Packaging of Olive Oil: Quality Issues and Shelf-life Predictions

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ABSTRACT

Olive oil has gained much appreciation among consumers worldwide leading to increased markets as well as greater consumer expectation and thus more challenges for the relevant food sector. By understanding the product, its interactions with the environment and the protective role of the package, decisions can be made on the barrier properties required of the packaging materials to achieve the desired shelf-life. To this end, the shelf-life of packaged olive oil under various storage and distribution environments can be predicted by mathematical modeling. This review examines the basic factors affecting the shelf-life of olive oil in different packaging systems and describes the main oxidative degradation mechanisms for them. Since an experimental investigation to correlate the basic quality factors and the shelf life of a product is time- and effort-consuming, the use of mathematical modeling for the prediction of packaged olive oil shelf-life is also discussed. In the presented works the shelf-life predictions were based on the most consumer related attributes i.e. on the evolution of olive oil flavour compounds under various packaging and storage conditions. The validation of the simulations against known experimental results, showed a very good correlation, confirming the great value of the mathematical approach for a quick and accurate prediction of oxidation sensitive products' shelf life.

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INTRODUCTION

Since antiquity, olive oil has played a major role in diet, health, economy, and social and religious issues for the civilizations developed around the Mediterranean Basin. Due to its unique composition, nutritional value, and health benefits, olive oil has gained world-wide acceptance by ever-more-conscious consumers seeking nutritious, natural and healthy foods. The increase in the consumption of olive oil parallels the intensification of research around the world in areas such as the cultivation of olive trees, collection of the fruits, processing techniques and technology, storage, bottling, distribution and preservation materials and practices. At the same time, a remarkable amount of knowledge has been gained through studies correlating constituents of olive oil to their health benefits results for humankind (Angerosa et al., 2004).

As in any other fat-containing product, rancidity of edible oil due to oxidative degradation is a serious problem in some sectors of the food industry. The degree of exposure to air, temperature and light, the oil extraction techniques, and the conditions and means of storage greatly influence the way that oxidation progresses and the type of by-products produced. As a result of the oxidation, the levels of naturally present antioxidants like polyphenols and tocopherols are reduced; olive oil may contain several by-products that are potentially toxic and harmful to the human body; and the unique flavour profile of the oil changes, mainly as a result of the presence of off-flavour compounds providing unacceptable odour notes.

From a consumer point of view, the most significant factor affecting the preference and acceptability of olive oil is the level of oxidation. It is critical that information about the oxidative stability of susceptible food be obtained before they are marketed. Among the methods employed to give reasonable and accurate prediction of the product's shelf-life, accelerated shelf-life tests have often been used. At the same time, serious doubts have been raised due to the fact that the oxidation is sped up using elevated temperatures, excess of oxygen, and catalysts including various metals. An erroneous prediction of the shelf-life, especially when predicted for lower temperatures, may thus result, entailing the need for real time studies in order to accurately estimate the shelf-life of the oil.

Packaging of olive oil has been one of the factors allowing its world-wide spread and retention of its quality for an extended period of time. Knowledge about packaging materials, their interactions with the oil, and a deeper understanding of the oxidation pathways under various storage conditions will provide the necessary information to be used towards improving the quality of packaged olive oil.

It is only due to the complex nature and composition of the product that the research concerning olive oil presents an endless area of opportunities, scientific challenges, innovative applications and even culinary experimentation. The goals set for this study have been strongly guided by the interest in packaged olive oil as an oxidation-susceptible product, mainly influenced by the availability of air and the presence of light reaching the product through the packaging materials. Based on the above, this study aims in presenting a mathematical approach for dealing with the description of the oxidation phenomena, in connection to the different oxidation stimulating factors in a sensitive, accurate and inexpensive way.

OLIVE OIL FLAVOUR COMPOUNDS DURING OXIDATION

After microbial spoilage, oxidation leading to overt rancidity is the second most important cause of food spoilage (Lindley, 1998). Extensive research has been done not only to identify the products of lipid oxidation and the conditions that influence their production, but also to study the mechanisms involved (Nawar, 1996). The well known initiation, propagation and termination steps are shown in Figure 1.

$$RH \xrightarrow{\text{initiation}} R^{\cdot} + H^{\cdot}$$
$$R^{\cdot} + {}^{3}O_2 \xrightarrow{\text{propagation}} ROO^{\cdot}$$
$$ROO^{\cdot} + RH \xrightarrow{\text{propagation}} ROOH + R^{\cdot}$$
$$RO^{\cdot} + ROOH \xrightarrow{\text{progpagation}} ROO^{\cdot} + ROH$$
$$RO^{\cdot} + RH \xrightarrow{\text{propagation}} ROH + R^{\cdot}$$
$$RH + {}^{\cdot}OH \xrightarrow{\text{propagation}} R^{\cdot} + H_2O$$
$$R^{\cdot} + R^{\cdot} \xrightarrow{\text{termination}} R - R$$
$$2RO^{\cdot} \xrightarrow{\text{termination}} ROOR$$
$$ROO^{\cdot} + R^{\cdot} \xrightarrow{\text{termination}} ROOR$$
$$RO^{\cdot} + R^{\cdot} \xrightarrow{\text{termination}} ROR$$
$$ROO^{\cdot} + ROO^{\cdot} \xrightarrow{\text{termination}} ROOR + {}^{1}O_2$$

Figure 1. Characteristic reactions during the initiation, propagation and termination steps of oxidative degradation of fatty acids including triplet oxygen.

