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Experimental and theoretical investigation of packaged olive oil: Development of a quality indicator based on mathematical predictions

F.A. Coutelieris [a], A. Kanavouras [b,*]

[a] *Unilever Research and Development, Oliver van Noortlaan, 3130 AT, Vlaardingen, The Netherlands*
[b] *Unilever Europe, Spreads and Cooking Products Category, Nassaukade 3, 3071 JL, Rotterdam, The Netherlands*

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Abstract

The experimentally defined oxidative alterations taking place in packaged olive oil stored in various packaging materials and storage conditions, were used as basic evidence in order to develop and support a descriptive mathematically expressed theory, and eventually to conclude on a predictive model. Hexanal was experimentally quantified for extra virgin olive oil packaged in 0.5 L glass, PET, and PVC bottles, and stored at 15 °C, 30 °C and 40 °C under fluorescent light or dark conditions for 12 months. A set of mass transport equations describing the chemical reactions occurring in the oil phase as well as the diffusion of oxygen in the oil phase and through the packaging material, was numerically solved for various combinations of temperatures, light conditions and packaging materials. In addition, the probability of the packaged olive oil not to reach the end of its shelf life during a certain time period, was estimated and proposed as a quality reduction indicator. The suggested model could be used as a tool for an accurate forecast of the quality issues for packaged olive oil.

Keywords: Olive oil oxidation; Shelf-life; Storage conditions; Packaging; Mass transport

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1. Introduction

Oxidation is a major factor for quality deterioration in edible oils. The rate of oxidation depends mainly on the storage conditions, such as temperature and presence of light, as well as on the availability of soluble and reactive oxygen into the oil's mass. Under favorable conditions, oxidation follows a free radical chemical process where the initially formed hydroperoxides may further decompose or even polymerize, resulting in a complex mixture of compounds that could be used to describe the oxidation level (Angelo, 1996).

The increasing use of plastic materials, has been related to their low weight, easier handling, and competitive cost (Kiritsakis, Kanavouras, & Kiritsakis, 2002). However, plastics offer limited protection regarding their gas barrier properties and migration of compounds, compared to steel and glass. Furthermore, the nature of the packaging material has a notable influence on the quality of olive oil (Guttierez, Herrera, & Guttierez, 1988; Mastrobaistta, 1990). Kiritsakis and Dugan (1984, 1985) concluded on the negative role of oxygen and the additional role of light in the oxidative deterioration process for olive oil stored in glass and polymeric containers (polyethylene) and glass bottles. Furthermore, olive oil stored in polyethylene bottles and exposed to diffused light for 3 months had developed an off-taste and had lost most of its original color (Gutti-

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* Corresponding author. Tel.: +31 104 393919; fax: +31 104 394658.
E-mail address: antonis.kanavouras@unilever.com (A. Kanavouras).

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erez, 1975). Data presented by Guttierez, Garrido-Fernandez, Gallardo-Guerrero, and Gondul-Rojas (1992) showed that samples stored in glass or PVC bottles, under light, undergo greater changes in sensory characteristics than those stored in darkness. Kaya, Tekin, and Öner (1993) concluded on the superiority of colored glass versus clear glass and PET in order of the protection provided for packaged olive oil.

Besides the comprehensive experimental work on the oxidation of olive oil, only a limited number of valuable mathematical models have been presented in the literature. Their major attempt was to predict the shelf life of packaged olive oil and to suggest new package designs after taking into consideration the role of oxygen, the geometrical and structural characteristics of the plastic container and the volume of the oil. Dekker, Kramer, van Beest, and Luning (2002) calculated the level of primary oxidation products and the headspace oxygen concentration in different packages containing edible oil, during their storage at various temperature conditions. Their model was based on the reaction kinetics of the food and the active ingredients, the film permeability, and the mass transfer rate within the product. Del Nobile, Ambrosino, Sacchi, and Masi (2003) and Del Nobile, Bove, La Notte, and Sacchi (2003) introduced a two-dimensional model for the oxidation process of olive oil packaged in plastic bottles. However the diffusion of the flavor compounds in the oil phase and the oil's oxidation reactions were not considered. Furthermore, their parametric analysis was limited in the dimensions of the bottles, without any further refinement in terms of storage conditions, i.e. temperature and light. After pursuing an analogous study, Kanavouras, Hernandez-Munoz, Coutelieris, and Selke (2004) presented an experimentally-based descriptive model for the shelf life of packaged olive oil. A broad variety of storage conditions such as temperatures, availability of light and different packaging materials were considered. Their model though, was limited to chemical processes occurring inside the oil mass with the inadequacy of not incorporating the mass transport of the most oxidation-characteristic compounds due to diffusion, as well as the interactions of the packaging materials with the flavor compounds.

