



IWIMSM-03: Iberoamerican Workshop on Model. and Simulation Methods, Valencia, Spain, 2019



Implementation of a method of analyzing the oxidative stability of margarines and improving it by adding plant species

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Graphical Abstract

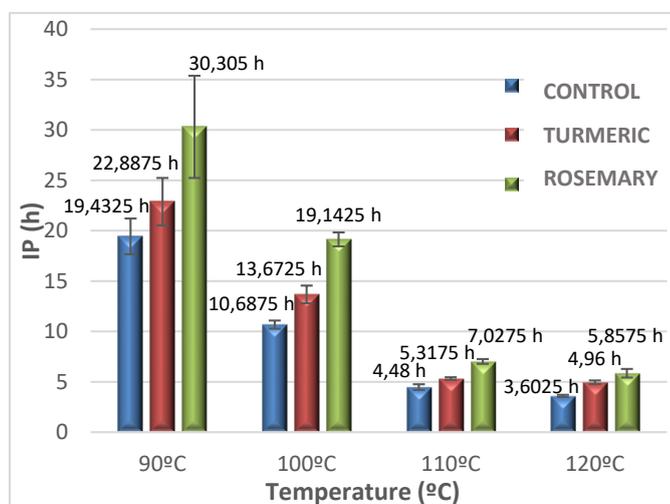


Figure 1. Comparison between the antioxidant efficacy of turmeric and rosemary in Tulipán margarine sample at different temperatures (90, 100, 110, 120 °C). The results are presented as mean ± SD.

Abstract

Lipid oxidation is the main process of deterioration of oils and fats that negatively affects the taste of food and its nutritional value. In this research, an implementation study of an oxidative stability analysis method of margarines was carried out, which turn out to be W/O emulsions. An analysis was made of two margarines of different composition in fatty acids at 90, 100, 110 and 120 ± 1.6 °C. In addition, it was decided to complete the investigation with the study of the oxidative stability of margarine in response to the addition of two different spices (rosemary and turmeric) through the Rancimat test. The study carried out with two margarines of different composition in SFA/UFA demonstrated how the

oxidative stability in margarines with higher content in SFA, is significantly higher with respect to margarines that present lower percentage of these.

The present investigation was completed through the study of the oxidative stability of margarine as a response to the treatment with turmeric and rosemary. Rosemary showed maximum antioxidant efficacy compared to turmeric. At 110 and 120 °C rosemary increased the IP of $2,5475 \pm 0,27$ h and $2,255 \pm 0,20$ h, compared to the control margarine.

KEY WORDS: antioxidant, emulsions, fat, lipid oxidation, margarine, oil, oxidative stability, Rancimat, rosemary, turmeric, SFA, UFA.

Introduction

To address some of the main current health problems and follow the most recent nutritional recommendations, in recent years the additional incorporation of polyunsaturated fatty acids (PFA) $\omega 3$ and $\omega 6$ into food (Ganesan, B *et al.*, 2014). However, the literature demonstrates how the oxidative stability of foods containing fats depends on the type and proportion of fatty acids (FA), the higher the saturation of fatty acids, the greater their stability (Tao, L., 2015). Lipid oxidation products have cytotoxic, carcinogenic properties and are considered risk factors for human health (Hosseini, H *et al.*, 2016). In order to control the oxidative process, the food industry uses synthetic antioxidants such as tert-butylhydroxyanisole, BHA (E-320) and butylhydroxytoluene, BHT (E-321). Due to reports on the possible toxic effects of these compounds, there is a growing consumer demand for natural products and interest in natural antioxidants has increased in recent years. Phenolic compounds are secondary metabolites characterized by their beneficial action for human health, since they play an essential protective role against oxidative phenomena and have therapeutic effects in a large number of pathologies (Mena, P. *et al.*, 2017).

Lipid oxidation has been widely studied in fats and oils and there is now a fairly good understanding of the factors that affect oxidation in such systems (Redondo, L. *et al.*, 2018). However, the understanding of the factors that affect lipid oxidation in certain types of systems such as food emulsions are still quite poor, considering the large amount of foods that consist entirely or partially of emulsions (milk, mayonnaise, margarine, ice cream, soups, baby food etc.).

Objectives

Recent studies have shown how the oxidative stability of different vegetable oils depended, in addition to other factors, on their fatty acid composition and improved when rosemary powder was added, a plant with a high content of polyphenols (Redondo, L. *et al.*, 2017; 2018).

