Oxidative Stability of Margarine Enriched with *Phoenix canariensis* L. Date Peel Extract

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ABSTRACT: *This paper concerns the oxidative stability of experimental reduced-fat margarine (EM) enriched with canariensis red date peel powder extracts. For this, the two phases intended for obtaining the margarines were used first as extraction solvents. Both enriched phases thus obtained are then employed to formulate different margarine samples. In addition to color and rheological behavior, margarine samples were characterized in terms of oxidative stability which was evaluated through the peroxide value, Q_{10}-factor and activation energy (Ea). Results showed that all the margarines formulated by addition of date peel extract presented high values of a* and b* parameters, compared with those of reference and commercial origin ($p<0.05$).The best oxidation resistance of different experimental margarines was obtained when the sample was added with: (i) the aqueous extract-ingredient, in the case of storage at 30°C, and (ii) the both aqueous and oil extract-ingredients, in the case of storage at 5°C. Results showed that the models applied (zero-order, first-order, polynomial, logarithmic and power law) differently described the oxidation kinetics ($R^2 \leq 0.993$), according to the margarine type and storage temperature. Globally, Q_{10} and Ea parameters varied within wide intervals of values (0.8-4.0 and 3.4-95.9kJ.mol^{-1}, respectively) according to margarine nature. So, the present study demonstrated the possible application of Phoenix canariensis red date peel extract as a natural colorant and antioxidant in margarine and other food formulations.*

KEYWORDS: *Experimental reduced-fat margarine; Phoenix canariensis L. Red date peel powder extract; Oxidative stability; Color; Rheology; Modeling; Extract-ingredient.*

INTRODUCTION

The margarine can undergo different types of deteriorations, the most significant one being the oxidation phenomenon. The oxidation products of lipids are known for their toxic effects on health, since they are associated with various physiological disorders, including cardiovascular diseases and cancers. As protection measure against oxidation, the addition of synthetic antioxidants such as butyl hydroxytoluene (BHT) are generally recommended, but consumers are now aware to what extent these chemicals may pose health risks [1]. This leads to the limitation of their industrial application and there is a trend to substitute them with natural plant

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antioxidants [2]. For instance, the sauge (*Salvia officinalis*) extract was recently found to be a natural health promoting antioxidant for sunflower oil [3].

To the best of our knowledge, only two works were devoted to the enrichment of margarine by plant extracts, namely date (*Phoenix dactylifera* L.) extract [4] and ethanolic extract of *Thymus vulgaris* [5]. Furthermore, *Lopes et al.* [6] have studied the antioxidant effect of various spices which were then added to margarine as substitutes of ordinary sodium chloride.

Substances from plants have recently attracted much attention with regard to human health, due to their antioxidant activity and low toxicity, among others [7]. This growing interest for natural antioxidants has led to the development of several methods for the extraction of bioactive compounds [8]. Regarding the extraction procedures, it is well established that chemical extraction involves organic solvents which are harmful to human and environment [9]. So, extraction procedure is one of the promising innovation themes that could contribute to sustainable growth of chemical and food industries [10].

The present work aims to investigate the oxidative stability of Experimental reduced-fat Margarine (EM) enriched by *Canariensis* Red Date Peel Powder (CRDP) extracts. For this, the two phases intended for obtaining the margarines were used first as extraction solvents. Both enriched phases thus obtained are then employed to formulate different margarine samples. It must be noticed that the date palm *Phoenix canariensis* L. (family of *Palmacea*) originated in the Canary Islands and it is now largely cultivated in all over the world as ornamental garden plant.

EXPERIMENTAL SECTION

Samples and chemicals

Sunflower, palm and stearin oils without any additive were supplied by COGB La Belle SPA /Algeria.

Phoenix canariensis L. date fruits were collected on a palm tree of the ORGM (National Office of Geological and Mining Research) garden, in Boumerdès city (40 km east of Algiers). Fruit samples were transported to the laboratory in polyethylene bags to avoid external contamination and were then stored at 5°C until analysis.

All the used solvents and reagents are of analytical grade and were purchased from Sigma-Aldrich, Co (Germany).