Numerous studies have reported on the analysis and identification of aroma compounds in olive oil (Flath et al. 1973; Olias et al., 1993). However, according to Tateo et al. (1993), it is the quantitative ratios among volatiles, rather than their absolute quantities, that are mostly correlated with the organoleptic characteristics of the product. Although the free radical triplet oxygen is the primary mechanism of the formation of volatile flavour compounds in edible oils (auto-oxidation), photosensitised singlet oxygen oxidation (photo-oxidation) initiated by chlorophyll has a significant role on the initiation of lipid oxidation. The interaction of light with triplet oxygen is the major source of the formation of singlet oxygen in foods. The effects of light on the oxidative stability of the oils can be explained either by the photolytic auto-oxidation or the photosensitised oxidation. Photolytic oxidation is the production of free radicals primarily from lipids during exposure to light. Photosensitised oxidation, however, occurs in the presence of photo-sensitizers and visible light. As light energy is absorbed, the sensitizer is transferred to an excited single state, while the energy is emitted with the removal of light. The sensitizer can be converted to an excited triplet state sensitizer via an intersystem crossing (ISC) mechanism. The excited triplet state sensitizer undergoes degradation and emits light. The type I pathway is characterized by hydrogen atom transfer or electron transfer between an excited triplet sensitizer and a substrate, resulting in the production of free radicals or free radical ions. The excited triplet state sensitizer is a reactive species and may undergo type I or type II reaction pathways, as shown in Figure 2.

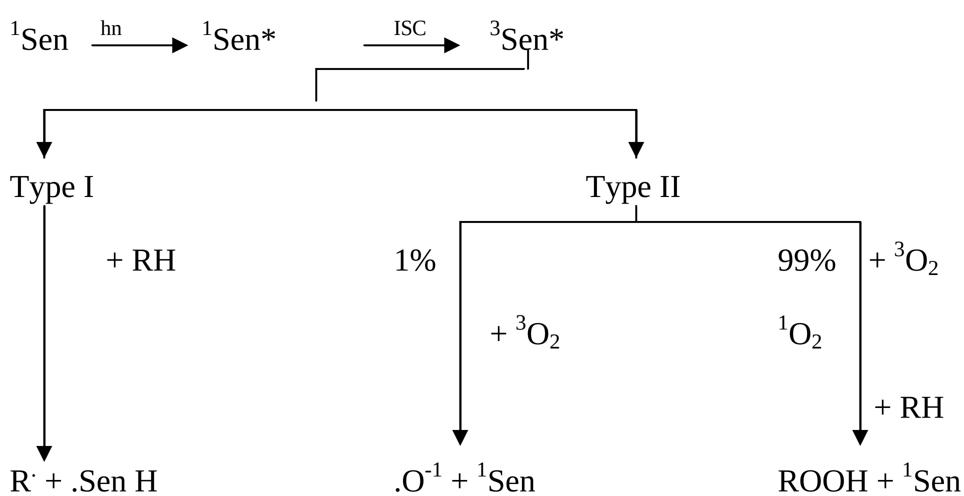

Figure 2. Type I and Type II pathways of an excited triplet state sensitizer.

In the type II pathway, the excited triplet sensitizer reacts with triplet oxygen via a triplet-triplet annihilation mechanism to form singlet oxygen and singlet sensitizer. The rate of the type II reaction mainly depends on the solubility and concentration of oxygen present in the food system. The competition between substrate and triplet oxygen for the excited triplet sensitizer is the major factor determining which pathway will dominate. Once singlet oxygen is formed, it may react with singlet state unsaturated fatty acids, which contain high densities of electrons, and form a mixture of conjugated and non-conjugated hydroperoxides that readily break down to produce undesirable oxidation by products (Min, 1998). The primary oxidation products are (odourless and flavourless) mono-hydroperoxides which are precursors of unpleasant odours and flavours developing in oils thus diminishing the quality of the olive oil (Labuza, 1971; Kochhar, 1993; Morales et al., 1997; Crapiste, 1999). Based on the oxidation conditions, a variety of hydroperoxides can derive from the corresponding fatty acids. Table 1 shows the proportions of monohydroperoxides formed by auto-oxidation and photo-oxidation of the three most important and well studied unsaturated fatty acids, that also dominate olive oil's composition and significantly contribute to its oxidative degradation (Kochhar, 1993).