Anticipating a further contribution in the interesting and ever advancing area of shelf life modeling for olive oil, the present work aims to present an analytical model for the mass transport phenomena taking place in the oil-package system. The model was developed by considering a set of mass transport equations in a representative circular ring, which consisted of both olive oil mass and packaging material surface. An experimental investigation on the oxidative deterioration of extra virgin olive oil, when packaged in glass and plastic containers and stored at light or dark for a year, was the essential data employed in order to evaluate the proposed model. The evolution of hexanal over time was used as the main indicator of the oxidative alterations taking place inside the oil phase during time. The introduction of the probability for the packaged olive oil not to reach the end of its shelf life when stored under specific conditions, could have a great potential in designing and/or during the storage of product—packaging material interacting systems.

2. Materials and methods

2.1. Packaging of olive oil

Portuguese organic extra virgin olive oil was packed under nitrogen gas, without headspace, in cleaned and dried 500 mL PET drinking water bottles, in 500 mL PVC bottles (Novapack, Co. Paris, IL, USA), and in 500 mL glass bottles (Fisher Scientific Co. New Jersey, USA). The oxygen transmission rates for PET and PVC were to be approximately 8 cc/m^2/day and 9.8 cc/m^2/day at 0.21 atm driving force, respectively. Both materials seem to be effective barriers to wavelengths shorter than 340 nm while visible light was almost equally highly transmitted through either PET or PVC materials. Bottles were sealed tightly with standard polypropylene threaded caps. Half of the bottles were covered with aluminum foil and placed inside fiberboard boxes and the other half were exposed to fluorescent light. Filled bottles were stored in controlled environment chambers at 15, 30 or 40 °C and 60% RH. During the experiment, four 40 W fluorescent light bulbs were placed at 30 cm above the bottles. Weekly rearrangement of the bottles was applied to ensure uniform exposure to light. Two bottles per treatment were analyzed in triplicate monthly up to 12 months.

2.2. Instrumental analysis

An automatically operating stripping apparatus (Dynatherm 1000, Dynatherm Analytical Instruments Inc., Kelton, PA) was used to strip volatile compounds out of the oil, kept at 37 °C, into a Tenax-TA trap (Supelco, Bellefonte, PA). Compounds were desorbed using a desorption unit (Model 890 from Dynatherm Analytical Instruments Inc. Kelton, PA) connected to a gas chromatography apparatus (Hewlett Packard 5890 Series II, Hewlett Packard, Philadelphia, PA) with a 30 m × 0.32 mm ID × 0.25 mm film thickness, fused silica capillary column (SPB-5, Supelco, Bellefonte, PA). The temperature program was: initial temperature, 35 °C for 5 min, increased to 80 °C at a rate of 3 °C/min, held for 1 min, then increased to 180 °C at 10 °C/min, held for 1 min, and finally increased to 220 °C at 4 °C/min where it was held for 10 min. The carrier gas was maintained at a flow rate of 1.75 mL/min at 40 °C. Identification of compounds was performed with a Varian 2000 mass spectrometer (Varian, TX, USA) interfaced with the Dynatherm desorption unit. The tuning value for the ITMS was 100, using cedrol as the tuning standard. Other parameters were: tune sensitivity, 9000; acquisition parameters: full scan, scan range: 41–300 amu, scan time: 1.0 s, threshold: 1 count, multiplier from 1500 to 2300 V depending on multiplier conditions; transfer line temperature, 240 °C; exit nozzle 240 °C; manifold 240 °C. In addition, hexanal (Sigma-Aldrich, St. Louis, MO, USA) was injected in the GC for a further verification of the identified volatiles.

2.3. Model description

In order to explain the oxidation process, a representative model for the evolution of hydroperoxide in the packaged olive oil, based on the main chemical reactions related to the oxidative degradation inside the oil phase, was applied. Based on the original design, we can quite accurately describe the bottles as perfect cylinders with negligible end-effects in the long semi-axis. Thus, due to the indicated axial symmetry, the dimensions of the mathematical problem can be reduced to one, which is parallel to the short semi-axis of the cylindrical bottle. A graphical representation of the system including the packaging materials' thickness L_w, can be seen in Fig. 1.