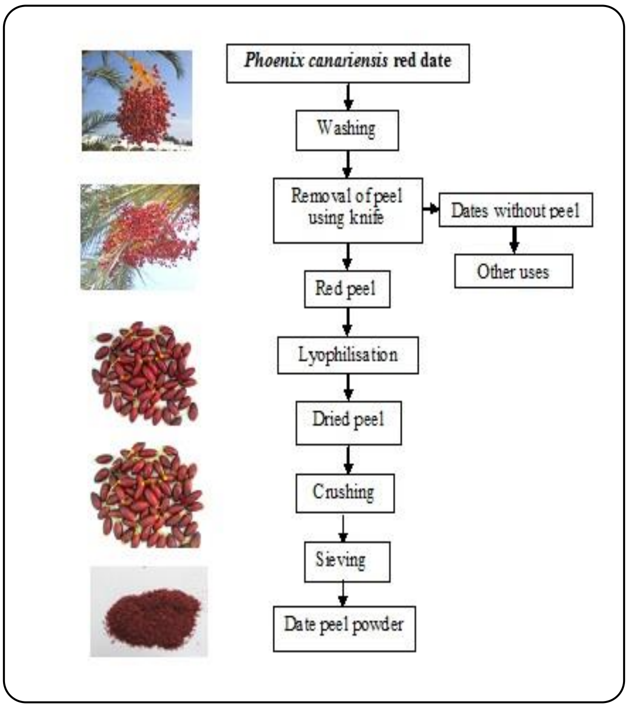


Fig. 1: Procedure of preparation of canariensis red date peel powder (CRDP).

Extracts-ingredients (E-I) preparation

First, the CRDP was obtained according to the diagram of Fig. 1. The peel was recovered by manual scraping with the home knife, while the freeze-drying was performed using a lyophilizer CRYODOS Telstar (Terrassa, Spain).

CRDP extracts which are intended to be incorporated in EM samples are designed here as extract –ingredients (E-I). For this, the two phases intended for obtaining the margarines were used first as extraction solvents. Both enriched phases thus obtained are then employed to formulate different margarine samples. So three types of extraction solvents were considered: (i) the fat phase, allowing to obtain fat-E-I, (ii) the aqueous phase, allowing to obtain the aqueous-E-I, and iii) the mixture of fat-E-I and aqueous-E-I (1:1, weight/weight).

The two basic E-I were prepared as follows:

- Fat-E-I: the fat phase was mixed with 1% (w/w) of CRDP. For this, the required CRDP amount was weighed in beaker, and then mixed with the melted at 50°C-oil phase (mixture of oils: sunflower, palm and stearin). The obtained suspension was maintained at 50°C during 20 min under continuous stirring. It was then filtered through a Whatman No. 1 filter paper to eliminate