The volatile aldehydes (Table 2) obtained from various unsaturated fatty acid monohydroperoxides and the vinyl ketones are mainly responsible for potent off-flavours, because their threshold levels are very low. There are two reaction pathways that could explain the volatile compounds derived for the decomposition of hydroperoxides. The first pathway, scission A, will result in the formation of an unsaturated aldehyde and an alkyl radical and a vinyl radical when reacting with a hydroxyl radical. The latter forms

1-enol, which tautomerises to the corresponding aldehyde. The other one, scission B, will yield a vinyl radical and a saturated aldehyde compound. The domination of a particular pathway depends on the oxidation state of the oil, temperature, oxygen pressure, the presence of pro- and antioxidative catalysts, and other factors (Kochhar, 1993).

Table 1. Proportions of monohydroperoxides formed by auto-oxidation and photo-oxidation of unsaturated fatty acids (Kochhar, 1993).

	Monohydroperoxides			
	Position of		Proportion (%)	
Fatty acid	-OOH group	Double bond	Auto-oxidation	Photo-oxidation
Oleic	8	9	27	
	9	10	23	50
	10	8	23	50
	11	9	27	
Linoleic	8	9, 12	1.5	
	9	10, 12	46.5	31
	10	8, 12	0.5	18
	12	9, 13	49.5	18
	13	9, 11	1.5	33
	14	9,12		
Linolenic	9	10, 12, 15	37	23
	10	8, 12, 15		13
	12	9, 13, 15	8	12
	13	9, 11, 15	10	14
	15	9, 12, 16		13
	16	9, 12, 14	45	25

Other volatile oxidation products such as furan derivatives, vinyl alcohols, ketones, alcohols, alkynes, short-chain fatty acids, etc., also contribute to undesirable flavours to varying extents. Characteristic flavour descriptions attributed to specific compounds arising during oxidation are presented in Table 3.

Table 2. Aldehydes obtained from various unsaturated fatty acid mono-hydroperoxides on the basis of beta-scission reaction routes (Kochhar, 1993).

Fatty acid	**Monohydroperoxide**	**Aldehyde formed**
Oleate	8-OOH	2-Undecanal; Decanal
	9-OOH	2-Decenal; nonanal
	10-OOH	Nonanal
	11-OOH	Octanal
Linoleate	9-OOH	3-Nonenal
		2,4-Decadienal
		Hexanal
Linolenate	9-OOH	2,4,7-Decatrienal
		3,6-Nonadienal
	12-OOH	2,4-Heptadienal
		3-Hexenal
	13-OOH	3-Hexanal
	16-OOH	Propanal
Arachidonate	8-OOH	2,4,7-Tridecatrienal
		3,6-Dodecadienal
	9-OOH	2,6-Dodecadienal
	11-OOH	2,4-Decadienal
		3-Nonenal
	12-OOH	3-Nonenal
	15-OOH	Hexanal

Unsaturated aldehydes and ketones are susceptible to further oxidation that gives rise to additional off-flavour compounds. Also, many non-volatile secondary products such as hydroperoxy epoxides, hydroperoxy cyclic peroxides and di-peroxides have been identified in oxidized oils. Decomposition of the above secondary compounds would further contribute to the complex volatile products influencing the flavours and odours of oils.

Table 3. Flavour description of characteristic oxidation derived compounds (Kochhar, 1993).

Ketones	**Flavour description**
2-butanone	Etheral, unpleasant
2-pentanone	Fruity, banana-like, pear drops
2-hexanone	Etheral
2-heptanone	Spicy, rancid almonds
2-octanone	Green, fruity, etheral
2-nonanone	Fruity, fatty, turpentine
3-buten-2-one	Sharp, irritating
1-penten-3-one	Sharp, fishy, oily, painty
1-octen-3-one	Mouldy, mushroom, metallic
1-*c*-5-octadien-2-one	Metallic, musty, fungal
3-*t*-,5-t-octadien-2-one	Fatty, fruity
3-*t*,5-t-octadien-2-one	Fatty, fruity
3,5-undecadien-2-one	Fatty, fried
Alcohols	
1-butanol	Oxidised
1-pentanol	Oxidised
1-hexanol	Oxidised, green bean
1-heptanol	Oxidised, green bean
2-pentanol	Etheral
2-hexanol	Turpentine
2-heptanol	Rancid coconut
2-nonanol	Musty, stale
2-*t*-hexen-1-ol	Sweet wine
2-*t*-octen-1-ol	Fatty
1-penten-3-ol	Oxidised
1-hexen-3-ol	Rubbery rancid
1-octen-3-ol	Musty, foreign
Acids	
Butyric (C4)	Buttery, cheesy, rancid
Caproic (C6)	Fatty, rancid, goat-like
Caprilic (C8)	Soapy, rancid, musty
Capric (C10)	Sour, cheesy, soapy
Lauric (C12)	Fatty, soapy
Hydrocarbons	
Nonane	Buttery, creamy, grassy
1-nonene	Buttery, nutty, rancid
1-hexyne	Buttery, rubbery
1-decyne	Buttery, beany, grassy, melon-like
1,3-nonadiene	Buttery, beany, rancid

THE EFFECT OF PACKAGING MATERIALS ON THE QUALITY OF OLIVE OIL

Proper packaging of olive oil will provide conditions to assure adequate product life for distribution and marketing. Physico-chemical characteristics of the packaging material may significantly affect the quality of oil, depending on the extent of interactions. Migration and scalping are interactions that can occur between the olive oil and the packaging material which further affect the quality and safety aspects of the oil (Kiritsakis, 1998).