2.3.1. Oil-phase

It is widely approved that the oxidation reactions taking place in the oil phase, which can be summarized as follows (Kanavouras et al., 2004):

$$O_2 \xrightarrow[h\nu]{k_a} O_2^\circ \tag{1a}$$

$$RH + O_2^\circ \xrightarrow{k_b} ROOH \tag{1b}$$

$$RH + O_2 \xrightarrow{k_c} ROOH \tag{2}$$

with RH being any fatty acid serving as the oxidation substrate, ROOH the derived hydroperoxide, and k_a, k_b and k_c the reaction constants influenced by temperature. The simultaneously occurring reactions (1a) and (1b) take place only in the presence of light. Hydroperoxides are eventually transformed to off-flavor compounds, among which the most prominent one with the higher impact on the sensory evaluation for the olive oil can be safely assumed to be hexanal. Thus, we may presume that ROOH is actually hexanal, which sorption by the polymeric packaging materials ("scalping") we will consider.

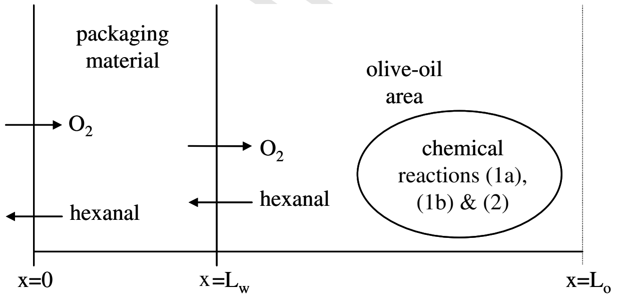

Fig. 1. Graphical representation of the P_{safe} concept.

Under this respect, the assumptions made for the oil phase are as follows:

1. The oil is quiescent.
2. All the hydroperoxide (ROOH) taking place in the above-mentioned reactions, finally is transformed to hexanal.
3. Initially (at $t = 0$) there is a measurable certain amount of oxygen, fatty acid and hexanal in the oil-phase.
4. The packaging materials adsorb hexanal according to Langmuir isotherm.

By assuming a quasi-steady state for the intermediate product O_2° (Atkins, 1998), the mass transport phenomena (diffusion of O_2 and hexanal) in the oil phase, can be described by the following set of differential equations when a negligible diffusion of RH in the oil phase is considered:

$$\frac{\partial C_{O_2}}{\partial t} = D_{O_2,\mathrm{mix}} \frac{\partial^2 C_{O_2}}{\partial x^2} - \xi k_a C_{O_2} - k_c C_{O_2} C_{RH} \tag{3}$$

$$\frac{\partial C_{RH}}{\partial t} = -\xi k_a C_{O_2} - k_c C_{O_2} C_{RH} \tag{4}$$

$$\frac{\partial C_{\mathrm{hexanal}}}{\partial t} = D_{\mathrm{hexanal,\,mix}} \frac{\partial^2 C_{\mathrm{hexanal}}}{\partial x^2} + \xi k_a C_{O_2} + k_c C_{O_2} C_{RH} \tag{5}$$

where C_i is the concentration of species i (namely: O_2, RH and hexanal), $D_{i,\,\mathrm{mix}}$ denotes the diffusion coefficient of species i in the mixture represents the olive oil, ξ is the light indicator ($\xi = 0$ corresponds to dark, $\xi = 1$ corresponds to light) and x, t are the spatial co-ordinate and time respectively. The light is treated as Boolean function because of the lack of experimental data for intermediate light amounts.

