Effect of the ozonization process on the quality of peanuts and crude oil

Ernandes R. de Alencar1, Lêda R. D. Faroni2, Nilda F. F. Soares3, Marta C. S. Carvalho3 & Katiane F. Pereira3

ABSTRACT
The purpose of this study was to evaluate the effect of ozone on the quality of peanut grains and crude oil extracted from these grains. Peanut samples of 1 kg were used, with a moisture content of 8.0% w.b. and stored in 3 L glass recipients. The ozonization process utilized ozone gas concentrations of 13 and 21 mg L⁻¹, temperature of 25 ºC, exposure periods of 0, 24, 48, 72 and 96 h, and a flow rate of 1.0 L min⁻¹. Evaluation of peanut quality consisted of analysis for moisture content, electrical conductivity, lipid concentration and peanut color. The qualitative parameters of the crude oil evaluated were free fatty acids, peroxide index and iodine index. In general there was no alteration in peanut quality due to ozone, except for the coloration of the peanuts. With regard to parameters related to the crude oil extracted from the peanut, there were no qualitative alterations due to ozone exposure. It was concluded that, despite depigmentation of the skin surrounding the peanuts, the quality of the peanuts and the extracted crude oil is not affected by exposure to ozone gas at concentrations up to 21 mg L⁻¹, for up to 96 h.

Key words: ozone, qualitative changes, coloration

Efeito do processo de ozonização na qualidade dos grãos e do óleo bruto de amendoim

RESUMO
O propósito deste trabalho foi avaliar o efeito imediato do ozônio na qualidade dos grãos de amendoim e do óleo bruto extraído desses grãos. Utilizaram-se amostras de 1 kg de grãos, com teor de água de 8,0% b.u., acondicionadas em recipientes de vidro com capacidade de 3 L e no processo de ozonização, as concentrações de 13 e 21 mg L⁻¹, temperatura de 25 ºC, períodos de exposição de 0, 24, 48, 72 e 96 h e vazão do gás de 1,0 L min⁻¹. Para avaliação da qualidade dos grãos foram analisados os parâmetros teor de água, condutividade elétrica, teor de lipídios e coloração dos grãos. Quantificaram-se, para a avaliação da qualidade do óleo bruto, o teor de ácidos graxos livres, o índice de peróxido e o índice de iodo. Em geral, não ocorreu alteração da qualidade do amendoim em virtude a exposição ao ozônio, exceto para a variável coloração dos grãos. Com relação aos parâmetros relacionados ao óleo bruto, não ocorreram alterações qualitativas devido a exposição ao ozônio. Concluiu-se que, apesar de ocorrer despigmentação da película que envolve os grãos de amendoim, a qualidade dos grãos e do óleo bruto extraído não é afetada pela exposição ao gás ozônio em concentrações de até 21 mg L⁻¹, por até 96 h.

Palavras-chave: ozônio, alterações qualitativas, coloração

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2 Faculdade de Agronomia e Medicina Veterinária/UnB, CEP 70910-970, Brasília, DF. Fone: (61) 3307-2803. E-mail: ernandesalencar@unb.br
3 DEA/UFV, Av. P. H. Rolfs s/n, CEP 36570-000, Viçosa, MG. Fone: (31) 3899-1874. E-mail: lfonari@ufv.br; marta.carvalho@ufv.br; katiane.ferreira@ufv.br
4 DTA/UFV. Fone: (31) 3899-2227. E-mail: nfssoares@ufv.br
Effect of the ozonation process on the quality of peanuts and crude oil

INTRODUCTION

Ozone gas (O$_3$) is an allotropic form of oxygen that can be produced synthetically by means of electrochemical discharge. During the production process of this gas, oxygen molecules (O$_2$) are separated, producing highly reactive free radicals, which react with other oxygen molecules, resulting in ozone gas (Novak & Yuan, 2007).

Features such as high reactivity and penetrability, and spontaneous decomposition into a non-toxic product (oxygen) make ozone gas an important alternative for the food industry. Another key feature is its high oxidation potential, making it one of the most potent sanitizers known, and a strong antimicrobial agent. In 2001, FDA (U.S. Food and Drug Administration) approved the use of ozone as an antimicrobial agent in food, both in the gas phase and dissolved in water (FDA, 2001). The exposure time required for the inactivation of microorganisms depends on the microbial species, and on the concentration of ozone, and any concentration smaller than 0.02 mg L$^{-1}$ is enough to treat pure water. The gas acts directly on the microorganisms and destroys their cell wall (Stucki et al., 2005).

