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Effect of vacuum thermoxidation on sunflower oil

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Abstract

In recent years vacuum frying was developed as an alternative methodology to traditional frying.

In this study, sunflower oil thermoxidation was evaluated using conventional process conditions (180 °C and atmospheric pressure) and vacuum technology conditions (130 °C and 0,1 bar). Traditional thermoxidation lasted 20 h while vacuum thermoxidation was completed after 56 h.

Total polar compounds reached 23 and 7,1 % at the end of atmospheric and vacuum thermoxidation respectively, while polymers content was 9,3 and 2,2 % for each oil. Tocopherols contents decreased 45 % for atmospheric thermoxidized oil and were reduced to 17 % for vacuum thermoxidized oil.

These results clearly proved vacuum thermoxidation achieved a significantly lower deterioration rate than atmospheric thermoxidation of sunflower oil, conferring it much longer useful life and better nutritional qualities. Accordingly, a significantly slower vanishing rate of tocopherols was observed in vacuum thermoxidation.

Keywords: Chemistry, Food science, Food technology

1. Introduction

Popularity of fried foods is related to the ease, speed and low cost of the preparation and because of the unique changes to the sensory and nutritional characteristics of the product, as well as for its preserving action.

The frying process leads to physical and chemical changes in both the oil and food. The changes produced occur simultaneously as a result of complex interactions between food and oil and are difficult to identify and analyze separately. Changes also depend on the characteristics of the food, oil type, history of thermal treatment, surface/volume ratio, rate of air incorporation, temperature, heating process, length of immersion, kind of material the frying container is made of, etc. The effects are difficult to estimate due to the variety of interfering factors. Some compounds are lost and others are produced during the process. Potentially toxic and/or carcinogenic compounds are developed and although widely studied, many have not been fully identified. In order to reduce the production it is very important to identify and study their formation.

Changes in the oil during the frying process have been studied and information has been compiled about the changes in food, but the details of the process are still a mystery. To fully understand the transformations produced by frying, the changes suffered by the oil in the absence of food must be studied as a first approach.

Traditional frying is conducted at atmospheric pressure and high temperatures around 180 °C. Over the last few years, vacuum frying was developed as an alternative methodology to traditional frying. In vacuum frying, foods are cooked in a closed reduced pressure system that decreases boiling point of frying oil and water present in the products. Water is rapidly eliminated when the temperature of the oil reaches water boiling point for the respective operating pressure. Considering foods cook at lower temperatures and with reduced exposure to oxygen, natural colors and flavors are preserved (Shyu et al., 1998). Therefore, many authors claim a quality improvement is achieved with vacuum frying.

Lately, this technology has been used for frying chips or crispy snacks. Some studies have been carried out to evaluate the influence of the process over the product, observing lower lipid absorption and smaller levels of acrylamide (carcinogenic potential), as well as good texture qualities, original color and flavor preservation and good retention of nutrients (Garayo and Moreira, 2002; Mariscal and Bouchon, 2008; Da Silva and Moreira, 2008; Yagua and Moreira, 2011; Crosa et al., 2014a; Belkova et al., 2018). Consequently, nutritional benefits of vacuum frying stand out. Considering the market's latest trends towards healthy eating, vacuum frying appears as a promising new technology.

Regarding the deterioration process suffered by the oil while frying, no reports have been made using procedures accepted by current regulations but exclusively employing quick measuring methodology, particularly for the estimation of total polar compounds (Shyu et al., 1998; Crosa et al., 2014b). A single article that compared oil deterioration in vacuum frying with oil thermoxidation in traditional frying was found (Crosa et al., 2014b).

To compare the two technologies adequately, equivalent thermal driving forces should be used in both experiments. This is accomplished by keeping a constant difference between oil temperature and water boiling point at the operating pressure (Mariscal and Bouchon, 2008). Therefore, given thermal driving force for traditional frying is 80 °C and the vacuum pump used in this study worked at 0,1 bar (with boiling temperature of water corresponding to 50 °C), vacuum thermoxidation operating temperature was 130 °C.

Sunflower oil is widely used in Uruguay. In particular, it is frequently employed for frying foods at home as well as in the restaurant business and the food industry (Pinchak et al., 2013). According to the manufacturer this variety comes in two versions, one with addition of antioxidants and the other exclusively with the natural antioxidants remaining after chemical refining. The second kind was used for this investigation.