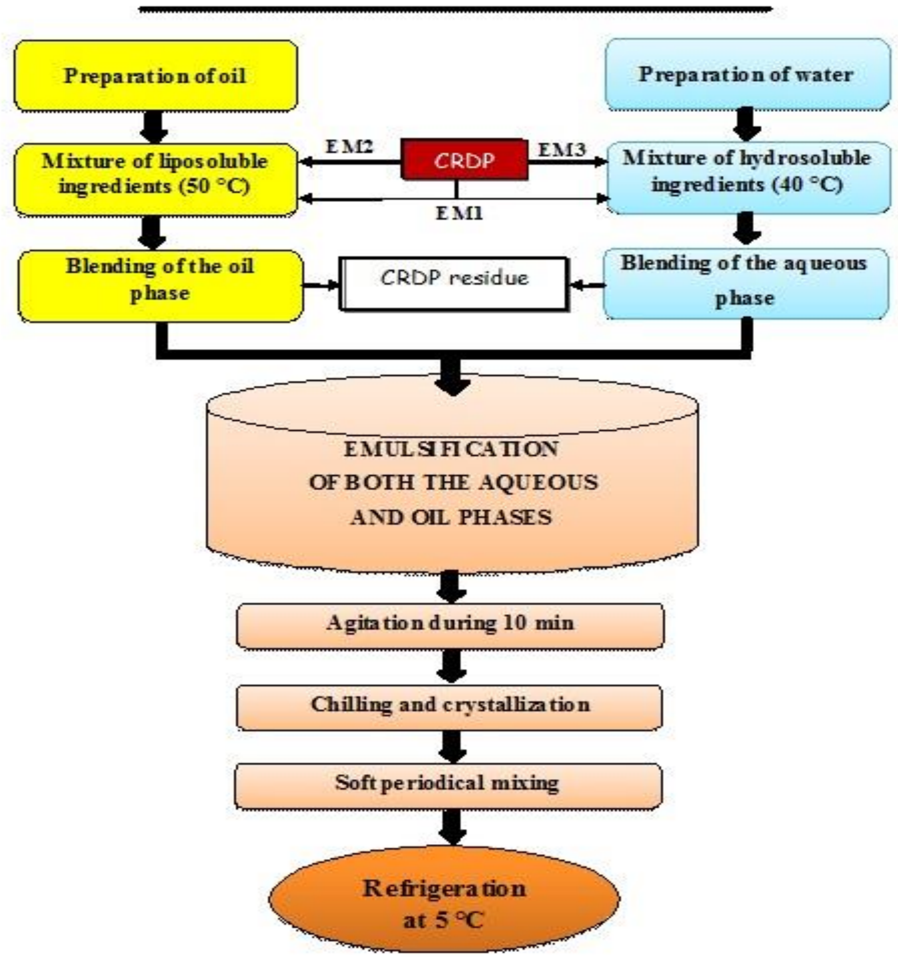


***Fig. 2:** Diagram of preparation of experimental reduced-fat margarine (EM), at laboratory scale. The EMs were added with canariensis red date peel powder (CRDP) extract using the following phases as solvents: both fat and oil phases (EM1), only the oil phase (EM2), and only the aqueous phase (EM3). EM0: standard margarine sample (not added with CRDP extract).*

the solid particles. The fat-E-I corresponds to the filtrate.

-Aqueous-E-I: the previous procedure was applied by replacing only the fat phase by the aqueous phase.

EM preparation

After several trials, the concentration of 1% of CRDP was retained for all elaborated margarine samples, taking into account the specific yellow color of the formulated EM which should be close to that of butter.

EM samples were prepared according to the technological scheme adapted from the classical one (Fig. 2).

The formula is as follow: fat phase (blend of sunflower, palm and stearin oils) (60%), water (38.25%), salt (0.1%), citric acid (0.15%), soy lecithin as emulsifier (1%, dissolved in oil phase) and CRDP (1%) in the case of EM1, EM2 and EM3 (see Fig. 2 and the paragraph below).

Three different EM samples were obtained according to the E-I type used:

- EM0: margarine of reference (not added with CRDP extract).
- EM1: added with both fat-E-I and aqueous-E-I. Here, each E-I was prepared from a suspension containing initially 0.5% (w/w) of CRDP.
- EM2: added with fat-E-I
- EM3: added with aqueous-E-I

Color and rheological properties of freshly obtained EM samples

It must be recalled that the food color is considered one of the most important external factors of food quality, able to influence consumer acceptance [11]. The color parameters of CIELab system were determined by means of colorimeter CR-10 Konica, Minolta (Japan). The significance of determined color parameters is as follows:

L*: from 0% (black) to 100% (white), a*: from –60 (green) to +60 (red) and b*: from blue −60 (blue) to +60 (yellow).

Rheological property of food products is very important for several aspects such as the effect on mouth feeling [12].

The rheological behavior of EM was assessed using a Thermo HAAKE viscometer, VT-550 (Haake, Germany), equipped with a rotation device and a cone-plate connected to data processing software (Win Rheo Data Manager, Pro 2.96). For comparison purposes, local commercial butter (mark SARL-Betouche) and margarines (CM), including reduced-fat (mark Bellat, Algeria) and ordinary (mark LaBelle) ones were also studied. EM samples were placed (at 20°C) between the plate (30 mm of diameter) and the cone with an angle of 1° (and 28 mm in diameter; PK1, 1°). The EM samples were then subjected to a short pre-shear of 10 s at low speed, followed by a shear stress that induces the rotational movement of shear (rates ranged from 0 to 200 s^{-1}). The flow curves ($\tau = f(\dot{\gamma})$) were recorded and subjected to various rheological models to see the best fit, using Rheo Win software.

EM oxidative stability and modeling

The stability of EMs was studied by monitoring the peroxide value (*PV*) according to AOCS method [13], at ordinary storage conditions (5 ± 1°C) and at accelerated oxidation conditions (30 ± 1°C) during 20 days. As a measure of primary oxidation products, namely fatty acid hydroperoxides, the *PV* represents the most popular indication of lipid oxidation [14] and it is accordingly taken here as the quality criterion.

According to the kinetic of physicochemical transformations occurring in foods, under isothermal conditions, the time- dependence of *PV* can be described by the following well known general differential equation:

$$d(PV)/dt = k(PV)^n$$

where t is the storage time, k is the rate constant and n is the order of the food transformation reaction. The typical integrated forms frequently encountered in food processing are the following zero- and first-order models:

- zero order:

$$PV = k\,t + PV_0$$

where PV_0 and PV are the PV values at initial and any time, respectively.

- First order:

$$\ln PV/PV_0 = k\,t$$

Such equation is for example proposed by *Özilgen and Özilgen* [15] for modeling the oxidation of animal food lipids. A first order equation was also applied to describe the autoxidation in the last half of the autoxidation process of polyunsaturated fatty acid esters [16].

