.6 | 1.3 | 1.5 | 1.6 | 1.7 | 0.8 | 0.9 | 1.0 | 1.2 | 1.4 | 1.5 | 1.6 | 1.7 | 2.3 | 2.7 | 3.0 | 3.2 |
| 120 | 3.1 | 3.5 | 3.2 | 5.2 | 1.1 | 1.2 | 1.6 | 1.7 | 1.0 | 1.0 | 1.3 | 1.4 | 1.7 | 1.7 | 1.9 | 1.9 | 2.5 | 3.0 | 3.1 | 3.8 |
| 150 | 4.1 | 4.0 | 4.8 | 4.4 | 1.3 | 1.2 | 1.4 | 1.5 | 1.6 | 2.0 | 2.2 | 3.3 | 1.7 | 1.8 | 2.0 | 2.1 | 3.0 | 3.3 | 3.3 | 4.3 |
| 180 | 3.1 | 3.0 | 2.9 | 1.8 | 1.5 | 0.9 | 0.6 | 0.6 | 1.7 | 2.1 | 2.4 | 3.8 | 2.4 | 3.0 | 3.3 | 3.8 | 3.0 | 3.1 | 3.2 | 4.3 |

[a]Initial oxygen concentration in the headspace, Test 1 = 0–3%; Test 2 = 5–6.5%; Test 3 = 7–9%; and Test 4 = >15%. For abbreviation see Table 1.

of PV in olive oil stored in PET packages for 60 d. Alves (11) observed a linear increase of PV in soybean oil packaged in PET containing different UV absorber concentrations during 6 mon of storage.

The secondary compounds originating from the breakdown of hydroperoxides, which are formed and accumulated during the propagation phase, can be determined by the AV. In all the conditions studied, the AV increase was dependent on the storage time ($R^2$ = 0.90; 0.91; 0.95; and 0.96 for Experimental tests 1–4, respectively), and the difference was significant ($P$ < 0.05). The highest AV (3.8) after 180 d of storage was observed in the samples from Experimental test 4.

Lipid oxidation is followed by carbon double-bond alterations, with the formation of conjugated compounds increasing the absorption at 234 nm because of the presence of conjugated dienes. There was a linear increase in the specific extinction during the storage period for all experimental conditions ($r$ = 0.96; 0.91; 0.99; and 0.93) showing a significantly high positive correlation ($P$ < 0.01). A significant difference was seen among Experimental tests 1, 3, and 4 ($P$ < 0.05).

Alves (11) observed a significant linear increase of the specific extinction at 232 and 270 nm in soybean oil packaged in PET and stored for 180 d. Espinoza-Atencia (12) studied the luminous radiation effect on the conjugated dienes in packaged soybean oil and found an increase of the conjugated dienes depending on the increase of the light emission in PET.

Results obtained for physical-chemical and sensorial data on storage of RBD soybean oil packed in PET bottles are presented in Table 4.

FFA and moisture levels increased in all the treatments during storage. The oil used in the treatments initially presented only traces of moisture, indicating that moisture permeation through the bottle wall could have occurred. Moisture in the oil at levels as low as 0.05% can speed up the hydrolysis reactions if the temperatures of storage and transportation are high (13). Among the four experimental tests, the FFA and moisture contents did not present significant differences, indicating that the different oxygen contents in the headspace did not affect the content of FFA in oil. After 180 d, the oil had FFA contents below that established by Brazilian legislation (8), i.e., a maximum of 0.03% for moisture and 0.03% for FFA. Fujisaki (14) reported a linear increase of the acid value in safflower oil with different oxygen concentrations (2, 4, 10, and 20%). Alves (11) observed a significant linear increase of FFA contents in soybean oil that was packaged in PET and stored for 180 d.

The smoke point decreased notably with time in all the treatments, independent of the initial oxygen amount in the headspace. The differences among the experimental conditions were not significant, indicating that the initial amount of oxygen in the free space did not affect the smoke point. The smoke point decreased with the accumulation of decomposition products such as FFA, glycerides, and volatile products.