In this study, the influence of vacuum thermoxidation (130 °C and 0,1 bar) on sunflower oil was evaluated and compared with its degradation in traditional frying conditions (180 °C and atmospheric pressure). For that purpose, total polar compounds, polar fraction composition, polymers content and tocopherol contents were determined in sunflower oil subjected under both thermoxidation processes.

2. Materials and methods

2.1. Raw material

Uruguayan refined sunflower oil (SFO) with no preservatives added was purchased from local market.

2.2. Vacuum thermoxidation of sunflower oil

600 g of SFO were placed in a vacuum flask with slow agitation by a magnetic stirrer and thermoxidized on a heating plate at 130 ± 5 °C and 0,1 bar of pressure. The heating time to reach test temperature was approximately 30 minutes. Considering the geometry of the flask and the height and diameters of the volume occupied by the oil, the surface/volume ratio was calculated as $0,073 \text{ cm}^{-1}$. Heating took place in food absence. The total time of thermoxidation was 56 hours.

Samples of about one gram were taken every four hours for further analysis. The surface/volume ratio of fat was not affected during the test since the intakes were very small in relation to the mass of material used. Thermoxidized samples were stored at -20 °C until the moment of their analysis.

2.3. Atmospheric pressure thermoxidation of sunflower oil

600 g of SFO were placed in an identical flask with slow agitation by a magnetic stirrer and thermoxidized on a heating plate at 180 ± 5 °C. The heating time to reach test temperature was approximately 30 minutes. The surface/volume ratio of the oil in the flask was $0,073 \text{ cm}^{-1}$, calculated as in 2.2. Heating took place in air presence and in food absence. The total time of thermoxidation was 20 hours.

Samples of about one gram were taken every four hours. The surface/volume ratio of fat was not affected during the test since the intakes were very small in relation to the mass of material used. Thermoxidized samples were stored at -20 °C until the moment of their analysis.

2.4. Determination of the total content of polar compounds

Standard method IUPAC 2.507 (IUPAC, 1992) was carried out but the technique was scaled down. The modification was verified and validated. Sample amounts of around $300 \pm 0,01$ mg were seeded in filtration columns (20 mL with septum, SUPELCO) loaded with 6,3 g of silica gel (dried at 160 °C for 4 hours, with water content adjusted to 5 %). The non-polar fraction was eluted with 65 ml of the elution mixture (petroleum ether:diethyl ether 90:10 v/v) into an evaporating flask. Polar compounds were then eluted with 50 mL of diethyl ether into a second flask. The solvents were removed by rotary evaporation. The polar fraction was stored for analysis by HPLC. Analysis were run in triplicate.

2.5. Polymers content

Standard method IUPAC 2.508 (IUPAC, 1992) was executed in thermoxidized samples to determine polymers levels. Samples were prepared in tetrahydrofuran (THF) at a concentration of 50 mg/mL. Determinations were carried out in a Shimadzu 20A HPLC with IR detector on Nucleogel GPC columns of 100 and 500 Å ($5 \mu\text{m} \times 300 \text{ mm} \times 7,7 \text{ mm}$). THF was used as mobile phase and the flow rate adjusted to 1 mL/min. Tests were run at least in duplicates.

2.6. Characterization of polar fraction

Polar fractions obtained in 2.4 were analyzed according to the method described by Dobarganes et al. (1988). Experiments were carried out at least in duplicates.

2.7. Tocopherol contents

Tocopherol contents in oil were determined according to the method used by Andrikopoulos et al. (1991). Determinations were performed at least in duplicates.

3. Results and discussion

3.1. Change in total polar compounds and polymers content

The SFO used in this investigation had a low content of total polar compounds (TPC) as shown in Fig. 1, and a peroxide value of $(1,9 \pm 0,1)$ meq/kg. The