Materials used for bottling and packaging olive oil include plastic, glass, tinplate, aluminum, stainless steel, fibre glass, and plastic-coated paperboard. The most common containers are tinplate, plastic, and glass bottles.

Synthetic polymers

Synthetic polymers, commonly known as “plastics”, are extensively used for packing and bottling of vegetable oils, even though they are not always suitable for this purpose (Ashby, 1998). Plastics offer limited protection against oxygen and chemical migration compared to steel and glass. However PVC is a popular packaging material for edible oils in many countries, mainly due to its adaptability to all types of closure, transparency, total compatibility with existing packaging lines, and potential for personalized design features (Dalpasso, 1991). The need for additives during the processing of PVC arises mainly from the inherently poor thermal stability of PVC in the processing temperature range. The function of lubricants in plasticized PVC is to reduce friction on surfaces, including the reduction of adhesion between the polymer melt and the metal surface of the processing equipment. A sterilization process applied to the material prior to use, such as for pharmaceutical products, encourages the migration of components from PVC (Fras et al., 1998).

Poly(ethylene terephthalate)-PET has been supplanting PVC in the edible oil market due to its wide availability, great properties during manufacturing, durability, clarity, design options and strength in blow-molded bottles, recyclability, higher tolerance against weather and less substances migration. Due to the fact that polyethylene has been the most popular polymer in the early days, a lot of studies were using this material in oxidation studies.

Glass

Glass is one of the most inert materials for bottles and demi-johns. Glass is easily cleaned, which helps to dislodge microbes adhering to the container walls. Transparent glass is widely used for bottling olive oil. This practice leads to the photo-oxidation of olive oil and to reduction of its shelf-life. The use of coloured glass bottles for bottling olive oil prevents or slows down the process of oxidation. Green bottles will protect oil from light rays with a wave-length of 300-500 nm (Mastrobattista, 1990; Kiritsakis, 1998). Changes occurring in 12 extra virgin olive oils produced by different extraction procedures and sealed in clear glass bottles, during storage of the half of those in cool and dark conditions and the other half at room temperature with changing light conditions. After 18 months, total chlorophyll, Peroxide values, diglycerides, and squalene showed the greatest changes. Oils stored in the dark kept well, while the oxidative process was well advanced in oil stored in the light. It was concluded that extra virgin olive oil kept in clear glass bottles can be stored in cool and dark conditions for 18 months, while over the same period, oil kept in the light loses some of its sensory and organoleptic characteristics (Leonardis and Macciola, 1998). Kaya et al. (1993) concluded the superiority of coloured glass compared to clear glass and PET for the protection of packaged olive oil.

Other materials

In the old days, Chestnut and oakwood had been used for packaging olive oil**.** Nowadays, aluminum is also employed as a packaging material. It is resistant to rusting and corrosion. In order to increase the mechanical resistance, combination with other metals (Al/Mg, Al/Mn, Al/Si/Mg) is recommended. Stainless steel (chromium content more than 12%) is mostly used for storage tanks and oil tankers for transportation of olive oil. It is highly resistant to mechanical damage and corrosion. Such materials mainly protect the oil from oxidative deterioration.

Actual shelf life estimations for packaged olive oil

The majority of the research, since the early days has been focusing on the comparative evaluations of olive oil stored in different packaging materials, while the determination of the quality was based on either chemical or sensorial properties. In the most common experiments polymeric containers were compared to glass under light or dark conditions. In such studies, it was generally recognised that significant changes take place in the oil stored in transparent glass bottles and exposed to light (Mastrobattista, 1990). As a result of three months light exposure, olive oil stored in polyethylene bottles developed an off-taste and lost most of its original color (Gutierrez, 1975). Kiritsakis and Dugan (1985) found that olive oil stored in colourless glass bottles and exposed to diffused light lost all of the chlorophyll and about 70% of the carotene content. Samples stored in glass or poly(vinyl chloride)-PVC bottles, under light, experienced greater changes in sensory characteristics than those stored in darkness (Min, 1998). Another key-parameter is the oxygen permeability of the container since it has been shown that olive oil bottled in low oxygen barrier materials such as polyethylene (PE) and polypropylene (PP) should be sold within four weeks (Boskou, 1996), in contrast to PVC bottles with lower oxygen permeability that can hold olive oil for three months without appreciable quality loss.

Among the studies that focused on the evolution of specific flavour compounds is the one by Kanavouras et al. (2004), who determined the identity and quantity of flavour compounds for extra virgin olive oil packaged in 0.5 L glass, PET, and PVC bottles and stored at 15^{o}C, 30^{o}C and 40^{o}C under fluorescent light or dark conditions for one year. The researchers concluded that mainly the presence of fluorescent light, followed by the elevated temperature, stimulated the oxidative alterations in olive oil. Separated and identified flavour compounds were recorded for all the olive oil samples. Based on their abundance and evolution in the oil samples, the most clearly describing the oxidation were: hexanal, nonanal, (E)-2-decenal, (E)-2-heptenal, 2-pentyl furan. It was assumed that these compounds might be used as markers of the oxidation process to quantitatively monitor and describe the quality of packaged olive oil.