The above differential equations are to be integrated with the following initial and boundary conditions:

$$C_{O_2}(x > L_w, t = 0) = C_{O_2}^{\infty,\mathrm{in}} \tag{6}$$

$$C_{RH}(x > L_w, t = 0) = C_{RH}^{\infty,\mathrm{in}} \tag{7}$$

$$C_{\mathrm{hexanal}}(x > L_w, t = 0) = C_{\mathrm{hexanal}}^{\infty,\mathrm{in}} \tag{8}$$

$$\left.\frac{\partial C_{O_2}}{\mathrm{d}x}\right]_{x=L_o,t>0} = 0 \tag{9}$$

$$\left.\frac{\partial C_{\mathrm{hexanal}}}{\mathrm{d}x}\right]_{x=L_o,t>0}=0 \tag{10}$$

$$C_{\mathrm{O}_2}(x=L_w^+,t>0)=C_{\mathrm{O}_2}(x=L_w^-,t>0) \tag{11}$$

$$D_{\mathrm{hexanal,\,mix}}\left.\frac{\partial C_{\mathrm{hexanal}}}{\mathrm{d}x}\right]_{x=L_w,t>0}=k_{\mathrm{ads}}C_{\mathrm{hexanal}}(x=L_w,t>0) \tag{12}$$

where $C_i^{\infty,\mathrm{in}}$, $C_i^{\infty,\mathrm{out}}$ is the initial concentration of species i at the inner and outer surface of the packaging material, respectively, L_o is the inner radius of the bottle and L_w is the packaging material thickness. Initial conditions (6)–(8) assure a constant initial spatial profile for the concentrations of O_2, RH and hexanal, respectively, while boundary conditions (9) and (10) impose the axial symmetry at $x = L_o$. Although oxygen partition between packaging material and oil-phase is not actually identical, the lack of experimental data on the partition coefficient for the specific materials and conditions, does not allow the use of a boundary condition regarding partitioning, and therefore, Eq. (11) simply constrains the continuity of the oxygen concentration on the wall surface. Finally, Eq. (12) expresses a typical Langmuir-type adsorption (Coutelieris, Kainourgiakis, & Stubos, 2003) which in the case of hexanal in the packaging material, can be described as follows. The diffusive flux approaching the adsorbing surface, $D\left.\frac{\partial c_A}{\partial r}\right]_{r=\alpha}$, should be analogous to the absorbed mass, $\frac{k}{K}c_s$, where c_s is the surface concentration, K is defined by the Langmuir isotherm:

$$\Theta_{\mathrm{eq}}=\frac{Kc_b}{1+Kc_b} \tag{13}$$

where k is a reaction rate defined from the relation:

$$R(c_s)=kc_b(c_{\mathrm{mx}}-c_s) \tag{14}$$

while $R(c_s)$ is the overall adsorption rate given as a function of the surface concentration c_s, c_b is the concentration of the diluted mass in the neighborhood of the solid surface, c_{mx} is the maximum concentration attained when the surface is completely covered by substance A and Θ_{eq} is ratio of the covered to the total surface, defined as:

$$\Theta_{\mathrm{eq}}=\frac{c_s}{c_{\mathrm{mx}}} \tag{15}$$

In conclusion, k_{ads} in Eq. (12) represents the overall rate of the hexanal adsorption by the wall.

2.3.2. Oil-package system

The assumptions made for the oil-package system are as follows:

1. Oxygen and hexanal are of constant concentration outside the bottles (at $x = 0$).
2. Initially (at $t = 0$), oxygen and hexanal concentrations inside the packaging material are zero.

Thus, the transport of oxygen and hexanal through the packaging material can be described by the diffusion equations:

$$\frac{\partial C_{\mathrm{O}_2}}{\partial t}=D_{\mathrm{O}_2,\mathrm{wall}}\frac{\partial^2 C_{\mathrm{O}_2}}{\partial x^2} \tag{16}$$

$$\frac{\partial C_{\mathrm{hexanal}}}{\partial t}=D_{\mathrm{hexanal,\,wall}}\frac{\partial^2 C_{\mathrm{hexanal}}}{\partial x^2} \tag{17}$$

where, $D_{\mathrm{O}_2,\mathrm{wall}}$ and $D_{\mathrm{hexanal,\,wall}}$ denote diffusion coefficients of the oxygen and the hexanal, respectively, through the packaging material.