**TABLE 4**
**Physicochemical and Sensorial Data on Storage of RBD Soybean Oil Packed in PET Bottles[a]**

| Time (d) | FFA (%) | | | | Moisture (%) | | | | Smoke point (°C) | | | | Color (Yellow/Red) | | | | Sensorial note | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Test | | | | Test | | | | Test | | | | Test | | | | Test | | | |
| | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 |
| 0 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 230 | 230 | 230 | 230 | 9/1.0 | 9/1.0 | 9/1.0 | 9/1.0 | 8 | 8 | 8 | 8 |
| 30 | 0.02 | 0.03 | 0.02 | 0.03 | 0.03 | 0.04 | 0.03 | 0.03 | 228 | 226 | 224 | 224 | 10/1.1 | 11/1.1 | 12/1.1 | 12/1.1 | 7 | 7 | 6 | 6 |
| 60 | 0.03 | 0.04 | 0.03 | 0.04 | 0.04 | 0.04 | 0.04 | 0.04 | 225 | 220 | 210 | 210 | 11/1.1 | 11/1.1 | 12/1.2 | 13/1.3 | 6 | 6 | 6 | 5 |
| 90 | 0.04 | 0.03 | 0.03 | 0.03 | 0.05 | 0.04 | 0.05 | 0.05 | 218 | 216 | 204 | 200 | 10/1.2 | 11/1.1 | 14/1.4 | 15/1.5 | 6 | 6 | 5 | 5 |
| 120 | 0.07 | 0.07 | 0.07 | 0.07 | 0.07 | 0.07 | 0.08 | 0.07 | 208 | 200 | 200 | 200 | 13/1.3 | 14/1.5 | 15/1.5 | 15/1.6 | 6 | 5 | 5 | 5 |
| 150 | 0.10 | 0.10 | 0.10 | 0.11 | 0.08 | 0.08 | 0.10 | 0.08 | 198 | 192 | 190 | 190 | 15/1.5 | 16/1.6 | 16/1.6 | 18/1.8 | 6 | 5 | 4 | 4 |
| 180 | 0.11 | 0.11 | 0.11 | 0.12 | 0.07 | 0.07 | 0.08 | 0.07 | 190 | 182 | 180 | 180 | 15/1.5 | 19/1.8 | 20/2.0 | 20/2.0 | 6 | 5 | 4 | 3 |

[a]Initial oxygen concentration in the headspace, Test 1 = 0–3%; Test 2 = 5–6.5%; Test 3 = 7–9%; and Test 4 = >15%. For abbreviations see Table 1.

**TABLE 5**
**Pearson Correlation Matrix for the Studied Parameters on Storage of RBD Soybean Oil Packed in PET Bottles[a]**

| | Time | PV | Head-space $O_2$ | Dissol. $O_2$ | AV | $K_{232}$ | Color Yellow | Color Red | Moisture | FFA | Smokepoint | SN |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Time | 1.00 | | | | | | | | | | | |
| PV | 0.84** | 1.00 | | | | | | | | | | |
| Headspace $O_2$ | –0.08 | 0.01 | 1.00 | | | | | | | | | |
| Dissol. $O_2$ | –0.56** | –0.51* | 0.57** | 1.00 | | | | | | | | |
| AV | 0.42* | 0.49* | –0.10 | –0.36 | 1.00 | | | | | | | |
| $K_{232}$ | 0.69** | 0.57** | –0.30 | –0.56** | 0.71** | 1.00 | | | | | | |
| Color Yellow | 0.58** | 0.52** | 0.02 | –0.34 | 0.91** | 0.83** | 1.00 | | | | | |
| Color Red | 0.54** | 0.51* | –0.11 | –0.35 | 0.90** | 0.86** | 0.98** | 1.00 | | | | |
| Moisture | 0.25 | 0.16 | 0.06 | –0.08 | 0.62** | 0.71** | 0.75** | 0.79** | 1.00 | | | |
| FFA | 0.23 | 0.23 | –0.05 | –0.24 | 0.82** | 0.73** | 0.85** | 0.87** | 0.88** | 1.00 | | |
| Smoke point | –0.48* | –0.40 | 0.03 | 0.22 | –0.87** | –0.83** | –0.95** | –0.96** | –0.84** | –0.89** | 1.00 | |
| SN | –0.69** | –0.85** | –0.20 | 0.36 | –0.48* | –0.51* | –0.53** | –0.48* | –0.15 | –0.32 | 0.43* | 1.00 |

[a](*) significant correlation; (**) highly significant correlation; Dissol. $O_2$, dissolved $O_2$; AV, anisidine value; $K_{232}$, specific extinction (232 nm); SN: sensorial note. For other abbreviations see Table 1.

