Systematic transition from description to prediction for the oxidation in packaged olive oil

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ABSTRACT

In this work, an oxidation predictive model was proposed, following a methodical consideration of the natural laws and principles that determine the phenomena occurring during the olive oil oxidation. A mathematical description was obtained via a road-map involving selected "food-packaging-environment" system descriptors. A straightforward transition from the phenomena description to the tool was also developed. For this work, oxidation of packed edible oil was tested against the developed methodology, as a characteristic exemplar to confirm and support it. In conclusion, the proposed, mathematically supported, methodology was proven to be highly appropriate and satisfactory for capturing the potential chemical-physical evolution of oxidation, and therefore, the effectiveness of the tool has been demonstrated for oxidation of edible olive oil.

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1. Introduction

Reactions of food constituents with species present in the environment are one of the most significant research interests around food preservation, impacting on health, cost and quality. A significant amount of research in pursuit of reaction mechanisms, parameters affecting them, significance, protective compounds, and risks and hazards involved, has been reported. A great number of studies and results in chemistry, physics, mathematics and modeling, packaging and material science, to name but a few, are available. Accordingly, new information is emerging following wider consideration of the existing data and knowledge with the aim of developing alternative applications or resolving existing challenges. In some cases, review of these challenges has established critical approaches for obtaining results in specific scientific activities.

Choe and Min (2006) reviewed mechanisms and factors for edible oil oxidation, and discussed aspects that affect oxidative stability of edible oils, namely free fatty acids, mono- and diacylglycerols, metals, chlorophylls, carotenoids, tocopherols, phospholipids, temperature, light, oxygen, oil processing methods. Descriptions of the interaction among certain oil and environmental parameters were reported to affect the outcome of oxidation, mainly evolution of off-flavor compounds, while others decrease the content of the

beneficial or desirable attributes and characteristics, mainly antioxidants and unsaturated fatty acids concentrations (Kanavouras, Hernandez-Múnoz, & Coutelieris 2004a; Kanavouras, Hernandez-Munoz, Coutelieris, & Selke, 2004b; Mistry & Min, 1988; Osborne & Akoh, 2003). The authors concluded that oxidation of edible oils could be minimized through temperature control, exclusion of light and oxygen through careful selection of packaging, and removal of metals. Furthermore, intrinsic concentrations of antioxidants and other minor compounds could have a significant role in the type of oxidized compounds present. Interestingly, on more than one occasion, the interaction of these factors on oxidation of oil was noted, along with the difficulty in differentiating their individual effects (Blekas, Tsimidou, & Boskou, 1995; Choe & Min, 1992; Velasco & Dobarganes, 2002). Yet, differences in qualities and varieties also hinder generalization of the oxidation outcome, requiring greater knowledge about edible oil type and variety (Dachtler, Van dePut, Stijn, Beindorff, & Fritsche, 2003; Guillen & Cabo, 2002).

Within a complex system where there is potentially limited control, such as the food-packaging environment, it is difficult to managing risks associated with deterioration. Such risks are particularly important when targeting consumer safety as well as quality and food attributes or characteristics related to consumer perception. The establishment of quality criteria and limits, and their retention, has impacted formulation, packaging materials and food chain logistics, leading to extended shelf-life and increased sales.

Accordingly, food scientists and researcher have sought to define what has to be measured or estimated to obtain deeper

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insight into specific phenomena. Within the vast majority of research fields, significant numbers of published works deal with either the same hypothesis or study phenomena using similar methodological approaches, influencing the macroscopic research outcome to some extent (Choe & Min, 2006; Kiritsakis, Kanavouras, & Kiritsakis, 2002 and references therein). Inevitably, many results presented in such works are similar in terms of the knowledge they bring. Furthermore, in many cases, there are particular difficulties in identifying the contribution of individual studies to the knowledge created through the years. From a certain point-of-view, these could be regarded as wasted effort – if their contribution is not clear – that generates vast quantities of data, which is increasingly difficult to manage.
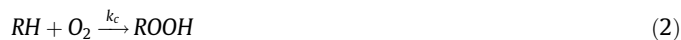
To overcome research efficiency barriers, reduce repetition and work specifically on oxidation of edible oils, the oxidation hypothesis and research objectives/questions have to be redefined. This could be supported by treating existing knowledge with a well-defined and mathematically constrained, classification framework. This approach would allow grouping of phenomena in a compact framework, which could help researchers seeking to describe universal phenomena, independent of their research field.