The above differential equations are to be integrated with the following initial and boundary conditions:

$$C_{\mathrm{O}_2}(x>0,t=0)=C_{\mathrm{O}_2}^{\infty,\mathrm{in}} \tag{18}$$

$$C_{\mathrm{hexanal}}(x>0,t=0)=C_{\mathrm{hexanal}}^{\infty,\mathrm{in}} \tag{19}$$

$$C_{\mathrm{O}_2}(x=0,t>0)=C_{\mathrm{O}_2}^{\infty,\mathrm{out}} \tag{20}$$

$$\left.\frac{\partial C_{\mathrm{O}_2}}{\mathrm{d}x}\right]_{x=L_w,t>0}=0 \tag{21}$$

$$C_{\mathrm{hexanal}}(x=0,t>0)=C_{\mathrm{hexanal}}^{\infty,\mathrm{out}} \tag{22}$$

$$C_{\mathrm{hexanal}}(x=L_w^+,t>0)=C_{\mathrm{hexanal}}(x=L_w^-,t>0) \tag{23}$$

where $C_{\mathrm{O}_2}^{\infty,\mathrm{in}}$, $C_{\mathrm{hexanal}}^{\infty,\mathrm{in}}$, $C_{\mathrm{O}_2}^{\infty,\mathrm{out}}$ and $C_{\mathrm{hexanal}}^{\infty,\mathrm{out}}$ are the initial equilibrium concentrations of oxygen and hexanal, respectively, along the two sides of the packaging material. Initial conditions (18) and (19) assure a constant initial spatial profile for the concentrations of O_2 and hexanal, respectively, according to the previously made assumptions. Eqs. (20) and (21) define the constant concentrations of oxygen and hexanal in the packaging outer boundary with the environment. Boundary condition (22) imposes the continuity of oxygen mass flux at the interface ($x = L_w$) while Eq. (23) assures the continuity of the hexanal concentration for the same boundary.

2.3.3. Simulations

The boundary value problem described by the partial differential equations (3), (4), (5), (16) and (17), along with the initial and boundary conditions (6)–(12) and (18)–(23), was discretized in space and time using a non-uniform finite-difference scheme (Press, Flanner, Teukolsky, & Vetterlling, 1986). A numerical algorithm, that involves a typical Newton method for non-linear systems (Burden & Faires, 1989) in conjunction with the finite differences scheme, was modified and adopted to handle the non-linearity of the system. The system was solved numerically with precision of order of 10^{-15} for a range of storage temperatures (15 °C, 30 °C and 40 °C), for various packaging materials (glass, PET, PVC) and light conditions (light, dark).

The values for the parameters used were taken from the relevant literature while numerical interpolation or extrapolation was implemented on the experimentally measured values when necessary. More specifically:

1. The reaction constant rates k_a and k_c were previously, (Kanavouras et al., 2004), given by the formulas $\ln k_a = -1030300/T + 394.8$ and $\ln k_c = -29347/T + 189.59$.
2. The oxygen diffusion coefficients in the oil-phase were 2.025×10^{-6} cm^2/s at 15 °C, 2.3×10^{-6} cm^2/s at 30 °C and 2.72×10^{-6} cm^2/s at 40 °C (Del Nobile et al., 2003; Del Nobile, Bove, et al., 2003; Schumpe & Luhring, 1990).
3. The oxygen diffusion coefficient in the packaging materials were:
   (i) Glass: 0 cm^2/s for any temperature.
   (ii) PET: 2.1×10^{-9} cm^2/s at 15 °C, 4.9×10^{-9} cm^2/s at 30 °C and 8.8×10^{-9} cm^2/s at 40 °C (Del Nobile et al., 2003; Del Nobile, Bove, et al., 2003; Toi, 1973).
   (iii) PVC: 1.17×10^{-9} cm^2/s at 15 °C, 4.01×10^{-9} cm^2/s at 30 °C and 7.56×10^{-9} cm^2/s at 40 °C (Hernandez-Munoz, Catala, & Gavara, 1999; Toi, 1973).
4. The hexanal diffusion coefficient in the packaging materials were:
   (i) Glass: 0 cm^2/s for any temperature.
   (ii) PET: 1.9×10^{-11} cm^2/s at 15 °C, 3.6×10^{-11} cm^2/s at 30 °C and 4.8×10^{-11} cm^2/s at 40 °C (Feigenbaum et al., 1991; Hernandez-Munoz, Catala, Hernandez, & Gavara, 1998).
   (iii) PVC: 3.2×10^{-11} cm^2/s at 15 °C, 4.0×10^{-11} cm^2/s at 30 °C and 5.1×10^{-11} cm^2/s at 40 °C (Feigenbaum et al., 1991; Hernandez-Munoz et al., 1998).
5. The hexanal adsorption coefficient to the plastic packaging material has not been measured experimentally, yet. On the other hand, it has been proven for Langmuir type adsorption that the mass transport coefficient becomes constant for rather high values of the adsorption rate, independently on the physical and chemical properties of the materials (Coutelieris et al., 2003). Thus, it has been fixed in 9 cm/s for the plastic containers. Obviously, for glass bottles $k_{ads} = 0$.