Overall, olive oil quality has been found to be influenced by the type of material (plastics, glass), conditions of storage (light, temperature), and time. Although a significant amount of results have been obtained, it still seems to be of great importance to conduct experiments by choosing different storage conditions and combinations thereof and to evaluate the ability of new polymers to extend the shelf-life and overall quality of olive oil. The influence of environmental relative humidity (RH) and the effect of the olive oil stored on plastic materials' properties have not been reported yet. Additionally, the use of active packaging that could scavenge oxygen from the packages headspace as well as the oxygen diffused through the packaging material have been proposed (Tawfic and Huyghebaert, 1999).

It is worth-noticing that all the aforementioned works do not include sufficient data in the direction of analytical and/or empirical description of oil-packaging interactions in terms of adsorption isotherms. This lack of information leads to weak modelling, since it is usually unable to accompany the transport equations with boundary conditions of von-Newman type.

SHELF-LIFE PREDICTIONS

In the case of packaged products the influence of the packaging material, the environmental conditions and the time of storage have a significant role in the retention of extra virgin olive oil's quality. Besides the oxidation progress within the oil, other parameters related to the polymers' barrier properties and degradation behaviour during contact with the oil should be taken into consideration in order to better estimate the food-package interactions and understand their influence in the shelf-life modeling of the product. Obviously, experimental investigation of such complicated processes is a very time- and effort-consuming task.

Basic flavour compounds, among other oxidation indicators were investigated as a useful tool in order to evaluate the oil's tolerance to oxidation or its oxidation level at a certain point and extrapolate the results to predicting the shelf-life of the product under various conditions. The flavour compounds produced during the oxidation of packaged olive oil were experimentally evaluated by Kanavouras et al., (2004), resulting on an extensive data-set of flavour profiles evolution. The characteristically different response of selected compounds under different storage conditions, contributed to their suggested employing as descriptors of the probability of the oil not to reach the end of its self-life. The profiles of five selected flavour compounds, namely hexenal, 2-pentyl furan (E)-2-heptenal, nonanal and (E)-2-decenal, were ordained, while evolving during the oxidation of extra virgin olive oil packaged in glass, PET, and PVC bottles and stored at 15^{o}C, 30^{o}C and 40^{o}C under light or dark conditions for one year.

Apart from the extended and comprehensive experimental work on the oxidation of olive oil, only a limited number of valuable mathematical models have been presented in the literature up to now. In the majority of these studies, the main focus 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 & Luning (2003) 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. Their model could not be consider as sufficient for general use because they have not taken into account diffusion processes in the oil phase.

Recently, Del Nobile, Ambrosino, Sacchi & Masi (2003) and Del Nobile, Bove, La Notte & Sacchi (2003) introduced a two-dimensional model for the oxidation process of olive oil packaged in plastic bottles with headspace occupied by air. However the diffusion of the flavour compounds in the oil phase and the oil's oxidation reactions were not considered in detail. 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.

In terms of mathematical description of transport processes, an attempt towards a more accurate modelling approach was initiated by Kanavouras, et al. (2004a) who presented an experimentally-based descriptive model for the estimation of the rate constants for the most commonly accepted oxidation reactions. A broad variety of storage conditions such as temperatures, availability of light and different packaging materials were considered in order to finally calculate the rate constants k_a and k_c of the reactions $O_2 \xrightarrow[h\nu]{k_a} O_3^-$ and $RH + O_2 \xrightarrow{k_c} ROOH$ as functions of temperature (see Figure 3). Their model was however limited to chemical processes occurring within 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 flavour compounds. The above rate constants in conjunction with other experimental results (diffusivities, permeabilities, etc.) were used for a detailed representation of the mass transport equations which describe the diffusion of the flavour compounds in the oil phase, the reactions taking place there (oxidation, photo-oxidation, etc) as well as the interaction with the packaging material (Coutelieris & Kanavouras, 2004).

T	T(K)	1/T(K)	$\ln k_c$	$\ln k_a$
15	288	3.47	87.577	360.333
30	303	3.30	93.035	577.383
40	313	3.19	95.644	639.143

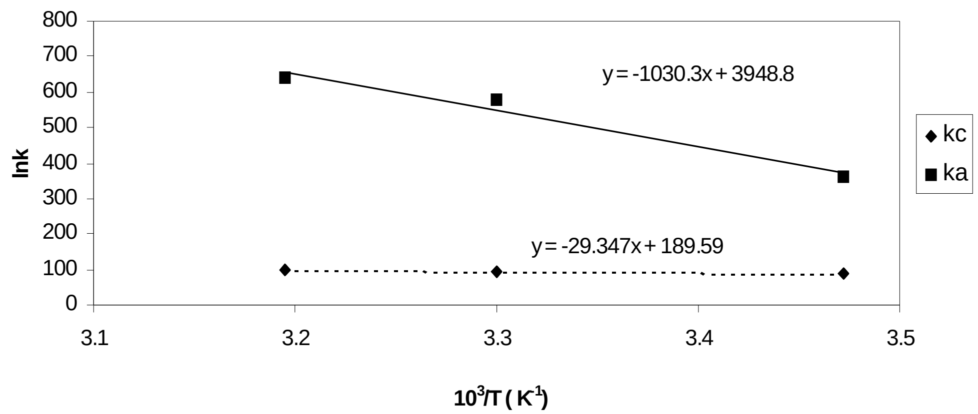

Figure 3. Plot of $\ln k_a$ and $\ln k_c$ as functions of 1/T (^{o}K).