In parallel, such an approach also requires a transition roadmap from description of the system to a predictive model. The roadmap has to take into account elementary mathematical expressions of fundamental principles in a given system. Therefore, such an approach must focus on cohesions among quantified factors (variables, parameters, etc.) rather than just the quantities present at any given time. Having achieved the transition and the road map, the outcome would be a tool (predictive model), permitting control, modification and improvement of the system.

Consequently, this work aimed to applying a structured approach for description of the overall oxidation process in a product system, including foods susceptible to oxidation, such as oil, packaging and environmental conditions. The laws and equations describing the physical and chemical oxidation were used to test the methodology in olive oil (scientific exemplar). The discussion focuses on the mathematical description of oxidation, which could satisfy a roadmap and lead to building of a working model describing the specific phenomena within a well-defined system such as edible oils.

2. Experimental

Virgin olive oil, packed without headspace in 500 ml bottles, was the main object of this work. In order to estimate product shelf-life, it was necessary to examine in depth the phenomenon of oxidation that affects negatively oil quality. Fatty acids (RH) in bulk phase (oil) produce hyperoxides (ROOH) through auto-oxidation and photo-oxidation, as follows:

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

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

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

where k_a, k_b and k_c are the reaction constants influenced by temperature. As far as reactions (1a) and (1b) take place only in the presence of light, it is obvious that the effect of storage conditions should be studied taking into account these crucial parameters (namely, temperature and light). Therefore, several storage conditions were considered in combinations including a range of practical potential temperatures (5–40 °C), and the presence and absence of light (Kanavouras et al., 2004a, 2004b). In order to estimate the impact of packaging materials, bottles made of poly(ethylene

terephthalate)- (PET), poly(vinyl-chloride)-(PVC) and glass were included.

Following a quiescent period, photo-oxidation reaction takes place when light is available. Auto-oxidation occurs simultaneously in oils stored in oxygen-permeable containers. Such oxidation processes significantly lower the quality of the oil, which reaches the end of its shelf-life after a definite period of time. Thus, quality is concerned directly with hyperoxide concentrations, meaning a detailed mass transport also has to be considered.

Regarding determination of oxidation, *hexanal* is widely accepted as an indicator, although its concentration does not describe quality or storage-degradation holistically because the decomposition mechanism from hyperoxide to hexanal is not clear (see Del Nobile, Ambrosino, Sacchi, & Masi, 2003a; Del Nobile, Bove, La Notte, & Sacchi, 2003b). In this context, relevant oxygen input and oxidation output mass transport equations proposed previously are as follows (Coutelieris & Kanavouras, 2006; Kanavouras & Coutelieris, 2006):

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

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

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

where C_i is the concentration of species i (namely: O_2, RH and hexanal), $D_{i,mix}$ denotes the diffusion coefficient of species i in the mixture (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. Light is treated as a Boolean function because of the lack of experimental data for intermediate light levels. These equations could be integrated numerically after posing appropriate initial and boundary conditions (see Coutelieris & Kanavouras, 2006), while the results are concentrations, as actually a function of space and time.

Likely issues include whether hexanal concentration can be safely related to oil quality. Since this correlation is not straightforward, Coutelieris and Kanavouras (2006) suggested olive oil should not to reach the end of its shelf-life during a given time period (P_{safe}) This indicator is analogous to the area cited between the concentration curve and a threshold line, arbitrarily defined by the highest acceptable concentration of hexanal in the oil. As far as concentration is a spatial distribution, the concentration curve used for estimation of P_{safe} was produced after spatial averaging, allowing for definition of only time-dependent concentrations. Moreover, the area related to P_{safe} can be expressed by integrals, meaning the potential to reach the end of shelf-life is defined as (Coutelieris & Kanavouras, 2006):

$$P_{safe} = \frac{\int_{t_1}^{t_2} \langle C_{hexanal}\rangle(t)dt}{\int_0^{t_2} \langle C_{hexanal}\rangle(t)dt} \tag{6}$$

where t_1 is the time when $C_{hexanal}$ reaches the critical value and the upper edge of the integrals, t_2, could be any time period.