Lately, *Xia et al*. [17] proposed the polynomial functions to investigate *PV* and epoxide content of oxidized oils. The second-order equation was adapted here as follows:

$$PV = k_1t^2 + k_2t + PV_0$$

where k_1, k_2 are the model constants.

In addition, two other mathematical equations were tested:

- Logarithmic model:

$$PV = k_3 \ln(t) + a$$

where k_3 and a are the model parameters.

This model was used for example to describe the kinetic of whey isolate proteins aggregation [18].

- Power law:

$$PV = k_4t^b$$

where k_4 and b are the model parameters.

The power law model is frequently used for investigation the diffusion kinetic of bioactive substances during liquid-solid extraction [19], knowing that the mass transfer of oxygen through the oil-water interface can significantly accelerate the autoxidation of oil-in-water emulsion [16].

In addition to the correlation coefficient (R^2), the model adequacy was verified by means of the following statistics:

Mean Relative Error (MRE):

$$MRE = \frac{100}{n}\sum_{i=1}^{n}\frac{\left(PV_{calc,i} - PV_{exp,i}\right)}{PV_{exp,i}}$$

Standard error (S):

$$S=\sqrt{\frac{\sum_{i=1}^{n}\left(PV_{exp,i}-PV_{calc,i}\right)}{n-m}}$$

Where $PV_{calc,i}$: the calculated by the model peroxide value, $PV_{exp,i}$: the experimental peroxide value, n : the number of experimental points and m: the number of parameters of the model.

Effect of temperature on oxidation rate

The temperature dependence of oxidation rate was studied through Q_{10} - factor defined as follows:

$Q_{10} = k_{T+10} / k_T$

where k_T and k_{T+10} are the rate constants at temperatures T and T+10°C, respectively. It can be calculated from at least two constant rates (k_1 and k_2) obtained at two temperatures (T_1 and T_2) regardless of whether or not they are 10°C apart [20], using the following equation:

$Q_{10} = (k_2/k_1)^{10/(T2-T1)}$

Q_{10} quotient is widely used to estimate the temperature dependence of food chemical reactions.

At last, the activation energy (E_a) was calculated, based on the relationship between E_a and Q_{10}:

$E_a = 0.1\ RT_1T_2 \ln Q_{10}$

Where, R = ideal gas constant = 8.31 J/mol.K, T_1 and T_2 = absolute temperatures (in K).

The latter equation can be easily reformulated as follows, considering the concrete values of T_1 and T_2 applied in the present work:

$E_a = 0.0001\times8.31\times303\times278\times0.4\ln(k_{30}/k_5)$ or

$E_a = 28 \ln(k_{30}/k_5)$

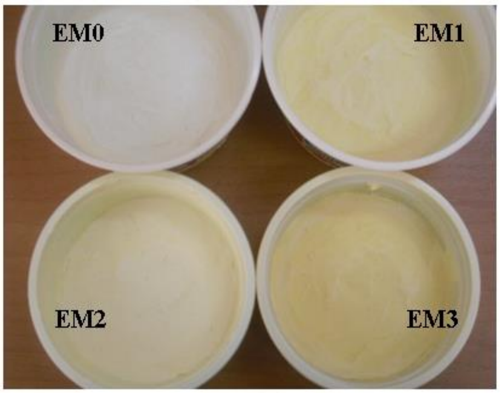
Statistical analysis

The results in triplicate were expressed as mean ± standard deviation. The analysis of variance (ANOVA) was performed by XLSTAT 2011 to determine the least significant difference at the level of $p<0.05$.

RESULTS AND DISCUSSION

Color and rheological properties of freshly obtained margarines

All the margarines formulated by addition of date peel extract (EM1, EM2 and EM3) present a specific colored aspect (Figure 3a), with high a^* (redness) and b^* (yellowness) values, compared with EM0 and CM ($p<0.05$) (Figure 3b).



(a)

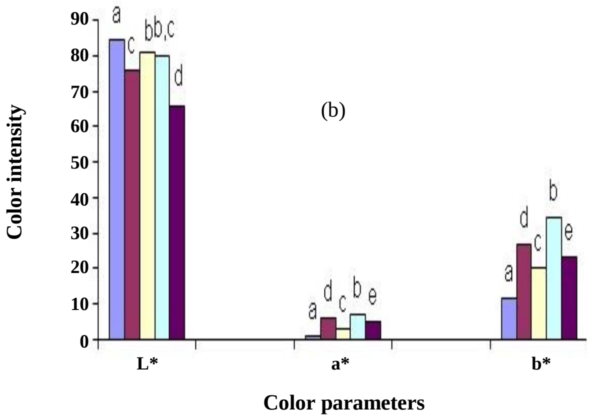


Fig. 3: Photographs of EM samples added with CRDP extracts (a) and corresponding color parameters in CIELab system (b) EM1, EM2 and EM3 represent enriched margarines. EM0 and CM are laboratory non-enriched and commercial margarines, respectively. See Fig.2 for more information.