By assuming that the oil is quiescent and that all the hydroperoxide taking place in the reactions finally is transformed to hexanal, at t=0 there is a measurable certain amount of oxygen, fatty acid (*RH*) and hexanal in the oil-phase, 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:

$$\frac{\partial C_{O_2}}{\partial t} = D_{O_2,oil}\frac{\partial^2 C_{O_2}}{\partial x^2} - \xi k_a C_{O_2} - k_c C_{O_2} C_{RH} \quad (1)$$

$$\frac{\partial C_{RH}}{\partial t} = -\xi k_a C_{O_2} - k_c C_{O_2} C_{RH} \quad (2)$$

$$\frac{\partial C_{hexanal}}{\partial t} = D_{hexanal,oil}\frac{\partial^2 C_{hexanal}}{\partial x^2} + \xi k_a C_{O_2} + k_c C_{O_2} C_{RH} \quad (3)$$

where C_i is the concentration of species i (namely: O_2, RH and hexanal), $D_{i,oil}$ denotes the diffusion coefficient of species i in the oil-phase, ξ is the light indicator (ξ =0 corresponds to dark, ξ =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 non-linear terms describe the mass transport due to chemical reactions related to the oxidative degradation inside the oil phase. More precisely, the reactions taken into consideration are

$$O_2 \xrightarrow[h\nu]{k_a} O_3^- \quad (4a)$$

$$RH + O_3^- \xrightarrow{k_b} ROOH \quad (4b)$$

$$RH + O_2 \xrightarrow{k_c} ROOH \quad (4c)$$

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 only by temperature. The simultaneously occurring reactions (4a) and (4b) take place only in the presence of light.

The above differential equations (1)-(3) were integrated with initial and boundary conditions that (a) assure a constant initial spatial profile for the concentrations of *O_2, RH* and hexanal, respectively, (b) impose the axial symmetry and (c) constrain the continuity of the oxygen concentration on the oil-packaging interface. 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, a typical Langmuir-type adsorption was simply assumed. This type of adsorption is rather common in such systems (Coutelieris, Kainourgiakis & Stubos, 2003) and can be described as follows. The diffusive flux approaching the adsorbing surface should be analogous to the absorbed mass, i.e.

$$D_{hexanal,oil}\mathbf{n}\cdot\nabla C_{hexanal} = \frac{k}{K}c^{s}_{hexanal} \quad (5)$$

where $c^{s}_{hexanal}$ is the surface hexanal concentration, K is defined by the Langmuir isotherm

$$\Theta_{eq} = \frac{Kc^{b}_{hexanal}}{1+Kc^{b}_{hexanal}} \quad (6)$$

where k is a adsorption rate constant defined from the relation:

$$R(c^{s}_{hexanal}) = kc^{b}_{hexanal}(c_{max} - c^{s}_{hexanal}) \quad (7)$$

By $R(c^{s}_{hexanal})$ is denoted the overall adsorption rate given as a function of the surface concentration $c^{s}_{hexanal}$, $c^{b}_{hexanal} = C_{hexanal}(x \rightarrow surface)$ is the concentration of the hexanal mass in the neighbourhood of the solid surface, c_{max} 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:

$$\Theta_{eq} = \frac{c^{s}_{hexanal}}{c_{max}} \tag{8}$$

By assuming that oxygen and hexanal are of constant concentration outside the bottles, the transport of oxygen and hexanal through the packaging material can be described by the diffusion equations:

$$\frac{\partial C_{O_2}}{\partial t} = D_{O_2,wall} \frac{\partial^2 C_{O_2}}{\partial x^2} \tag{9}$$

$$\frac{\partial C_{hexanal}}{\partial t} = D_{hexanal,wall} \frac{\partial^2 C_{hexanal}}{\partial x^2} \tag{10}$$

where, $D_{O_2,wall}$ and $D_{hexanal,wall}$ denote diffusion coefficients of the oxygen and the hexanal, respectively, through the packaging material. The above differential equations (9)-(10) were integrated with initial and boundary conditions that (a) assure a constant initial spatial profile for the concentrations of O_2 and hexanal, respectively, (b) define the constant concentrations of oxygen and hexanal in the packaging outer boundary with the environment and (c) impose the continuity of oxygen and hexanal concentration mass flux at the interface.