Interestingly enough, this approach produces mainly two essential categories, namely, an expression of the system behavior and a definition of the boundary conditions. Finally, at least one macroscopic quantity must be estimated, against which the phenomenon evolution can be evaluated.

3. Methodology background

Initially, in order to achieve a detailed description of the activities potentially in a well-defined system, it is proposed that any

packed food system of physical-chemical interest, could be described through a typical "in-process-out" context. The characteristic functionalities of such a system can only be established through the inherent relationships among the unique entities in the system. At a basic level, a systemic representation can be described using the following "categorical descriptors", expressed as:

$$\text{matter} + \text{energy} \xrightarrow{\text{relationships}} \text{outcome} \tag{7}$$

For a thorough description of a system, the physical principles involved and a validation step are needed. For such a consideration, and in order to obtain a holistic approach for the system, analysis both in-space and in-time need to be discrete, including the relationships among the phenomena. Furthermore, it seems important to move from purely a description of the system towards a predictive outcome, and consider both the laws and analytical results obtained. In that sense, the system will eventually represent the way human intelligence translates phenomena into universally accepted laws and norms. This could be obtained at a satisfactory level only when our understanding has no gaps or inconsistencies and either fills or reveals potential open issues (new hypothesis formation). It will be shown that a solid methodological process, which has been proposed and tested for oxidation, will eventually generate a classification scheme that correlates these four systemic categories (i.e. matter, energy, relationships, outcome) to three, empirically defined, levels. A combination of the above provides a framework, within which the hypothesis against which the phenomenon is studied, makes sense.

The classification scheme must align with the hypothesis while it should also consider both the context potential and determine the system's boundaries. Furthermore, when these four categories are expanded to three levels, the resulting four by three matrix will contain each of the "category X level" cells. Therefore, the matrix will also contain the distinct and particular conditions that may pre-define the overall systemic activity. Filling in such a matrix, might also result in a knowledge summary that, when properly managed and mathematically treated, may reveal emerging research areas, original hypotheses, and the essential experimentation approaches.

4. Results

Applying the aforementioned approach to olive oil oxidation generated Table 1 with three defined levels in the left-to-right direction. Preparation of Table 1 was supported by a thorough description of the elements and mechanisms of the phenomena and relevant, well-acknowledged, literature references. More precisely, when the olive oil shelf-life, baseline oxidation level, had to be studied, the system could be considered using the "oil-packaging material-environment" phases. Within these three phases, the mathematically described mass and energy balances allow for a judgment as to whether and/or when the hypothesis of a "high quality product" will not be valid anymore (time). The mathematical solutions of the relative differential equations (results), and their interpretation to at least one macroscopic quantity (quality index), allows for insight into the oxidation phenomenon. A detailed description of how the olive oil oxidation matrix could be filled-in.

4.1. Row 1 – Matter

For the simplest – single dimensional case – as shown in Column 1, we consider oxygen concentration, as a unique compulsory species involved in the oxidation evolution, (Korycka-Dahl & Richardson, 1978). In a number of studies, oxygen concentration

in oil has been studied. Its presence and activity dependents on its partial pressure in the headspace of the oil (Andersson, 1998), which affects the amount of oxygen dissolved in the oil, with oil oxidation increasing with the amount of dissolved oxygen (Min & Wen, 1983) but the oxidation rate independent of sufficiently high oxygen concentrations (Labuza, 1971). However, the reverse was found also to be true at low oxygen pressure (Karel, 1992), where the oxidation rate is independent of the lipid concentration while temperature promotes the oxidation rate, as do the presence of light and metals such as iron or copper (Andersson, 1998). Researchers have also calculated the amounts of oxygen sufficient to promote the oxidation in oils, as reported by Przybylski and Eskin (1988) and Min and Wen (1983), at various temperature ranges, suggesting an oxygen-presence to oxidation-by-products relationship. In particular, for rapeseed oil in the dark, temperature and oxygen are highly correlated with 2-pentenal and 1-pentene-3-one, at the relatively elevated temperatures of 50 °C but not at 35 °C (Andersson & Lingnert, 1999). Convection and solubility are other important pathways for oxygen penetration into the oil, affecting oxidation at high temperatures due to low solubility of oxygen (Andersson, 1998).

