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Evaluation of oil extracted from corn grains ozonized at different levels of grain mass temperature

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Abstract

Pest management in grain storage units must be based on control measures, which should be efficient, low cost and with the least possible environmental impact. Considering ozone gas as a new strategy of modified atmosphere for grain protection against insect-pest attack, this work was carried out to evaluate its immediate and latent effect on the quality of oil extracted from grains during storage. Corn grains were subjected to atmosphere modified with 50 ppm ozone, 8 L min-1 flow, for 168 hours, at grain mass temperatures of 20, 30, 35 and 40 °C. Atmospheric air was applied for 168 hours to the grain mass under the same conditions of the ozone gas treatment, as control. After exposition to ozone and atmospheric air at each temperature, the grains were individually homogenized and placed into 2.5-L glass bottles, which were stored in room conditions for 180 days. To evaluate the effect of the treatments on grain quality, acidity and peroxide values of the extracted oil were determined after the treatment and every 45 days. The peroxide and acidity values were not affected by ozone after treatment at any temperature. Therefore, ozonization did not induce immediate and latent alterations in peroxide and acidity values in fumigated grains at the studied grain mass temperature levels.

Key words: grain protection, storage, ozonization, acidity value, peroxide value.

Introduction

Protection and conservation of grains during storage constitute in a socioeconomic need. All the resources destined for feed-use should be carefully conserved during storage in order to maintain the nutritional value. The grain type and the treatment it was subjected during management and processing will define the correct procedures to be adopted for storage (Parizzi, 2005).

In the last years, the demand for alternatives to reduce the use of chemical products to control biological agents such as insects and fungi has been increasing. Among the main alternatives, the use of ozone gas (O_3) stands out as it can be produced at the workplace, eliminates tasks such as chemical handling, storage and disposal of containers, and mainly, it does not leave toxic residues in the grains, since the only product of degradation is oxygen (O_2) (Barbosa et al., 2005).

Although some authors have reported the efficiency of ozone to control stored grains insect-pests (Kells et al., 2001; Mendez et al., 2003; Zhanggui et al., 2003), little it is known about its influence on grain and byproduct quality during storage. Increasing knowledge on factors

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that can interfere with the exposition of grains to ozone, as well as the interaction with the common biotic agents found in the grain mass, allows a better understanding of the influence on the quality of grains and byproducts. Jay (1971) reported that the temperature effect on the period of time needed to obtain an efficient fumigation is as important as the techniques that use conventional fumigants.

The quality of the oil can be used as indicator of the grain quality. Traditional analyses as free fatty acid content, peroxide value, percent composition of fatty acids and iodide value, among others, have been used for crude oil evaluation (Napoleão, 1997).

Free fatty acid content or acidity value expresses the amount of fatty acids released from triglyceride structures. Peroxide value is used to evaluate the state of oxidation of oils. The oxidation of oils in grains or seeds can occur by the action of enzymes in damaged grains or the contact of the oil with the oxygen from the air, which is accelerated by the increase in temperature and moisture. High free fatty acid content or peroxide value indicate low oil quality, and also indicate low seed quality, caused by the presence of broken or moldy grains, resulted from inappropriate handling or processing (Napoleão, 1997).

Seeking alternatives to reduce the use of chemical products in grain storage units, the objective of this work was to study the immediate and latent effect of ozone gas application at different levels of grain mass temperature on grain quality. The evaluated parameters were acidity and peroxide values of oil extracted from corn grains.

Materials and methods

The experiments were conducted at the Sector of Pre-processing and Storage of Agricultural Products, Department of Agricultural Engineering, Federal University of Viçosa (UFV). The influence of growing mass grain temperature (20, 30, 35 and 40 °C) combined with ozone exposition periods of 24 and 48 h on *S. zeamais* mortality, using 50 ppm ozone for 168 h, and on the quality of oil extracted from grains over a period of 180 days of storage.

Ozone and atmospheric air supply

Ozone gas was obtained from a generator developed by the Physics Department of the Aeronautics Technological Institute (ITA). In the gas generation process, dry atmospheric air (dew point below -40 °C) was used as input, passing through a dieletric barrier discharge (DBD) refrigerated reactor. This type of discharge is produced by applying a discharge voltage between two parallel electrodes, having between them a glass dieletric capacitator and a free space where the dry air or the oxygen flows through. In this free space a filament discharge is produced, where electrons are generated with enough energy to break down the oxygen molecules forming ozone (O_3).