Among the three enriched margarines, EM3 (added with aqueous extract-ingredient) shows the great a^* and b^* values ($p<0.05$), demonstrating the hydrophilic character of CRDP pigments. The L^* values of the three fortified margarines are close to those (72-76) found by *Tiwari et al.* [21] regarding laboratory margarines added with a blend of palm stearin and coconut oil.

The rheological models associated with different samples appear to be significantly influenced by the dissolution phase of the CRDP (Table 1). Thus, Bingham model related to visco-plastic fluid was found to be the most adequate for EM0 (R^2~0.80). Its mathematical expression is as given below:

$\sigma = \sigma_0 + \eta\gamma$

where σ_0 = yield stress, needed by the product to go from high viscosity to low viscosity; η = Bingham plastic viscosity.

Table 1: Parameters of rheological models related to elaborated margarine samples.

Margarine	Model	Parameter						R^2	χ^2
		σ_0	η	η_0	η_∞	m	n		
EM0	Bingham	167.6	0.374	-	-	-	-	0.808	<0.1
EM1	Cross	-	-	182.9	-0.2219	2.734	1.038	0.987	-
EM2	Cross	-	-	69.07	0.1778	15.69	1.368	0.972	<0.1
EM3	Cross	-	-	48.38	0.0725	14.02	1.532	0.990	<0.1
Butter	Cross	-	-	144.3	-0.3809	6.873	1.122	0.830	<0.1
CM Labelle	Cross	-	-	151.9	-95.64	7.497	0.109	0.757	<0.1
CM Bellat	Cross	-	-	132.3	-3.546	24.12	1.124	0.962	< 0.1

σ_0 = yield stress, η = Bingham plastic viscosity, η_0 = zero-shear viscosity, η_∞ = viscosity at infinite shear rate, m = constant time, and n = dimensionless exponent which controls the rate of thinning.

The Cross model which is described by the following four-parameter equation [22] correctly fits experimental data of EM1 (R^2~0.98), EM2 (R^2~0.97), and EM3 (R^2~0.99), indicating their pseudo-plastic or shear-thinning behavior:

$$(\eta - \eta_\infty)/(\eta_0 - \eta_\infty) = 1/[1+(m\gamma)^n]$$

$$\text{or } \eta = \eta_\infty + (\eta_0 - \eta_\infty)/[1+(\gamma/\gamma_c)^n] \text{ with } m = 1/\gamma_c$$

where η_0 = zero-shear viscosity, η_∞ = viscosity at infinite shear rate, m = constant time related to the relaxation times of the polymer in solution, γ_c = critical shear rate associated with sudden onset of shear thinning, n = dimensionless exponent which controls the rate of thinning.

These findings demonstrate the incontestable impact of the CRDP extract on the rheological behavior of different margarine samples. In fact, it is well-known that rheological properties of food emulsions can vary from low viscosity Newtonian liquids to plastic materials, such as margarine [23]. Thus, among investigated margarine samples, only EM0 showed a Bingham plastic behavior which is well established to be the most appropriate to describe flow curves of soft foods like margarine. For such products a predetermined shear stress is needed in order to start flowing. Cross model characterize flow behavior of polymer dispersions and other shear-thinning fluids. We think that CRDP phytochemicals present in fortified EMs induced such flow behavior. This was confirmed by the tendency of *n* values to unity (Table 1). Furthermore, the Cross model fit experimental data more accurately (R^2 = 0.99) in the case EM3. This may be explained by the fact that the CRDP bioactive substances are hydrophilic and they are subsequently better extracted and dispersed by the margarine aqueous phase. It can be also noted that globally, the Cross equation produces better fit than the Bingham model does (Table 1). The applicability of the former equation is also verified by *Hayati et al.* [24] for O/W emulsions from blends of soybean oil and palm kernel olein.

EM oxidative stability and modeling

The evolution of the margarine *PV* during storage at 30 and 5°C is illustrated in Figs. 4a and 4b, respectively.