Ozonation has been used in Europe to sanitize water for human consumption. Currently, this technology is being used for other purposes, such as to treat swimming pool water; to sanitize gallons of water, surfaces of food, plants, and food processing equipments; to disinfect carcasses; to preserve fruits and vegetables; to control pests of insects in stored grain; to reduce aflatoxin levels in food (Mckenzie et al. 1998; Prudente & King, 2002; Mendez et al., 2003; Pereira et al., 2008; Sousa et al., 2008).

The ability of the ozone to inactivate or inhibit the growth of microorganisms, and reduce aflatoxin levels in foods, makes this gas an important alternative to peanut, as far as food safety is concerned. The peanut, which has high nutritional value, is considered an ideal substrate for the development of the fungi Aspergillus flavus, A. parasiticus and A. nomius, and the presence of this mycotoxin is one of the factors that most compromise the quality of peanut (Pitt, 2000; Blesa et al., 2003; Ehrlich et al., 2007; Nakai et al., 2008). The aflatoxins which are produced by these fungi are highly carcinogenic, teratogenic, and mutagenic, and the four main primary mycotoxins are aflatoxins B1, B2, G1 and G2 (Li et al., 2009). Out of these four primary mycotoxins, aflatoxin B1 has the most toxicity and is considered to have greater carcinogenic potential, classified by the International Agency of Research on Cancer as group I compound, in other words, with the potential to cause primary hepatocellular carcinoma in humans (IARC, 1993; Williams et al., 2004; Baird et al., 2006).

Considering that ozone can be an alternative for the quality control of peanuts, as far as food safety is concerned, operating both in the inhibition of the potentially aflatoxigenic fungi, and in the reduction of the aflatoxin levels; more work is needed to evaluate the effects of this gas in the quality of peanut grains and peanut sub-products. The need for more works on this subject is justified by the fact that the ozone gas is able, according to Victorin (1992), to oxidize organic cellular components, such as amino acids and polyunsaturated fatty acids. Therefore, it is necessary to establish concentrations of the gas, and appropriate exposure periods of time, so that the quality of peanut is preserved, regarding the physical and chemical aspects. Hence, the aim of this study is to evaluate the quality of the peanut grains and of the crude peanut oil extracted from these grains, after the process of ozonation in different combinations of concentration, and in different exposure periods of time.

MATERIAL AND METHODS

The work was carried out at the Department of Pre-Processing and Storage of Agricultural Products in the Department of Agricultural Engineering - DEA, and at the Packaging Lab of the Department of Food Technology - DTA, both located at the Federal University of Viçosa - MG.

To assess the effect of the insertion of ozone gas in peanut (Arachis hypogaea L.), grains with moisture content (m.c.) of about 8.0% of w.b. were used. The ozone gas was obtained through an ozone generator, based on the method of Dielectric Barrier Discharge (DBD), developed by the Department of Physics, from the Instituto Tecnológico de Aeronautica (ITA), in São José dos Campos, Brazil. In the process of ozone generation, oxygen with purity of 90 ± 3%, and free of humidity, was used as input. It was obtained from the Mark 5 Plus Oxygen Concentrator.

The concentration of ozone was determined through the iodine method, described by Clesceri et al. (2000), which is the bubbling of ozone in 50 mL of potassium iodide solution (KI) 1 N, with production of Iodine (I$_2$). To ensure the displacement of the reaction to the production of I$_2$, it was necessary to acidify the mean with 2.5 mL of sulfuric acid (H$_2$SO$_4$) 1 N. The solution was then titrated with sodium thiosulfate (Na$_2$S$_2$O$_3$) 0.005 N, using a solution of 1% starch, as an indicator.

During the process of ozonation, 1 kg of peanuts, packed in 3L glass recipients at temperature of 25 °C, were ozonized at concentrations of 13 and 21 mg L$^{-1}$, with gas flow of 1.0 L min$^{-1}$, for periods of 0, 24, 48, 72 and 96 h. During the control treatment (0 mg L$^{-1}$), the grains were exposed to oxygen gas.