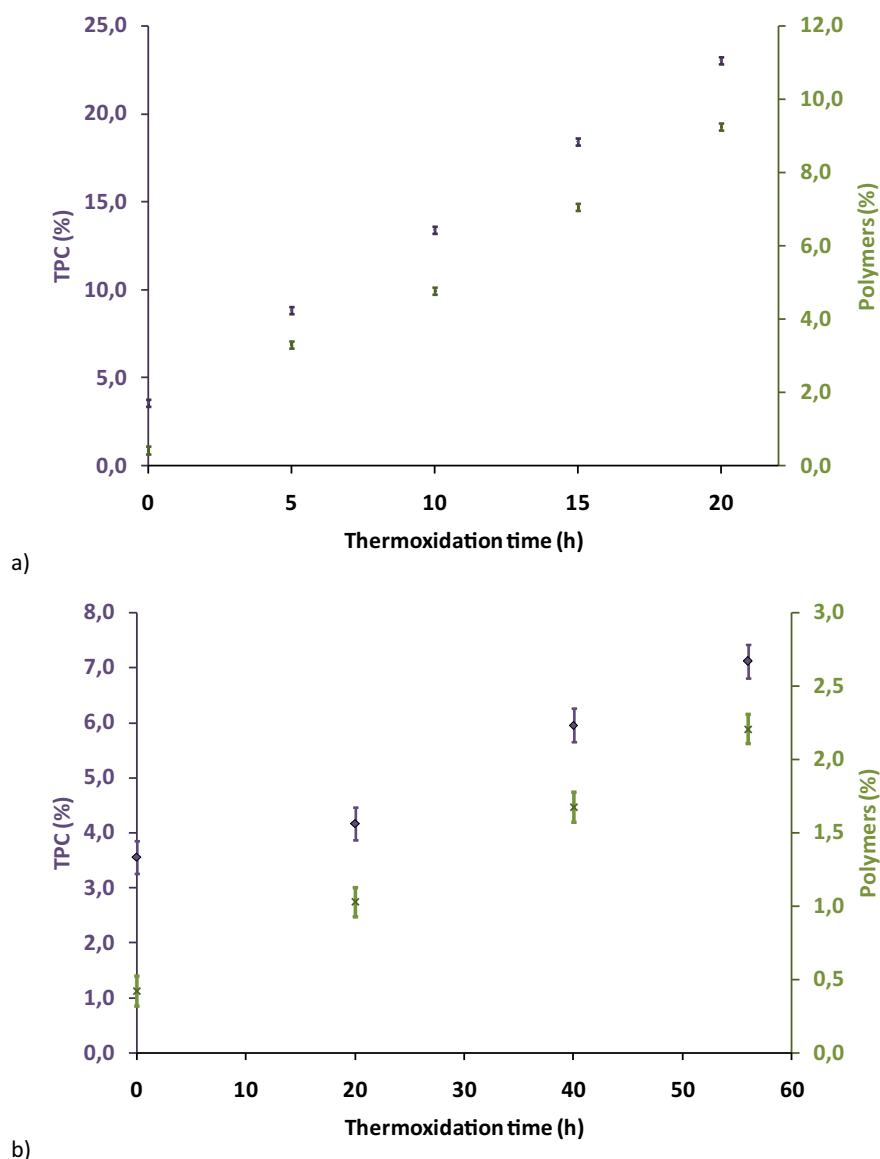


Fig. 1. Evolution of polar compounds and polymers with time of thermoxidation a) 180 °C and atmospheric pressure, b) 130 °C and 0.1 bar.

composition profile showed a high content of linoleic and oleic acid, with values among the typically found for this kind of oil and for regional varieties (35–75 and 14–55 % for each fatty acid respectively according to [Norm IRAM 55:29 Revision 2013-01-10](#)). As already mentioned, the SFO used for the experiments had no preservatives added but only the natural antioxidants that remained after chemical refining, with a total tocopherol content of (820 ± 20) ppm. Therefore, a high inherent oxidative stability was not expected but on the contrary a relatively rapid effect with thermal treatment was anticipated.

According to [Fig. 1](#) an increase in TPC and polymers content with time of thermoxidation was observed in both vacuum and traditional processes. These alteration compounds formed by oxidative and thermal reactions during the frying process, contribute to reduce the quality and modify the nutritional value of frying oils and fats ([Dobarganes et al., 2002](#)). At the end of atmospheric pressure thermoxidation total polar compounds reached a 23 % value while in vacuum thermoxidation only got to 7,1 %. Meanwhile, total polymers content was 9,3 and 2,2 % at the end of the operation for each oil respectively.

From this perspective, sunflower oil presented longer durability when used in vacuum frying conditions, reaching a TPC equivalent to 5 hours of atmospheric pressure thermoxidation at the end of the process. Roughly, sunflower oil could be used for vacuum frying for over 200 hours before reaching TPC values that made it ready for disposal.

3.2. Polar fraction characterization

With regards to the polar fraction composition with thermoxidation time, a decrease in hydrolytic and oxidative deterioration products contents (diglycerides + free fatty acids and oxidized triglycerides respectively) in both vacuum and traditional processes was observed, while thermal and secondary oxidative deterioration products contents (dimer and polymers) increased ([Fig. 2](#)).