The dry air used as input was obtained from an air compressor installed together with an aluminum filter. A two-outlet connection was installed in the filter outlet: one passing through the ozone generator and the other going directly to the atmospheric air system (control). Ozone production was regulated as a function of applied power, adjusted by the generator power variator. Dry airflow was monitored by an air flow meter. Ozone concentration was accurately measured through an espectrophotometer with 0.1 g m^{-3} accuracy. To increase the accuracy of O_3 concentration readings, a multimeter was connected to the espectrophotometer to enable the establishment of a relationship between the values read in the espectrophotometer (g m^{-3}) and the electric current (mA).

Exposition of corn grains to ozone gas and atmospheric air

For ozone and atmospheric air exposition, type 1 corn grains (25 kg) were placed into 20 cm diameter x 100 cm high PVC cylindrical containers. At the top and bottom cylinder lids

connections for a gas injection-exhaustion system were installed. A metallic screen was placed 10 cm above the bottom of each container to hold the grains and form a chamber for a better gas distribution. Corn grains were exposed to ozone and atmospheric air during 168 h.

Grain mass temperature control

The cylinders containing corn were taken to climatic chambers with air temperature controlled according to the grain mass temperature, which was monitored by a *1-Wire*™ Temperature/Data Logger system. This system consists of a data transmission network using software to allow the communication between the computer and the grain mass temperature sensors with only one conductive cable (Martins et al., 2004).

Grain storage and oil evaluation

After 168 h of exposition, grains at the temperatures 20, 30, 35 and 40 ºC were homogenized separately, distributed into 120 2.5-L glass flasks and stored in room conditions. The grains were ground in a Fritsch Pulverisette mill, 1600-rpm revolution speed, using a 2-mm stainless steel sieve, subsequently the oils were extracted. For evaluation of oil qualitative characteristics, the free fatty acid contents and peroxide values were analyzed every 45 days, over a period of 180 days of storage.

Oil extraction

The oils from the samples were soxhlet extracted with petroleum ether according to the AOCS Bc 3-49 (1988) methodology modified to compensate the low oil content in the samples. In each extraction, approx 40 g corn were ground in disk mill, placed into Whatman no. 2 filter paper cones and extracted in period of distillation of twelve h. After solvent evaporation on hot plate (below 60 °C), the Erlenmeyer flasks were taken to oven at 100 °C, for 20 to 60 minutes, to complete evaporation. The flasks were cooled in a dissecator and weighed to quantify the extracted oil, 2 to 5 g per flask.

Acidity and peroxide values

Free fatty acid content determination followed the AOCS Ca 5a-40 (1988) norm, with modification. Two grams of oil were dissolved in neutralized alcohol and 3 drops of phenolphthalein 0.01 % was added as indicator, titrations were then performed using 0.1 N NaOH. Free fatty acid (FFA) content, expressed as percent oleic acid, was calculated using equation:

$$agl = \frac{(A-B)xNx\,28,2}{m}$$

Where:

A = volume (ml) of 0.1 mol/l NaOH required for the sample;

B = volume (ml) of 0.1 mol/l NaOH required for the reagent blank

N = normality; and

m = sample mass (g)

Peroxide value determination followed the AOCS Cd 8-53 (1988) norm, with modification. Two grams of oil were poured in an Erlenmeyer flask with 30-ml acetic acid chloroform solution (3:2 v/v), 0.5 ml KI saturated solution and 30 ml distilled water. Titration was performed with $Na_2S_2O_3$ solution, using 2 %starch as indicator. The peroxide value was calculated by equation:

$$vp=\frac{(A-B)xNx1,000}{m}$$

Where:

A = volume (ml) of 0.1N $Na_2S_2O_3$ required for the sample;

B = volume (ml) of 0.1N $Na_2S_2O_3$ required for the reagent blank;

N = exact normality of the $Na_2S_2O_3$ solution; and

m = sample mass (g).