The choice of the temperature of 30°C is justified by the fact that at this condition, the oxidation is accentuated while the destabilization of the margarine structure as emulsion is avoided. Moreover, this temperature expresses the highest temperature reached during certain periods of the year in the north of Algeria. In contrast, the temperature of 5°C is the refrigeration temperature recommended for margarine storage.

From curve shapes of Fig. 4a, it can be easily noticed that, compared to enriched samples, the control margarine sample is more susceptible to the oxidation during the entire observation period. The classification of

the oxidation resistance of EMs can be expressed in the following order (based on PV values): EM3> EM1> EM2> EM0. There is a significant difference between PV values of all EM samples ($p<0.05$) at the 20th day. From these results, EM3 (margarine containing aqueous-E-I) appears to be the most stable, proving, therefore, the polar character of antioxidant molecules from CRDP.

The evolution of the PV of EM versus storage time, at 5°C, is shown in Fig. 4b. Again, enriched margarine

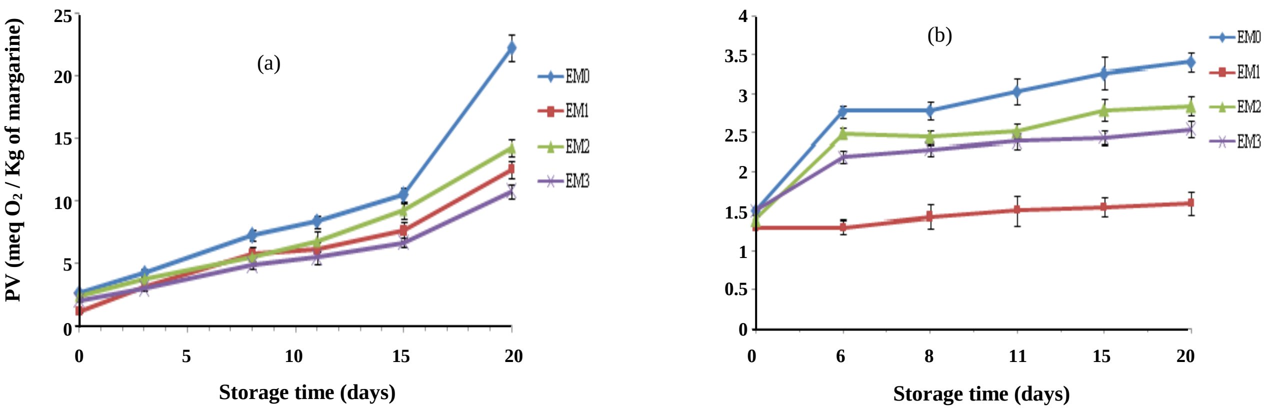


Fig. 4: Peroxide value (PV) of experimental reduced-fat margarine (EM) versus storage time: (a) in oven (30°C), and (b) in fridge (5 ± 1°C).

at 5°C, is shown in Fig. 4b. Again, enriched margarine samples remain more stable, compared with EM0, during over the observation period (20 days). The following classification of the oxidation resistance capacity of EM samples can be given: EM1 (containing the blend of aqueous-E-I and oil-E-I)> EM3> EM2> EM0, indicating the synergistic effect between the two types of E-I.

The high oxidative stability of enriched margarines (EM1, EM2 and EM3) with respect to the non-enriched margarine (EM0), for the two temperatures (5 and 30 ° C) considered, clearly demonstrates the antioxidant potential of the peel of red date of the canariensis variety. It is worth noting that canariensis red date peel was investigated for its phytochemical composition, color parameters and antioxidant potential and it was found that the peel presents an exceptional reducing power (about 44 mg ascorbic acid equivalent per g of dry matter) (own unpublished observations).

From data of Fig. 4, the stabilizing effect of refrigeration can be easily observed since at any time, the PV level at 5 °C is lower than that at 30 °C whatever the EM sample. In addition, at both storage temperatures, the induction period is absent, demonstrating the complex structure of margarine samples. Our results are in concordance with those communicated by *Chong et al.* [25] concerning the high oxidative stability of sunflower oil when added with mangosteen peel extracts. Furthermore, the stability at 5 °C of enriched EM is comparable to that found by *Tiwari et al.* [21] for two laboratory margarines containing a blend of palm stearin and coconut oil in different proportions. In fact, these authors have found that the peroxide value of studied margarine samples stored at 24°C changed approximately from 1.5 (1st day) to 2.5 meq O_2/kg (8th day).