3. Results and discussions

3.1. Experimental results and comparisons to simulations

The measured hexanal content in the olive oil samples during storage is shown with discrete points in Fig. 2. It can be mentioned that:

(i) Storage at lower temperatures under light results in lower amounts of hexanal in the oil;
(ii) The amount of hexanal in olive oil stored in glass containers was quite similar to that kept in PVC when stored at low temperature (15 °C), while it was significantly deviating when stored at 30 °C and at 40 °C;
(iii) For any temperature, hexanal content in oil stored in PET was always statistically different from the amount recorded in the oil stored in glass;
(iv) Olive oil samples stored in the darkness at any temperature did not contain significantly different amounts of hexanal over time, independently of the container.

Since, for the samples stored at light the amount of hexanal was almost twice as for the samples stored at the dark, it can be concluded that fluorescent light had a significant influences on the evolution of hexanal, while the availability of oxygen passing through the plastic containers was less influential, especially at lower temperatures of storage. Results also showed that after 12 months that olive oil had been stored at light, the samples kept in PET and at 40 °C contained the highest amounts of hexanal followed by those stored in glass at 40 °C, while the oil stored in PVC containers had a lower hexanal content.

The experimentally measured hexanal concentration was used for the validation of the mathematical model; its predictions are also presented in Fig. 2 with solid (glass), dashed (PET) and dotted (PVC) lines. The agreement between model predictions and experimental data can be considered as sufficient since the averaged relative difference varies from 5.6% to 32.8% (see Table 1). Due to the very low concentrations of hexanal in oil stored at dark and any temperature, model predictions diverged significantly from the experimental results as their values were comparable with the numerical accuracy. In this respect, the model could be used for any practical exploitation.

3.2. Shelf life predictions

Based on the hexanal concentration profiles, the probability for the olive oil to reach the end of its shelf life during a certain time period, is analogous to the ratio of the areas below and above an arbitrarily defined quality threshold. According to the graphical represen-