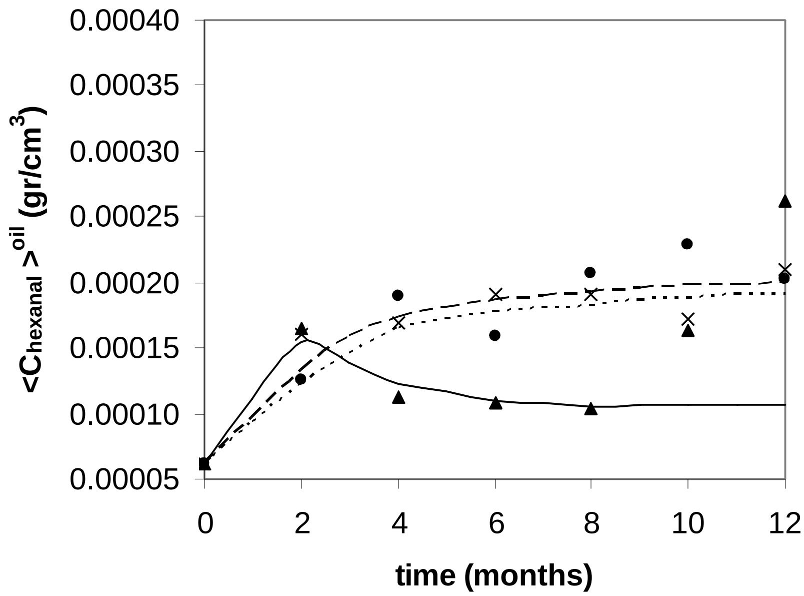

Figure 4. Typical time evolution of the spatially averaged hexanal concentration in the oil phase for various packaging materials (30^{o}C, light).

This set of mass transport equations was numerically solved for various combinations of temperatures, light conditions and packaging materials. The numerical solution was based on a non-uniform space discretization where a 5-point finite-difference scheme was applied. A typical iterative Newton method for non-linear systems has been embedded in the original finite differences system in order to handle the non-linearity coming from the reaction terms. As a result, the time evolution of the concentrations of the compounds under question has been produced. (A typical representative graph of these results is presented in Figure 4). 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). Furthermore, the conclusion came from the experiments were in excellent qualitative agreement with the predictions of the model in terms of concentration trends and the consequent effects on shelf-life through the presence of Hexanal in the olive oil.

In addition, the probability of the packaged olive oil not to reach the end of its shelf-life during a certain time period, P_{safe}, was estimated and proposed as a quality reduction indicator (Coutelieris & Kanavouras, 2004 and Kanavouras & Coutelieris, 2004). 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 defined by arbitrary quality criteria posed by several aspects like producer, consumer, market indicators etc., is analogous to the ratio of the areas below and above an arbitrarily defined quality threshold. 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 the end of its shelf-life period during the same time period [t_1,t_2], as:

$$P_{safe} = 1 - \frac{\int_{t_1}^{t_2} \langle C_{hexanal} \rangle (t) dt}{\int_{0}^{t_2} \langle C_{hexanal} \rangle (t) dt} \quad (11)$$

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.

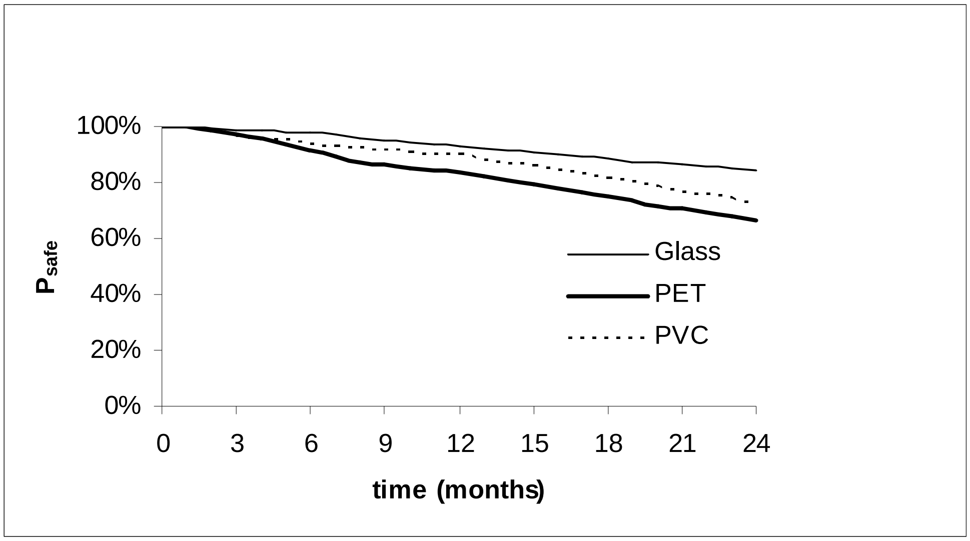

Figure 5. Time evolution of P_{safe} for oil stored at temperatures of 15, 30 and 40^{o}C alternating every 4 months under continuous dark.

By joining the model's predictions with this probability, reliable estimations of the qualitative changes of packaged olive oil stored at various conditions for prolonged periods of time have been produced. These quality degradations were expressed through the time evolution of the probability P_{safe}, as typically presented in Figure 5. In addition, the critical time periods after bottling at which this probability becomes 70%, 50% and 30%, were calculated, while this probability was also interrelated to temperature, presence of light and oxygen during storage. Obviously, results from a more extensive 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.