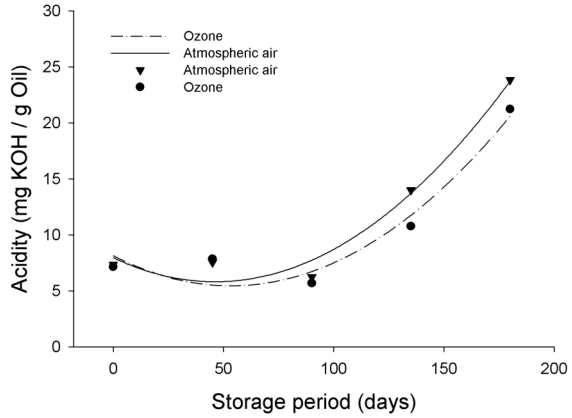
Data analysis

The experiment was arranged in completely randomized design, in a 2 x 5 factorial arrangement, two treatments with and without ozone and five storage periods (0, 45, 90, 135 and 180 days), three repetitions per temperature (20, 30, 35 and 40 ºC). Data were analyzed by regression analysis as a function of time, for all the determinations, in order to compare possible differences among treatments.

Results

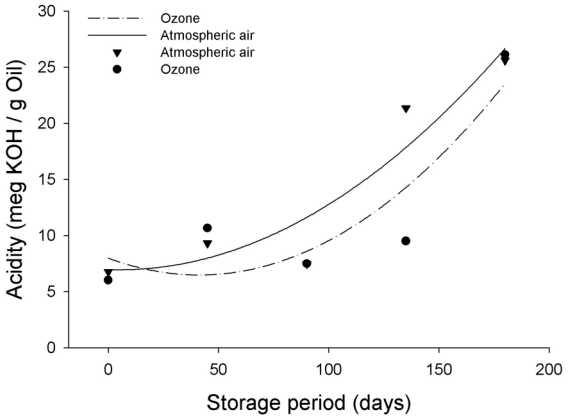
Oil acidity values were not changed after grain ozonization at none of the levels of grain mass temperatures (Figure 1). Acidity values of oils

(20 ºC)



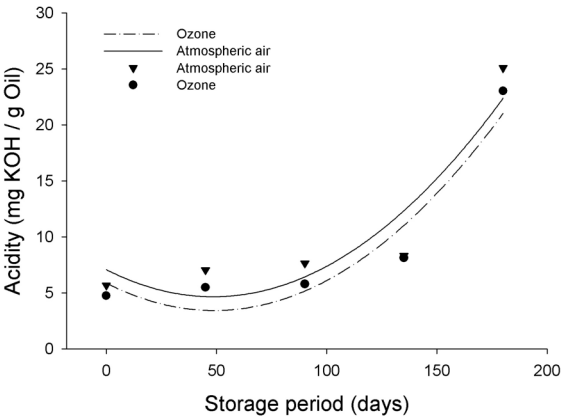
($Y_{(a)\ AR}$= 0,0010X^2-0,0926X+7,95)
(R^2 = 0,95; P<0,0001; F=121,32);
($Y_{(a)\ OZ}$= 0,0009X^2-0,1007X+8,13)
(R^2 = 0,74; P = 0,0003; F=17,36); where:
Y= Acidity value X = Storage period

(30 ºC)



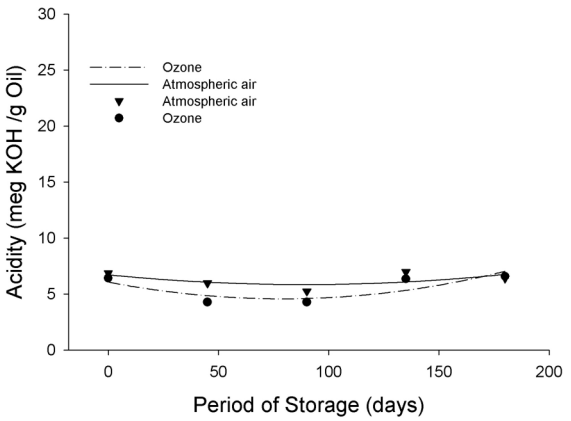
($Y_{(b)\ AR}$= 0,0006X^2-0,0061X+6,95)
(R^2 = 0,83; P = 0,0003; F = 22,82);
($Y_{(b)\ OZ}$= 0,0009X^2-0,0728X+7,97)
(R^2 = 0,73; P = 0,0023; F = 12,77); where:
Y= Acidity value X = Storage period