Presently, the modeling consists of predicting the oxidation rate of EM as a function of time, at different temperatures. This allows a better shelf life estimation and management. The modeling results (Tables 2 and 3) indicate that the adequacy of models depends on both the nature of the margarine and the applied storage temperature. At 30°C (Table 2), the first order (case of EM0 and EM3) and polynomial (cases of EM1 and EM2) models are the most appropriate (R^2= 0.962-0.993, MRE = 6.327-10.431, S = 0.455-1.502). At 5°C (Table 3), the power (EM0 and EM2), polynomial (EM1) and logarithmic (EM3) models correctly describe the experimental data (R^2 = 0.950-0.993, MRE =1.042-4.032, S = 0.036-0.203). These findings are partially in concordance with available literature data. Thus, *Crapiste et al.* [26] have communicated the goodness of the first order model (R^2 ~ 0.95), regarding sunflower oil oxidation at 30, 47 and 67°C. In all cases, this model is often adequate to describe experimental data, concerning the peroxidation of vegetable oils at temperature range of 25-180°C [27].

Whatever the temperature, the model constants related to EM0 (except for the polynomial model) are higher than those of models related to EM1, EM2 and EM3 (Tables 2 and 3), confirming the positive effect of CRDP extracts on the oxidative stability of margarines. At the same time, the model constants obtained at 30°C (Table 2) are higher than those obtained at 5°C (Table 3), confirming

Table 2: Modeling of oxidation kinetic of margarine during storage at 30°C.

Margarine	Applied model	Parameter							R^2	MRE	S
		K	k_1	k_2	k_3	k_4	a	b			
EM0	Zero order	0.869	-	-	-	-	-	-	0.852	27.191	2.998
	First order	0.097	-	-	-	-	-	-	0.970	10.431	1.502
	Polynomial	-	0.050	0.125	-	-	-	-	0.955	16.849	1.916
	Logarithmic	-	-	-	2.373	-	5.687	-	0.448	53.884	5.805
	Power law	-	-	-	-	4.556	-	0.323	0.754	26.578	5.223
EM1	Zero order	0.513	-	-	-	-	-	-	0.950	10.797	0.968
	First order	0.103	-	-	-	-	-	-	0.879	23.107	1.354
	Polynomial	-	0.009	0.322	-	-	-	-	0.962	16.319	0.988
	Logarithmic	-	-	-	1.599	-	3.671	-	0.652	42.083	2.573
	Power law	-	-	-	-	2.647	-	0.401	0.934	46.407	3.531
EM2	Zero order	0.563	-	-	-	-	-	-	0.948	14.190	1.092
	First order	0.085	-	-	-	-	-	-	0.987	50.68	0.313
	Polynomial	-	0.020	0.155	-	-	-	-	0.993	6.327	0.477
	Logarithmic	-	-	-	1.613	-	4.592	-	0.549	39.806	3.222
	Power law	-	-	-	-	3.887	-	0.285	0.785	23.953	2.807
EM3	Zero order	0.403	-	-	-	-	-	-	0.943	9.980	0.823
	First order	0.077	-	-	-	-	-	-	0.977	6.497	0.455
	Polynomial	-	0.013	0.147	-	-	-	-	0.977	6.912	0.593
	Logarithmic	-	-	-	1.179	-	3.734	-	0.567	33.451	2.270
	Power law	-	-	-	-	3.250	-	0.261	0.784	19.991	2.022

k, k_1, k_2, k_3, k_4, a, and b are the model constants, MRE = mean relative error, S = standard error.

the strong effect of temperature on PV rate increase as already demonstrated by *Vaidya and Eun* [28] regarding the oxidation kinetics of walnut and grape seed oils.

Temperature sensitivity of EM oxidative stability

Results of temperature dependence of margarine oxidation were summarized in Table 4, through Q_{10} and Ea values.

Q10 factor indicates the increasing margarine oxidation rate with 10 °C increase of storage temperature. Thus, a Q10 value close to unity indicates that the concerned physicochemical process is less sensitive to temperature. Although the Q10 values generally range between 2 and 3 for chemical reactions, they can sometimes take extreme values depending on the nature of the reaction. In this context, *Gama-Arachchige et al.* [29] reported Q10 values close to zero, concerning the study of physical dormancy-break in seeds.

Presently, Q10 values found vary over a wide interval (0.866-4.00), indicating that this parameter depends on the nature of margarine, the model constant used, as well as the appropriateness of this model.

Table 3: Modeling of oxidation kinetic of margarine during storage at 5 ± 1°C.