By adding additional significant reacting species (e.g. fatty acids and hyperoxides), and taking into account the packaging material (glass, PVC, PET), it should be possible to move to a multi-dimensional space of finite dimensions (Column 2), which would be expected to produce more accurate results.

This may be supported by the fact that, extra-virgin olive oil is usually in glass, tin or plastic bottles. The primary advantages for the first two are their impermeability to gases, but the glass and plastic bottles also had disadvantages, favoring the photo-oxidation (Méndez & Falqué, 2007). Through the years, various oils have been evaluated for their oxidative degradation over in time (Ramezan, 2004; Kaya, Tekin, & Oner, 1993). Such studies, along with generalized approaches to describe oxidation (Del Nobile et al., 2003a, 2003b) for olive oil packaged in bottles and the results reported (Caponio, Bilancia, Pasqualone, Sikorska, & Gomes, 2005; de Leonardis & Macciola, 1998; Méndez & Falqué, 2007) and many more, allow us to conclude with high confident that darkness, diffuse light or direct sunlight at room- or elevated temperatures, and exposure to air and air/light, are among the major factors to be considered for selection of packaging materials and storage conditions of edible oils.
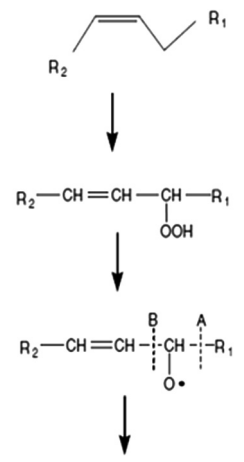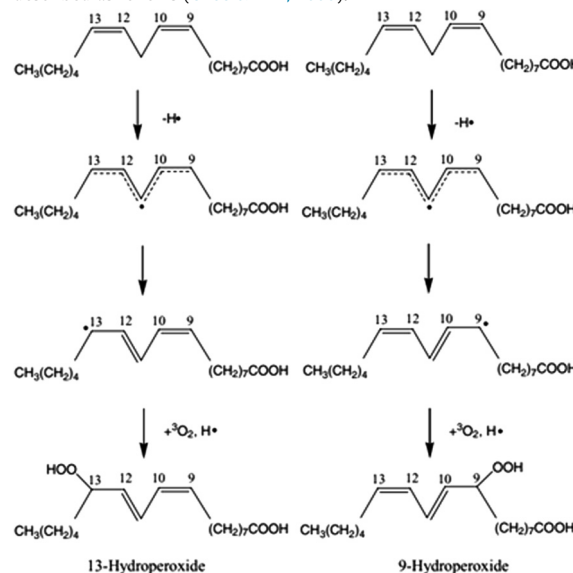
Finally, to approach a vector space of infinite dimensions (Column 3), it is necessary to consider all the species, i.e. identify the totality of factors involved in the system as a whole. For example, the various alkyl-hydroperoxides produced via each of the oxidation pathways, may according to Choe and Min (2006) to a certain extent be predicted in theory.

4.2. Row 2 – Energy

Autoxidation of oils and the decomposition of hydroperoxides increase as temperature increases (Marquez-Ruiz, Martin-Polvillo, & Dobarganes, 1996; St. Angelo, 1996). A higher decomposition of primary oxidation products, and the formation of dimers or oxidized compounds, in addition to the production of hydroperoxides, has been reported for higher temperature (Velasco & Dobarganes, 2002). Temperature also has an effect on the oxidation of unsaturated fatty acids since they are more susceptible to oxidation than saturated fatty acids, primarily due to their low activation energy for the formation radicals (Przybylski et al., 1993), while antioxidants also decrease the activation energy of oil oxidation (Choe & Min, 2006).