Qualitative analysis of ozonized peanuts
Moisture content

The moisture content of peanut grains was determined by the gravimetric method in a forced-air circulation oven and temperature of 130 ± 1 °C, as recommended by ASAE (2002), S401.1 method.

Lipid content

The lipid content of peanuts was determined according to the norms of AOCS (2009), Ac 3-44 method in soxhlet apparatus for 6 h using petroleum ether as solvent. The lipid content was calculated as a function of the dry matter mass of the sample and the lipid fraction extracted, according to Eq. 1:

$$\text{Lipids} \, (\%) = \frac{L}{m} \times 100$$

where:

$m$ is the weight of the sample in g.

$L$ is the weight of the organic fraction, in g.

L - mass of lipids in the sample, g
m - mass of the sample in terms of dry matter, g

Electrical conductivity

The electrical conductivity of the solution containing peanut grains was performed using the system of glass or mass conductivity (Vieira et al., 2001), aiming to evaluate the increase in membrane permeability, as grains deteriorate.

Color of grains

The evaluation of the color of peanut grains was performed with the ColorQuest™II Tristimulus Colorimeter, reaching the coordinate values L, a, and b from the Hunter system. With the values of coordinates L, a, and b, it was possible to obtain parameters related to the hue angle h (Eq. 2), to the color saturation or chroma C (Eq. 3), and to the color difference ΔE (Eq. 4) (Little, 1975, Francis, 1975).

\[ h = \arctan(b/a) \]  
\[ C = \sqrt{a^2 + b^2} \]  
\[ \Delta E = \sqrt{(L - L_0)^2 + (a - a_0)^2 + (b - b_0)^2} \]

where:
L - measurable in terms of intensity from white to black
a - measurable in terms of intensity of red and green
b - measured in terms of intensity of yellow and blue
L_0, a_0, b_0 - coordinates obtained before the ozonation of peanut grains

Qualitative analysis of the crude oil extracted from ozonized peanut grains

Free fatty acids

The free fatty acids (FFA) were determined in accordance with the norms of AOCS (2009), Method Ca 5a-40 and expressed as % of oleic acid. The FFA was calculated using Eq. 5:

\[ \text{FFA} = \frac{N \times 28.2 \times (V_a - V_s)}{m} \]  

where:
N - normality of NaOH solution
f - correction factor of the NaOH solution
V_a - volume of NaOH 0.01 N spent for the sample, mL
V_s - volume of NaOH 0.01 N spent in titration without oil sample, mL
m - mass of sample, g

Peroxide Index

The peroxide index (PI) was determined according to the norms of AOCS (2009), Cd 8-53 Method. The PI (mEq kg⁻¹) was calculated through Eq. 6:

\[ \text{PI} = \frac{N \times f \times 1000 \times (V_a - V_s)}{m} \]  

where:
f - correction factor of the NaOH solution
V_a - volume of NaOH 0.01 N spent for the sample, mL
V_s - volume of NaOH 0.01 N spent in titration without oil sample, mL
N - normality of NaOH solution

Iodine index

The determination of iodine was performed in accordance with AOCS (2009) norms, Method Cd 1b-87. The iodine value was obtained by Eq. 7:

\[ I = \frac{1.27 \times f \times (V_a - V_s)}{m} \]  

Experimental outline

The experiment was conducted in split plots, in which there were concentrations of (0.13 and 21 mg L⁻¹), and in the subplots the periods of exposure to gas (0, 24, 48, 72 and 96 h), in a completely randomized outline with three replications. Initially the variance at 5% of probability was analyzed, and then there was the analysis of regression. In the analysis of variance the SAEG Software 9.0 was used. To obtain the regression equations and the plotting of graphs, the software SigmaPlot 2001 was used.

RESULTS AND DISCUSSIONS

Quality of ozonized peanut grains

On Figure 1, there is the regression curve that describes the behavior of the moisture content of peanuts in different periods of exposure. Regardless of the exposure of peanuts to oxygen gas (control), and ozone gas (13 and 21 mg L⁻¹), there was a significant decreasing (p < 0.05) of moisture content of the grains in the different periods of exposure. The estimated mean value of moisture content of the grains decreased from 7.6% to 4.4% when the exposure time was 96 h.