With respect to color, an increase in red and yellow Lovibond values for the four experimental conditions was observed, indicating oil darkening during the storage. The definitive color among the tests was significantly different ($P < 0.05$). The soybean oil samples that presented the most intense yellow and red compounds were those that contained greater initial amounts of oxygen in the headspace, indicating that oxidative rancidity modifies the color during the storage at room temperature in the absence of light. The oil can become dark because of the oxidation reaction that promotes the decomposition of carotenoid pigments (responsible for the yellow and red color in soybean) by a free-radical mechanism. After 180 d, only the samples of Experimental test 1 (0–3% of $O_2$ in the headspace) were within the limit set by Brazilian legislation (8).

In the sensorial analysis, the soybean oil samples conditioned with different levels of initial oxygen were significantly different after 6 mon of storage, indicating different odor and flavor perceptions. According to the quality standard specification for sensorial analysis, grade six is the lowest acceptable score for good-quality oil during its useful life; therefore, the oil with >15% oxygen in the headspace was considered rejected after 60 d of shelf life; this time increased to 90, 120, and 180 d with the decrease of the initial oxygen concentration to 7–9, 5–6.5, and 0–3%, respectively. In a study performed on soybean oil, Medina-Juárez *et al*. (15) reported that after 90 d of storage the oil presented a substantial change in flavor, from nutty/bland to strong buttery flavor. In a study made with soybean oil packaged in PET, Azeredo (16) observed that the increase of the 234 nm UV absorber concentration from 0.05 to 0.15% did not significantly increase the oil sensorial grade after 6 mon of storage. Alves (11), studying soybean oil packaged in PET with different concentrations (0, 0.12, and 0.24%) of 234 nm UV absorber found that the sensorial score decreased during the storage time in all the experiments, however, the differences among the tests were not significant and the oils were considered rejected after 156 d of storage, before the physical-chemical tests detected greater alterations.

*Correlation among analytical methods.* In Table 5, the correlations between the studied parameters and time, determined using a Pearson matrix correlation, are presented.

The Pearson matrix correlation showed that PV presented highly significant correlations ($P < 0.001$), being positively related with specific extinction and yellow color and negatively with sensorial score. The PV evolution during storage presented a significant correlation ($P < 0.05\%$), being positively associated with AV and negatively with dissolved oxygen. According to White (17), the PV measures primary oxidation products and has a good correlation with anisidine, a fact that can be confirmed by the significant correlation presented.

According to Pearson's correlation matrix, oxygen evolution in the headspace presented a highly significant positive correlation ($P < 0.01$) with the dissolved oxygen level in the oil, indicating that the more oxygen that is available in the headspace, the more that dissolves in the oil.

The change of moisture content during storage presented a highly significant ($P < 0.01$) positive correlation with FFA and a negative correlation with the smoke point, indicating that moisture may have caused hydrolytic reactions in the TG of the oil, decreasing the smoke point temperature. The correlation analysis showed highly significant inverse correlations of FFA with moisture content and smoke point.

Statistical analysis indicated a highly significant negative correlation among smoke point, AV, specific extinction, color, moisture, and FFA and also among sensorial evaluation, PV, and yellow color. For values such as anisidine, extinction, red color, and smoke point, the negative correlation verified was significant.

The behavior of the specific extinction parameter presented a highly significant inverse correlation with the dissolved oxygen, indicating that, as the dissolved oxygen is consumed by the oxidation reaction, the conjugated diene content increases.

The PV and AV behave similarly, indicating that these compounds are accumulated in the system until the beginning of decomposition, which can be proved by the significantly positive correlation ($P < 0.05$) between these two values.

The smoke point reduction presented a good correlation with the increase in FFA and moisture value of the oil and did not have a relation with oxidative deterioration.

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