Although deterioration rate was much slower under reduced pressure, the deterioration products observed were the same in both processes. For vacuum thermoxidation the non-variability of the TAGox content after a first decrease was surprising. Dimer formation observed during the same period ruled out the possibility of TAGox not deteriorating. Instead, TAGox were formed in a way that compensated the loss. [Crosa et al. \(2014b\)](#) and [Shyu et al. \(1998\)](#) inform accumulation of peroxides during vacuum frying for different fatty materials. This could explain the plateau observed for the TAGox content under reduced pressure.

3.3. Change in tocopherol content

At the end of the atmospheric pressure thermoxidation process, a degradation of about 45 % of tocopherols was observed in sunflower oil, while for the vacuum

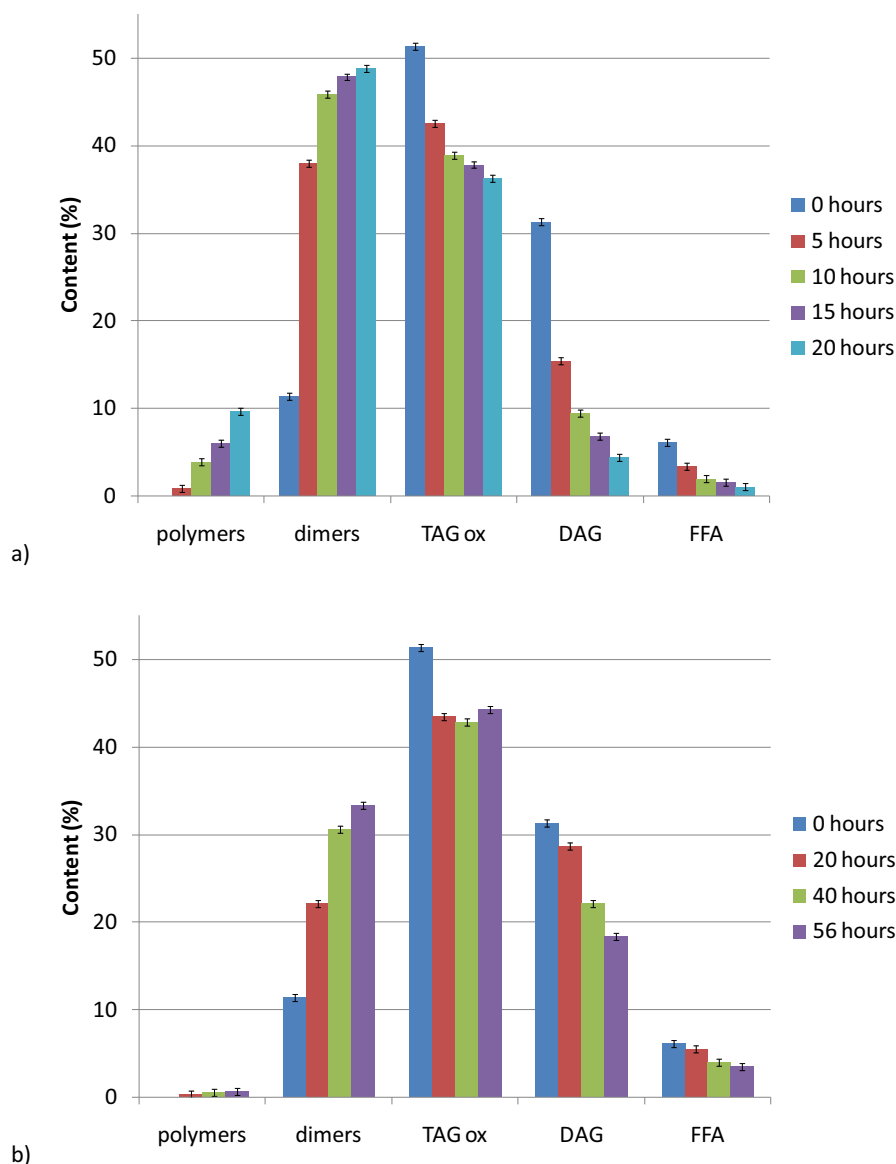


Fig. 2. Evolution of polar fraction composition with time of thermoxidation a) 180 °C and atmospheric pressure, b) 130 °C and 0,1 bar. TAG ox: oxidized triacylglycerides; DAG: diacylglycerides; FFA: free fatty acid.

process tocopherols decreased 17 % (Fig. 3). Once more, at the end of vacuum thermoxidation tocopherol values were similar to those obtained for 5 hours of traditional thermoxidation.