(35 ºC)



($Y_{(a)\ AR}$= 0,0010X^2-0,0995X+7,06)
(R^2 = 0,63; P = 0,0039; F = 9,58);
($Y_{(a)\ OZ}$= 0,0010X^2-0,1001X+5,86)
(R^2 = 0,89; P < 0,0001; F = 47,11); where:
Y= Acidity value X = Storage period

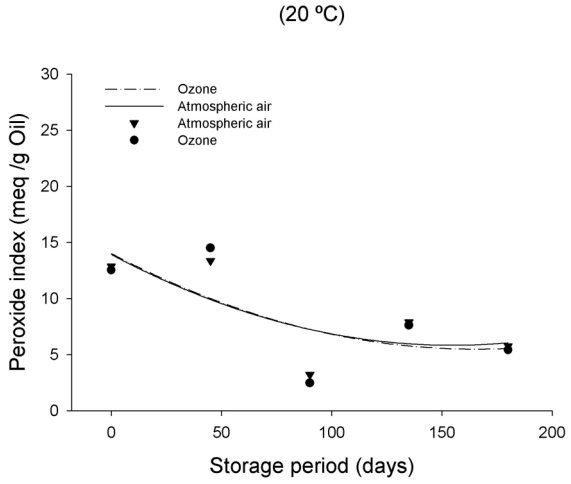
(40 ºC)



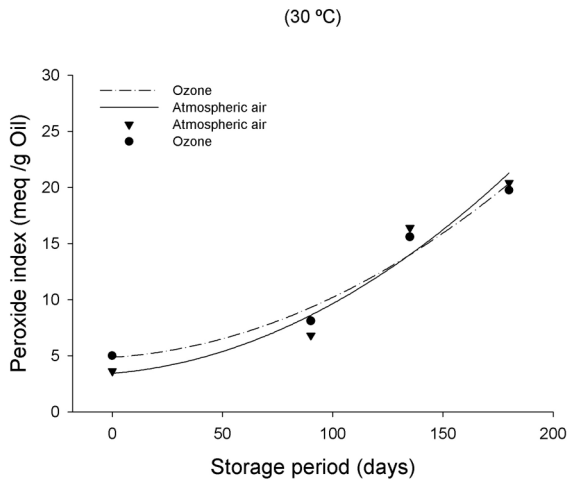
($Y_{(b)\ AR}$= 0,0001X^2-0,0195X+6,70
(R^2 = 0,13; P = 0,4237; F = 0,92);
($Y_{(b)\ OZ}$= 0,0002X^2-0,0379X+6,06
(R^2 = 0,52; P = 0,0109; F = 6,73); where:
Y= Acidity value X = Storage period

Figure 1. Acidity values of oil extracted from corn grains subjected to fumigation with ozone gas and atmospheric air at the levels of grain mass temperature of 20, 30, 35 and 40 ºC, over the exposition period of 168 h.

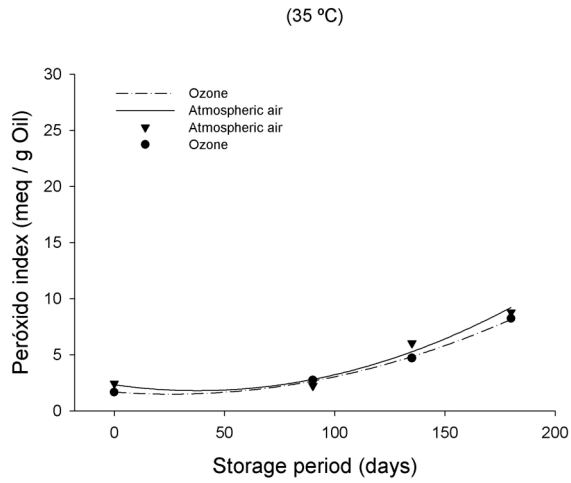
extracted from ozonized and non-ozonized grains at grain mass temperature of 20, 30 and 35 °C increased proportionally with the storage period, with the lowest values found during all the storage period for ozonized grains (Figure 1). At 40 °C, the oil acidity values were also lower in the ozonized grains, however the values kept practically constant over the storage period (Figure 1). Regarding peroxide values, it was found that the ozonized and non-ozonized grains showed similar values after treatment and over storage, with tendency for proportional increase with the storage period, mainly at the grain mass temperature of 30 °C (Figure 2).