Margarine	Applied model	Parameter							R^2	MRE	S
		K	k_1	k_2	k_3	k_4	a	b			
EM0	Zero order	0.078	-	-	-	-	-	-	0.730	11.833	0.397
	First order	0.032	-	-	-	-	-	-	0.644	13.608	0.454
	Polynomial	-	0.005	0.179	-	-	-	-	0.839	8.220	0.354
	Logarithmic	-	-	-	0.341	-	2.287	-	0.968	3.115	0.136
	Power law	-	-	-	-	2.161	-	0.422	0.974	3.245	0.203
EM1	Zero order	0.016	-	-	-	-	-	-	0.954	1.586	0.033
	First order	0.011	-	-	-	-	-	-	0.946	1.743	0.036
	Polynomial	-	0.000	0.023	-	-	-	-	0.966	3.419	0.092
	Logarithmic	-	-	-	0.052	-	1.249	-	0.968	4.192	0.084
	Power law	-	-	-	-	1.366	-	0.036	0.661	4.036	0.122
EM2	Zero order	0.057	-	-	-	-	-	-	0.651	11.059	0.348
	First order	0.027	-	-	-	-	-	-	0.588	12.346	0.380
	Polynomial	-	0.004	0.137	-	-	-	-	0.767	8.270	0.328
	Logarithmic	-	-	-	0.259	-	2.031	-	0.947	3.983	0.135
	Power law	-	-	-	-	1.941	-	0.358	0.950	4.032	0.164
EM3	Zero order	0.042	-	-	-	-	-	-	0.700	8.124	0.232
	First order	0.021	-	-	-	-	-	-	0.645	55.310	1.554
	Polynomial	-	0.003	0.109	-	-	-	-	0.857	6.138	0.208
	Logarithmic	-	-	-	0.191	-	1.946	-	0.993	1.042	0.036
	Power law	-	-	-	-	1.900	-	0.098	0.989	1.251	0.142

k, k_1, k_2, k_3, k_4, a, and b are the model constants, MRE = mean relative error, S = standard error.

Values less than 1 indicate inverse temperature dependence (case of EM0/polynomial model-k_2).

As Q10, the activation energy also varies over a wide range of values, from about -10 (EM0 / Polynomial model-k_2) to about 97 kJ/mol (EM1 /Zero order-k). From data of Table 4, it is easy to see the correlation between the Q10 and Ea values (see also the formula given in the experimental section). As has been explained above for Q10 value below 1, negative activation energy indicates inverse temperature dependence. Obtained Q_{10} values are in agreement with the literature data regarding some food alterations: anthocyanins (1.3-1.7) [30], ascorbic acid (1.06-1.58) [31] and sunflower oxidation at different conditions (~2) [3]. At the same time, the activation energy was in the range (5-117 kJ/mol) of values found for oxidation of different lipid foods [32, 33].

CONCLUSIONS

A new procedure of preparation of enriched margarines has been successfully tested. In fact, the two phases intended for obtaining the margarines were used first as extraction solvents. Both enriched phases thus

Table 4: Temperature effect on margarine oxidative stability, according to Q10-factor and activation energy (Ea).

Margarine	Model constant	Q_{10}	Ea (kJ mol^{-1})
EM0	Zero order-k	2.623	67.496
	First order- k	1.558	31.051
	Polynomial-k_1	2.512	64.471
	Polynomial-k_2	0.866	-10.054
	Logarithmic-k_3	2.173	54.320
	Power law-k_4	1.348	20.884
EM1	Zero order-k	4.003	97.093
	First order- k	2.447	62.630
	Polynomial-k_1	/	/
	Polynomial-k_2	2.874	73.892
	Logarithmic-k_3	3.937	95.923
	Power law-k_4	1.303	18.523
EM2	Zero order-k	2.500	64.125
	First order- k	1.582	32.110
	Polynomial-k_1	1.904	45.063
	Polynomial-k_2	1.051	3.456
	Logarithmic-k_3	2.078	51.212
	Power law-k_4	1.320	19.444
EM3	Zero order-k	2.471	63.314
	First order- k	1.682	36.379
	Polynomial-k_1	1.798	41.057
	Polynomial-k_2	1.127	8.374
	Logarithmic-k_3	2.071	50.963
	Power law-k_4	1.240	15.030

obtained are then employed to formulate different margarine samples.

The best oxidation resistance of different EM was obtained when the sample was added with: 1) the aqueous extract, in the case of storage at 30°C, and 2) the both aqueous and oil extracts, in the case of storage at 5°C.

The adequacy of models related to the oxidation kinetic and rheological behavior of EM was found to be a function of storage temperature and of margarine type.

Finally, these results highlighted the possibility of valorization of *Phoenix canariensis* L., a biomass widely available and underutilized. In particular, the possible application of CRDP extract as a natural colorant and antioxidant in margarine and other food formulations can be envisaged at industrial scale.

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