Preservation of natural antioxidants for longer periods probably gave greater protection and longer stability to the oil when working with reduced pressure. Therefore, this technology should be taken into account while developing fatty food products with better oxidative stability to extend shelf life after cooked.

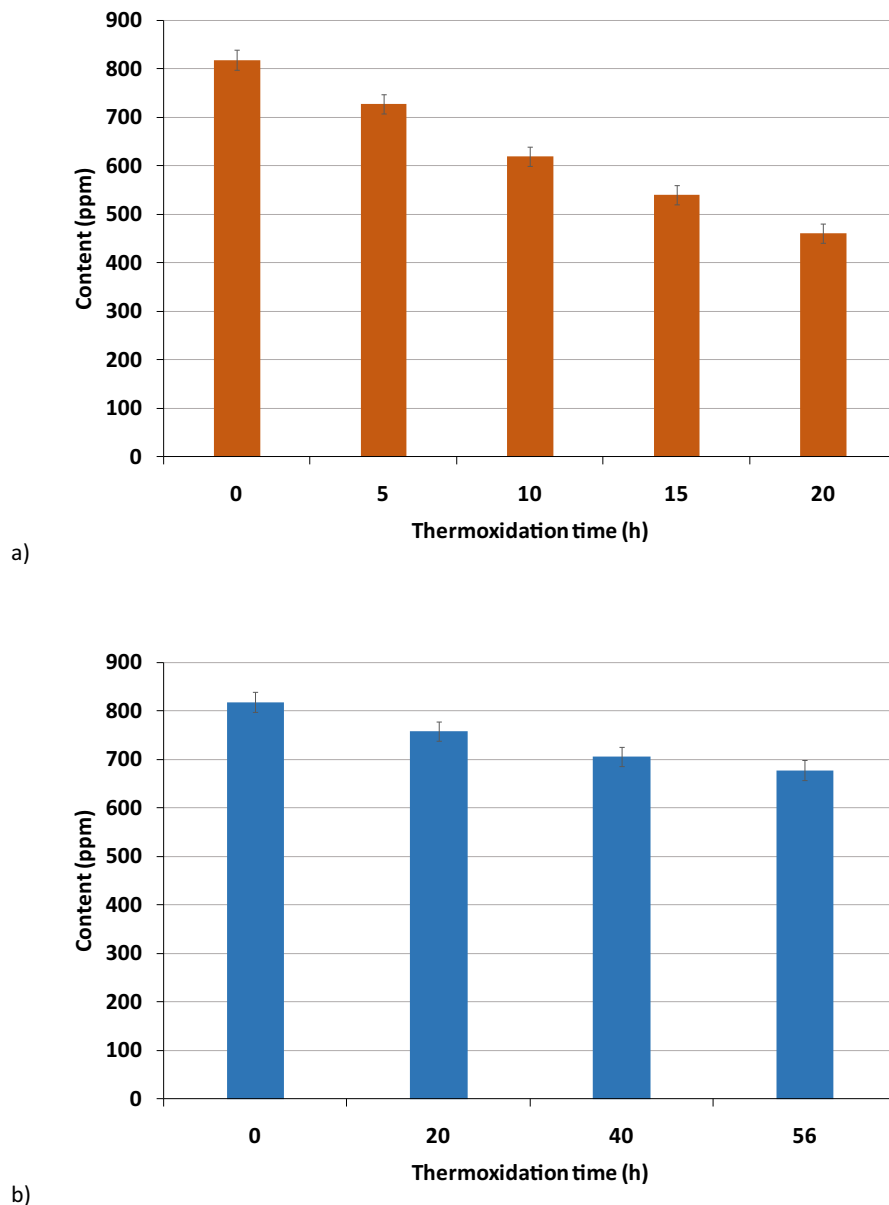


Fig. 3. Evolution of tocopherol contents with time of thermoxidation a) 180 °C and atmospheric pressure, b) 130 °C and 0,1 bar.

4. Conclusions

The results obtained clearly demonstrated a significantly slower deterioration rate of sunflower oil for vacuum thermoxidation than for traditional frying conditions, accordingly with the slower loss of tocopherols observed in the first scenario. In conclusion, vacuum frying process causes much less deterioration of the oil and therefore it is an encouraging methodology for the preservation of existing bioactive compounds in the frying oil such as antioxidants among others, as well as for producing healthier food alternatives.

Declarations

Author contribution statement

Nadia Segura: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Jimena Lázaro: Performed the experiments; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Bruno Irigaray: Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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