The use of oxygen, which is free of humidity, as input for the generation of ozone, and in the control treatment, explains the reduction of moisture content in peanuts (Figure 1). The loss of water during the ozonation process is due to the high hygroscopicity of peanut grains. It is important to note that in other products, such as fruits, ozone can react with the cuticle.
which is a structure whose main function is to control the loss of water through transpiration, and with lipoprotein components, accelerating the loss of water (Rao et al., 2000).

The lipid content in peanuts remained around 45%, regardless of their exposure to oxygen and ozone gas, at different periods of exposure (p > 0.05). The implication of this behavior is that the ozone gas does not affect the chemical composition of peanuts. Corn, soybeans, and wheat grains, were ozonated by Mendez et al. (2003), at the concentration of 50 ppm for 30 days. These authors also found no change in the chemical constitution of the ozonized grains, and there were no alterations in the content of amino acids and lipids.

Regarding the variable electrical conductivity of the solution that contained the peanut grains, there was no significant variation by the interaction of ozone gas concentration and exposure periods and these two factors were analyzed separately (p > 0.05). The average values of the electrical conductivity of the solution that contained the grains, exposed or not to the ozone gas, at different periods of exposure, remained within the range of 80 and 90 μS g cm⁻¹.

The variable electrical conductivity is directly related to the cell membrane integrity, and to the physiological quality of the grains; poorly structured membranes and damaged cells are associated to the process of deterioration (Heslehurst, 1988). The peanut grains which were exposed to the ozone gas at concentrations of 13 and 21 mg L⁻¹, for up to 96 h, were not affected physiologically. Similar results concerning the physiological quality of the grains were obtained by Santos (2008) for maize exposed to ozone gas at concentration of 100 ppm, for 180 min. Instead, Rozado et al. (2008) observed a significant increase in the electrical conductivity of the solution that contained the grains which had been exposed to ozone gas at concentration of 50 ppm, for 264 h.

Regarding the color saturation parameter, there was no significant variation by the interaction with the ozone gas concentration and exposure period, nor with any of these two factors, when analyzed separately (p > 0.05), however, the process of ozonation of peanuts in the different combinations of gas concentration and exposure periods, resulted in a significant change (p < 0.05) of hue angle and color difference. Changes in hue angle and color difference, regarding the grain that were exposed to oxygen and to ozone gas at concentrations of 13 and 21 mg L⁻¹, at different periods of exposure are shown in Figures 2 and 3, respectively.

The adjusted regression equations and their respective coefficients of determination relative to the hue angle and to the difference in color of peanuts that were exposed to oxygen and to ozone gas, at concentrations of 13 and 21 mg L⁻¹, in different periods of exposure, are presented in Tables 1 and 2, respectively.

The change in the color of peanuts grains can be explained by the depigmentation of its skin, of reddish color, by the ozone gas. Some pigments such as tannins, leuco-anthocyanins, flavanone and phlobaphene are found in the skin of these grains.
The peroxide value of crude peanut oil did not change significantly as a result of the concentration interaction of ozone gas, and exposure period, was not significant (p > 0.05). There was also no significant variation due to factors related to either ozone gas concentration, or exposure time, when analyzed separately. The mean iodine value was 96.8 g I\(_2\) 100 g\(^{-1}\) of sample, staying, therefore, within the maximum and minimum limits established by the Brazilian legislation in order to sell this product, despite the high potential of the ozone to oxidize unsaturated fatty acids (Gómez et al., 2008). According to the Brazilian laws, the iodine index of crude peanut oil should remain within the range of 80 and 105 g I\(_2\) 100 g\(^{-1}\) of sample (ANVISA, 1999). These results confirm the studies of Mendez et al. (2003), who found no significant change in the profile of saturated and unsaturated crude oil extracted from corn, soybean and wheat which were ozonized at a concentration of 50 ppm, for 30 days.

**Conclusions**

1. The analysis and interpretation of the data showed that despite the high oxidizing power of the ozone gas and its ability regarding the depigmentation of the skin of the peanuts, the quality of the grains, and the quality of the crude peanut oil are not affected by the ozone, at concentrations of up to 21 mg L\(^{-1}\), and at exposure periods of up to 96 h.

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