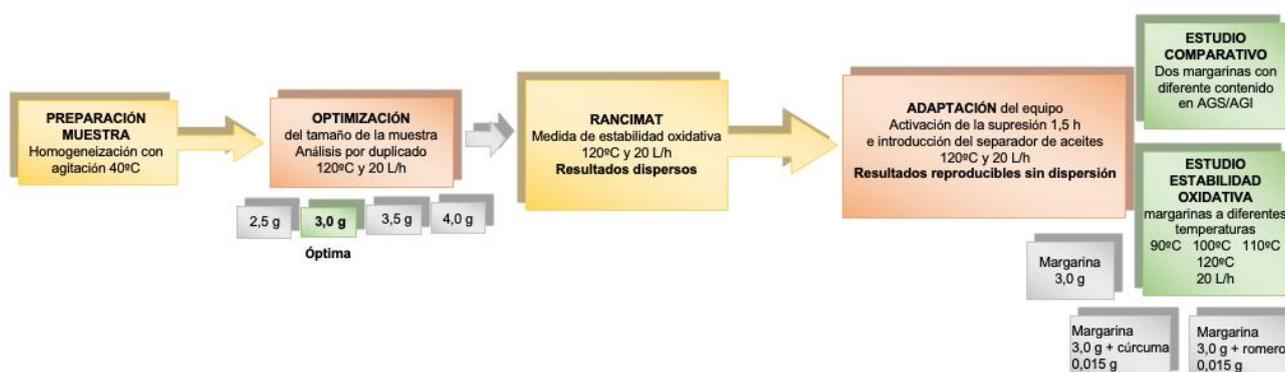
This led to the following objectives for the present study:

1. Design and execute an oxidation stability analysis protocol suitable for margarines that includes the optimization of the sample quantity, the determination of the appropriate test temperature, the adaptation and improvement of the equipment.
2. Relate the chemical composition of two margarines (content of saturated and unsaturated fatty acids) with the oxidation period.
3. Add spices selected for their documented antioxidant activity and see the effect on the oxidative stability of margarines at different temperatures.
4. Compare the results obtained in margarines with those obtained in oils.

Materials and Methods

The Rancimat model 892 automated device (Metrohm, Switzerland) was used.

To achieve the objectives, the work plan described below is developed:



Results and Discussion

The samples of 3.5 ± 0.001 g (0.885 ± 1.15 h) and 4.0 ± 0.002 g ($1,025 \pm 1.33$ h) showed negligible IP values ($P < 0.05$) and outside the time range required, which is between 2-6 h (892 Professional Rancimat Manual, 2017). The samples of 2.5 ± 0.001 g (3.185 ± 0.65 h) and 3.0 ± 0.001 g ($4,035 \pm 0.92$ h) were kept within the expected IP interval. In the absence of statistically significant differences between the two quantities, it was decided to determine 3.0 ± 0.001 g as the optimal amount to compensate water losses by evaporation. However, the dispersed results led us to propose an adaptation work. It was assumed that the water content present in the margarines could affect the detection of IP.

The IP results at $120 \pm 1,6$ °C of the Rancimat optimization ($3,415 \pm 0.42$ h), obtained by activating the 1.5 h suppression and using the oil separator, presented statistically significant values ($P < 0.05$), the trials showed reproducibility and consistency. If samples with a high content of highly volatile compounds, such as margarine, are used, there is a risk that it will be transferred to the measuring vessel in the vapor phase.

The study of Tulipán margarine (15% SFA, 15% MFA and 26% PFA) and Naturlí margarine (26% SFA, 33% MFA and 12% PFA) indicated how long it took for the Naturlí sample to oxidize at 120 °C ($10,415 \pm 0.45$ h) was significantly higher than that at the same temperature of the Tulipán sample (3.65 ± 0.20 h). The results were consistent with those obtained with oils (Redondo, L. *et al.*, 2018). Fewer unsaturated components generate less radical oxidation products and therefore have greater oxidative stability and longer induction time. The study at 90 °C ($20,455 \pm 3.05$ h), showed more variability with an SD of 3.05 h. It is likely that since no evaporation phenomenon occurred at these temperatures, the water content present in the sample could have affected the

detection of IP. These results indicated that 90°C is not an acceptable temperature when working with margarines using the Rancimat method, so a study at temperatures $\geq 100^\circ\text{C}$ is advised.

The treatment of the Tulipán sample with turmeric and rosemary showed an evident improvement in the oxidative stability of margarine (fig.1). Rosemary treatment showed maximum antioxidant efficacy compared to turmeric. The results obtained showed the highest antioxidant efficiency at $90 \pm 1.6^\circ\text{C}$ with an increase in the IP of $10.8725 \text{ h} \pm 7.42 \text{ h}$ with respect to the control sample, however, the results were not significant ($P < 0.05$). At 110 and $120 \pm 1.6^\circ\text{C}$ rosemary increased the IP of $2,5475 \pm 0,27 \text{ h}$ and $2,255 \pm 0,20 \text{ h}$, respectively. The results are statistically significant, they show reproducibility and significance, although the increase in IP with respect to the other temperatures turns out to be less evident.

Conclusions

1. The optimal amount of margarine was 3.0 g. The 1.5 h suppression together with the use of the oil separator, prove to be essential for the study of the oxidative stability of margarines. $T \leq 90 \pm 1.6^\circ\text{C}$ are not ideal when working with margarines using the Rancimat method.
2. The study carried out with the Naturlí and Tulipán margarines confirmed that the type of FA (in addition to other factors) determines oxidative stability in margarines and that the IP in margarines with a higher content of SFA is significantly higher.
3. Turmeric can be used as a source of effective natural antioxidants. The addition of rosemary significantly increased the oxidative stability of margarine compared to that studied with turmeric.
4. When comparing corn oil with Tulipán margarine that have similar % SFA, margarine is more stable because it has lower % UFA. In general, the oxidative stability of the margarine studied is greater than that of a pure vegetable oil with and without spices. This demonstrates the different behavior of oils and margarines against oxidative stability as predicted in our initial hypothesis.

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