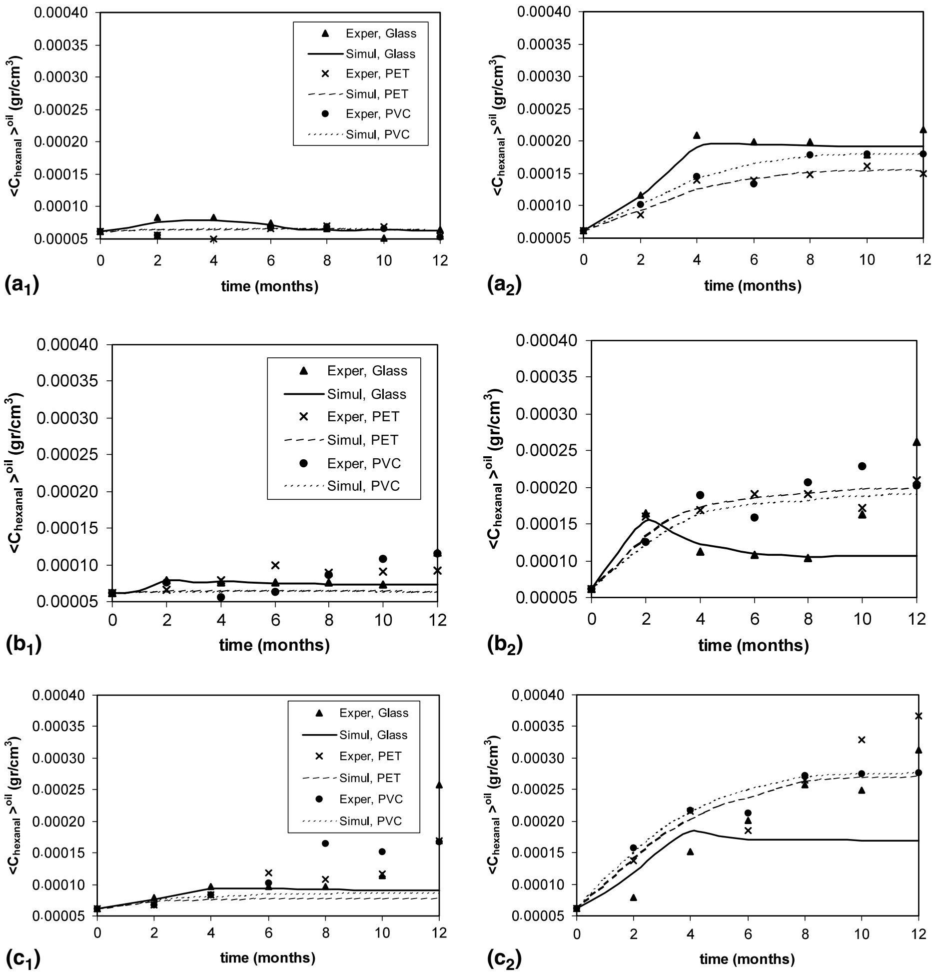

Fig. 2. Time evolution of the spatially averaged hexanal concentration in the oil phase, $\langle C_{\text{hexanal}}\rangle^{\text{oil}}$, for various packaging materials at 15 °C (a_1, a_2), 30 °C (b_1, b_2) and 40 °C (c_1, c_2). Subscripts indicate the light conditions (1 = dark, 2 = light). Comparison of the experimental measurements (discrete points) with the simulations (solid lines).

Table 1
Relative difference between numerical simulations and experimental data in terms of $\langle C_{\text{hexanal}}\rangle^{\text{oil}}$

Case	Relative difference averaged for 12 months (%)
Glass/15/light	5.6
PET/15/light	4.8
PVC/15/light	4.4
Glass/15/dark	8
PET/15/dark	12.4
PVC/15/dark	12.8
Glass/30/light	18.8
PET/30/light	7.2
PVC/30/light	10.4
Glass/30/dark	7.6
PET/30/dark	23.6
PVC/30/dark	24.4
Glass/40/light	32.8
PET/40/light	13.6
PVC/40/light	4
Glass/40/dark	16
PET/40/dark	28
PVC/40/dark	28.4

tation of the concept (see Fig. 3), the probability of the oil to reach its self-life during the time period $[t_1, t_2]$ is analogous to the ratio of the surfaces defined by the curves CDFEC and ABFEA. Since the above-mentioned areas can be expressed by integrals of the spatially averaged hexanal concentration, we can now define the probability, P_{safe}, for the oil not to reach

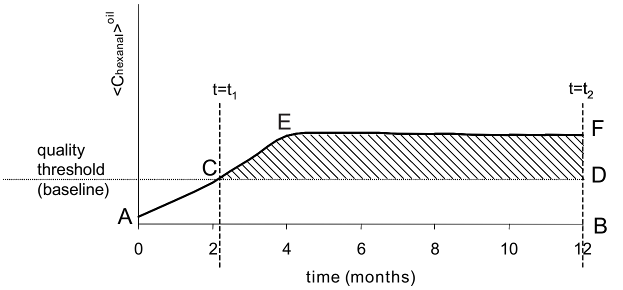

Fig. 3. Definition of the probability for the stored olive oil not to reach the end of its shelf life during a certain period.

the end of its shelf life period during the same time period $[t_1, t_2]$, as:

$$P_{\mathrm{safe}} = 1 - \frac{\int_{t_1}^{t_2} \langle C_{\mathrm{hexanal}} \rangle (t)\,\mathrm{d}t}{\int_{0}^{t_2} \langle C_{hexanal} \rangle (t)\,\mathrm{d}t} \tag{24}$$

where t_1 is the time when concentration reaches one defined critical value, perceived as an upper limit for the oil's quality acceptance. The brackets denote spatial averaging; the upper edge of the integrals, t_2, has been set to 12 months in this study. In general, P_{safe} is a simply estimated quality indicator, depended on the evolution history of hexanal. Further on, it will be employed in this study for the analysis of the results.

Fig. 4 presents the probability (see Eq. (24)), for the olive oil placed in glass, PET and PVC, and stored for 12 months at 15 °C, 30 °C and 40 °C under continuous light or dark. Temperature has a negative effect on the quality of the olive oil as the probability P_{safe} after 12 months decreased significantly with the temperature increment, independently on the light conditions and the material. On the other hand, storage in dark seems to be always better, since probability increased by a factor between 6 and 9. Finally, the role of packaging material appears to be different under different light conditions: glass was the best for oil stored under light, while for oil stored at dark, all the materials seem to have a similar effect.