Light accelerates oxidation, especially in the presence of sensitizers, such as chlorophylls, mainly via singlet oxygen (Lee & Min, 1988), which can be considered as much more important than

Table 1
Classification matrix for olive-oil oxidation.

Categories	Levels		
Matter	Oxygen	Unsaturated fatty acids, hyperoxides, O_2, container material	Hydroperoxides and deriving flavor profile compounds for temperature and oxygen concentration
Energy	Fatty acids (RH) produces hyperoxides (ROOH) through auto-oxidation and photo-oxidation reactions, as follows: $O_2 \xrightarrow[h\nu]{k_a} O_2^\circ$	Chemical reactions for auto-oxidation:	The produced hyperoxides follow a decomposition mechanism to produce several compounds, including hexanal. This mechanism is described as follows (Choe & Min, 2006):

The photo-oxidation mechanism to produce radicals, as follows:

$$O_2^- \cdot + O_2^- \cdot + 2H^+ \longrightarrow H_2O_2 + O_2$$
$$H_2O_2 + O_2^- \cdot \longrightarrow H_O \cdot + OH^- + {}^1O_2$$

Fick's Law for oxygen diffusion through packaging materials:
$$j_{O_2} = -D_{O_2,bottle}\nabla C_{O_2}$$
Mass flux for oxygen through packaging material: $j_{O_2} = U_{O_2} C_{O_2}$, and its velocity (Darcy's Law): $U_{O_2} = -K_{O_2}\nabla P_{O_2}/\mu_{O_2}$

Energy (column 1 continued):
$$RH + O_2^\circ \xrightarrow{k_b} ROOH$$
$$RH + O_2 \xrightarrow{k_c} ROOH$$

Energy (column 3 continued): For each species i, Fick's Law for oxygen and hyperoxides diffusion through packaging materials: $j_i = -D_{i,bottle}\nabla C_i$
Oxygen and hyperoxides mass fluxes for species i: $j_i = U_i C_i$, and their velocity (Darcy's Law): $U_i = -K_i\nabla P_i/\mu_i$

Categories	Levels		
Relationships	Single reaction term mass transport eq.: $\frac{dC_{ROOH}(t)}{dt} = k_a(T)C_{O_2}(t) + k_c(T)C_{RH}(t)C_{O_2}(t)$ Initial condition: $C_{O_2}(t=0)=C_0$, $C_{RH}(t=0)=C_1$ & $C_{ROOH}(t=0)=0$.	System of mass transport equations (diffusive, convective and reaction terms), where $i=1,2,\ldots,N$, with initial and boundary conditions. $\frac{dC_i}{dt} + \underline{U}_i \cdot \nabla C_i = D_{i,mix}\nabla^2 C_i \pm \sum_{j=1}^{N} k_{i,j}(T)C_iC_j$ $\quad\quad j\neq i$	Mass transport statistics for all the species influencing oxidation in oil phase & from the outer environment: $\frac{dC_i}{dt} + \underline{U}_i \cdot \nabla C_i = D_{i,mix}\nabla^2 C_i \pm \sum_{j=1}^{\infty} k_{i,j}(T)C_iC_j$ $\quad\quad j\neq i$ where $i=1,2,\ldots,\infty$ & i initial and boundary conditions.
Outcome	Hexanal concentration $C_{hexanal}(x,t)$, assumed equal to $C_{ROOH}(x,t)$, since the decomposition mechanism is not included in the current consideration.	Hexanal concentration, averaged over space, as follows $\langle C_{hexanal}(t)\rangle = \iint_V C_{hexanal}(\underline{r},t)dr$. It is also assumed that the hyperoxide concentration equals to that of hexanal since the decomposition mechanism is not included in the current consideration.	(P_{safe}): $P_{safe}(t) = 1 - \frac{\int_{t_{critical}}^{t}\langle C_{hexanal}\rangle(t)dt}{\int_0^t \langle C_{hexanal}\rangle(t)dt}$

temperature in $^1O_2$ oxidation, especially at shorter wavelengths (Sattar, DeMan, & Alexander, 1976) and lower storage temperatures (Velasco & Dobarganes, 2002). On the other hand, temperature has little effect on $^1O_2$ oxidation due to the low activation energy requirements (Rahmani & Csallany, 1998).