Flavour compounds as oxidation markers

In an attempt to identify the flavour compounds that could be highly related to the oxidation process, Morales et al. (1997) investigated the volatile components during the thermo-oxidation process and proposed the ratio of hexanal/nonanal as an indicator of the level of oxidation of olive oil. In other words, as the amount of hexanal was diminishing in the olive oil headspace and the amount of nonanal was increasing, the oil was moving towards higher oxidation levels and consequently lower acceptability. Additionally, the assessors agreed that although the peroxide value was low (PV=3.2), the oil had lost the fresh virgin olive oil volatile components while nonanal was exponentially rising. During the oxidation process, there was also an initial increase in 2-farnesene and aldehydes. Later hexanal, 2-heptanal, nonanal, and decanal were the major volatile compounds. Aliphatic acids and aliphatic ketones came much later to dominate, together with furans and alcohols. The increase in alcohols appeared to cause a reduction of potent off-flavours, since they derive from transformation of aldehydes (Kochlar, 1993).

Kanavouras at al., (2004b) used the introduced probability (P_{safe}) to allow the formation of a set of selection criteria that could be used to specifically interrelate the flavour compounds with the main storage abusing factors and eventually identify simple selection criteria for compounds that could be employed as quality indicators for the packaged olive oil. The storage conditions selected in this study were based on three major contributors to the oxidative degradations within the packaged olive oil: temperature, availability of light and presence of oxygen. These factors were further classified into groups to allow for an additional investigation of the effect of each one on the oil. In this case, P_{safe} assisted the simplified distinction among the oxidation favouring factors and was used for a quick evaluation of the oxidation level of packaged olive oil with potential applications to other oxidation sensitive packaged food components (Kanavouras et al., 2004b).

A suggested correlation outline was presented to describe the "storage history" of the product and identify the oxidation-promoting element, using the optimal number of compounds. Thus, a limited, accurate and quick evaluation of the quality level of stored olive oil, and a consequent estimation of its shelf-life, can be achieved. The overall conclusions could be presented by forming two main groups, based on the oxygen availability (oxygen/no oxygen), each one including all the possible combinations of low or high temperature and light or dark. A summary of the compounds for each group of conditions are presented in Table 4, where plus (+) is used when more than one compound were selected as markers. Researchers concluded that a limited, accurate and quick evaluation of the quality level of stored olive oil, and a consequent estimation of its shelf-life, can be achieved.

Table 4. Summary of the flavour compounds selected as markers for the formed groups of storage conditions, Kanavouras at al., (2004b).

	Storage conditions	**Compound(s)**
No oxygen	Low temperature and light	nonanal + hexanal
	High temperature and light	hexanal + nonanal
	Low temperature and dark	hexanal
	High temperature and dark	2-pentylfuran + hexanal
Oxygen	Low temperature and light	hexanal + nonanal + (E)-2-heptenal
	High temperature and light	2-pentylfuran + nonanal + (E)-2-heptenal
	Low temperature and dark	(E)-2-heptenal
	High temperature and dark	Nonanal

GENERAL CONCLUSIONS

Based on the need to build a more reliable and trustworthy relationship between ever increasingly demanding consumers and the olive oil as a product, it is becoming more and more evident that a methodology is needed for the accurate determination and estimation of product quality. Such a methodology should be based on sensitive, accurate and inexpensive “indicators” that will be able to provide an accurate shelf-life prediction by taking into account (monitoring of the product) the parameters influencing the deteriorative reactions leading to alterations in its flavour compound profile. Significant effort has been put on the development of such a methodology, mainly in terms of defining the effect of packaging materials and their interaction with the food, as well as the supply chain and logistics involved during storage and distribution. It could be concluded that the knowledge of the deteriorative mechanisms that reduce product’s quality over time, would allow for the selection of appropriate packaging materials to assure adequate protection under the most realistic conditions the product/package system is likely to face. In that sense, the above-mentioned efforts actually aim in the higher level of protection with the minimum cost, i.e. how to avoid over packaging at the mostly justified expenses.

Throughout the theoretical and experimental studies presented here, it becomes evident that modelling is a very powerful tool for predicting shelf-life of olive oil when a satisfactory agreement with the experimental results could be obtained. More specifically, simulations based on the mass transport equations produced results that allow the introduction of P_{safe}, which is a simple and easy-to-use marker for the quality of packaged olive oil. Thus, important conclusions about the packaging materials and the storage conditions of olive oil came out:

- The longer shelf life corresponds to storage of olive oil under continuous dark and low temperatures.
- Elevated temperatures are not as significant as the presence of light at continuous or alternating patterns.
- Elevated temperatures, although stimulate the deteriorative reactions, they were not as significant as the presence of light at continuous or alternating patterns.

Further investigation and incorporation into the model of the polymer properties as they might change in relation to prolonged food contact and storage conditions, could allow us to introduce a valuable quality-predicting methodology for packaged foods, an appropriate selection of packaging materials as well as to recommend the mostapropriate storage conditions.

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