In order to comment on the sensitivity of the model on the selection of the quality threshold Fig. 5 summarizes P_{safe} values for samples stored at 30 °C in glass, PET and PVC, at light or dark. P_{safe} values are compared for different thresholds, i.e. for 15%, 20%, 25% and 30% over the initial concentration of hexanal. In general, the lower the quality threshold, the higher the probability for the oil not to reach the end of the shelf life during the 12 months of storage. When the baseline was tested for a 5% step-wise increment, the probability raise was rather low. There are some certain combination of the storage conditions (PET/15 °C, dark, PVC/15 °C/dark, PET/30 °C/dark, PVC/30 °C/dark) where the higher concentration of hexanal, as estimated by the model, was less than 5% over the initial one and, thus, P_{safe} was close to 100%. These storage conditions correspond to the cases that model had the poorest agreement to the experimental results (see Table 1). The approach presented in Fig. 5 on the influence of the quality threshold selection on the P_{safe}, may allow the quality threshold positioning, based on any experimental or simulated data set, regarding storage conditions and packaging materials.

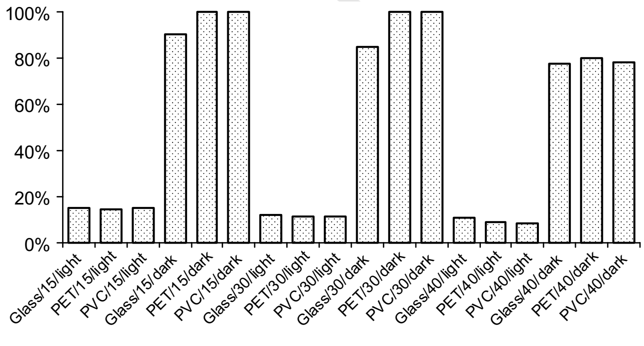

Fig. 4. Probability for the stored olive oil not to reach the end of its shelf life period for the same conditions as in Fig. 2.

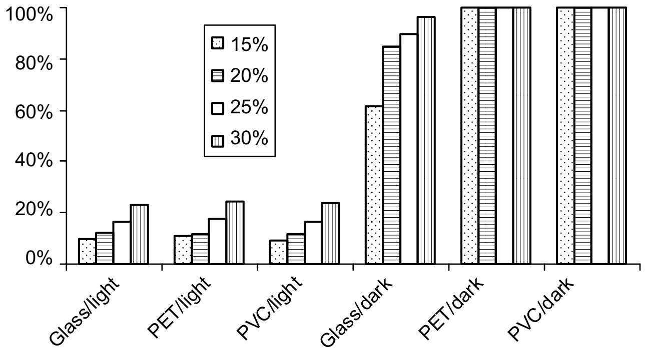

Fig. 5. Sensitivity of P_{safe} on the quality threshold (baseline).

4. Conclusions

The concentration of hexanal in olive oil stored in various packaging materials and storage conditions, was used as the basic indicator for olive oil's quality. In this study, the identity and quantity of hexanal was experimentally determined for extra virgin olive oil packaged in 0.5 L glass, PET, and PVC bottles and stored at 15 °C, 30 °C and 40 °C under fluorescent light or dark conditions for 12 months. A mathematical predictive model was introduced to describe the mass transport from and to the oil phase through various packaging materials for several temperatures and light conditions. It was found that olive oil stored at lower temperatures under light contained the lower amounts of hexanal, while when stored in the dark at any packaging material had comparable amounts of hexanal. A satisfactory agreement of the model to the experimental results was shown through the low values of their relative differences, (less than 20% for the majority of the examined combination of storage conditions).

One of the model's limitations is that due to the very low concentrations of hexanal in oil stored at dark and any temperature, model predictions diverged from the experimental results for the specific conditions, as their values were comparable with the numerical accuracy.

By joining this accurate model with the probability of the oil not to reach the end of its preferred shelf life during a certain time period, introduced in this work as P_{safe}, we may safely conclude on the qualitative changes of packaged olive oil stored at various conditions for prolonged periods of time, otherwise requiring extensive experimental effort and time. Results from an experimental investigation on oil-package interactions and the influence of storage conditions (light, humidity) on the packaging materials could provide more reliable parameters for the shelf life modeling of packaged olive oil stored at various conditions.

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