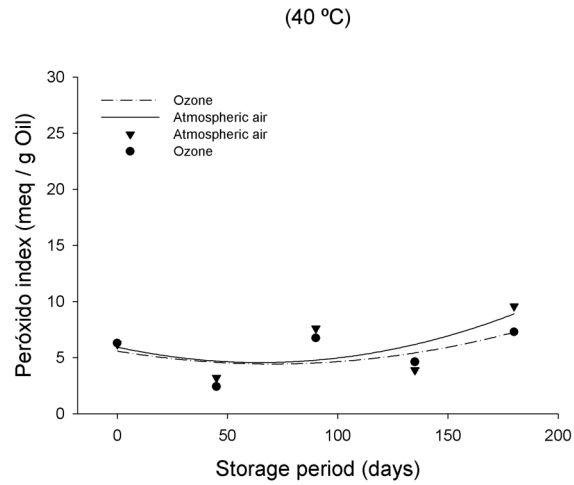
($Y_{(a)\ AR}$= 0,0003X^2-0,1046X+13,92)
(R^2 = 0,52; P = 0,0115; F = 6,63);
($Y_{(a)\ OZ}$= 0,0003X^2-0,1031X+14,00)
(R^2 = 0,48; P = 0,0180; F = 5,72); where:
Y= Peroxide value X = Storage period.



($Y_{(b)\ AR}$= 0,0005X^2-0,0157X+43,42)
(R^2 = 0,94; P = 0,0001; F = 56,48);
($Y_{(b)\ OZ}$= 0,0004X^2-0,0126X+4,85)
(R^2 = 0,84; P = 0,0036; F = 16,57); where:
Y= Peroxide value X = Storage period.



($Y_{(a)\ AR}$= 0,0004X^2-0,0277X+2,32)
(R^2 = 0,84; P = 0,0005; F = 23,23);
($Y_{(a)\ OZ}$= 0,0003X^2-0,0143X+1,66)
(R^2 = 0,96; P < 0,0001; F = 96,62); where:
Y= Peroxide value X = Storage period.



($Y_{(b)\ AR}$= 0,0003X^2-0,0424X+5,93)
(R^2 = 0,25; P = 0,1724; F = 2,04);
($Y_{(b)\ OZ}$= 0,0002X^2-0,0328X+5,57)
(R^2 = 0,23; P = 0,2054; F= 1,81); where:
Y= Peroxide value X = Storage period.

Figure 2. Peroxide values of oil extracted from corn grains subjected to fumigation with ozone gas and atmospheric air at the levels of grain mass temperature of 20, 30, 35 and 40 ºC, over the exposition period of 168 h.

Discussion

In this investigation the results for acidity value were similar to the ones reported by Barbosa et al. (2005). These authors also found that treating the grains with ozone in the concentration of 0.0132 kg O_3/m^3 air, for exposition periods up to 120 h, did not cause significant differences in the acidity value of oils extracted from corn grains. These results were already expected, since the production of free fatty acids in seeds is due to the action of lipases, or it is produced and released by fungi and other microorganisms (Norris, 1979). Consequently, the highest acidity values found in non-treated grains might have been caused by the action of biological agents such as insects and fungi.

A possible explanation for the similarity of peroxide values found between ozonized and non-ozonized grains, after the treatment and over storage, is a low oxidative degradation that might have occurred during the ozonization process, as the peroxide value is related with oxidative degradation of oils, which are described as the initial products of this type of reaction (Vergara et al., 2006). Peroxides are very sensitive indicators in their initial stage of oxidation. When peroxide concentration reaches a determined level, complex changes take place, forming low molecular weight compounds derived from the degradation. Thus, this measurement is limited by the peroxide's transitory nature, and its decomposition to secondary products can underestimate the level of oxidation. Low peroxide values can represent the initial or advanced stage of oxidation (Araújo, 2004). Therefore, based on this analysis, it is difficult to evaluate at which extension ozone affected the product final quality, and further analyses are needed to complement these results.

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