Following what was previously stated for Column 1, the consideration of one important species (namely, hexanal) imposes a simple set of related chemical reactions (oxidation and photo-oxidation). Besides, chemical reactions occurring in the system, and included in Column 1, more complicated phenomena, such diffusion and convection, must be also considered if a better understanding of the system is to be achieved (Column 2). The same increased complexity also applies for Column 3, where all the potentially present species, as well as the interactions between them (physical/chemical processes), are involved.

4.3. Row 3 – Relationships

In the case where only a single species is assumed to be produced, through only chemical reactions (Column 1), then only a single governing transport equation could be produced through a single mass balance. In Column 2, an amount of N species is considered and, therefore, N equations are necessary to describe mathematically the system (where N is an infinite integer). Following the previous analysis for Row 2, these equations should moreover include both convection and diffusion terms and, therefore, they form together a system of N differential equations with N unknown species' concentrations. Clearly, the above mathematical system has to be integrated, along with the appropriate set of N initial and 2 N boundary conditions, to assure the uniqueness of the solution. In brief, the transition from Column 1 to Column 2 takes place by describing a system of equations rather than a single equation.

In support of the above, we considered that synergies and antagonistic effects inside the oil mass define the outcome of the system of edible oil, which often contains multi- interacting components, thus altering the antioxidant performance when together rather than when used separately (Brimberg & Kamal-Eldin, 2003). Improved oil oxidation tolerance, via a combination of components, also differs various stages in oxidation (Choe & Min, 2006).

Thus, in the case of Column 3, we can consider an infinite number of species involved in the same phenomena and, therefore, an infinite system of equations could be produced. To overcome the barrier deriving from the point that such a mathematical system has no analytical solution or numerical approximation, it seems necessary to describe this system through stochastically produced formulations and, therefore, to produce solutions that include probabilistic and statistical characteristics.

4.4. Row 4 – Outcome

The "output" of a systemic activity has to be a macroscopic indicator that allows for an adequate description of the oxidation status. Hence, Column 1 counts on the hexanal concentration as such an indication, being the outcome with most potential. The selection of hexanal was based on studies on the decomposition products of hydroperoxides, which are considered responsible for the main off-flavors in oxidized edible oil, and correspond to sensorial threshold values affecting consumer perception with a rather diverse impact compared with the concentration of the compounds *per se* (Frankel, 1985).

Hydroperoxides formed by $^1O_2$ oxidation are expected to be decomposed by the same mechanisms as the hydroperoxides formed by $^3O_2$ in autoxidation. $^1O_2$ oxidation mainly produces 2-decenal and octane, two of the decomposition products of hydroperoxides in oleate (Frankel, 1985). The contents of octanal and 10-oxodecanoate in autoxidized oleate were higher than those

of $^1O_2$-oxidized oleate. 2-Heptenal and 2-butenal were noticeable in $^1O_2$-oxidized linoleic and linolenic acids, but negligible in autoxidized linoleic and linolenic acids. Heptenal was formed only in $^1O_2$-oxidized soybean oil in the presence of chlorophyll and light (Min, Callison, & Lee, 2003). A beany-flavor, which is a unique and undesirable flavor in soybean oil with low peroxide value, can be attributed to 2-pentylfuran and pentenylfuran (Ho, Smagula, & Chang, 1978; Smagula, Ho, & Chang, 1979). The growth rate of various oxidation-derived off-flavor compounds, as well as the equilibrium oxidation reaction constants when oil was stored in various polymeric and glass containers, was calculated by Kanavouras et al. (2004a).

In additional studies, hexanal, and 2-decenal and 2-heptenal and trans-2-octenal were the major volatile compounds detected in soybean and corn oils (Steenson, Lee, & Min, 2002). Pentane, hexanal, propenal, and 2,4-decadienal were present in high amounts in canola oil (Vaisey-Genser, Malcomson, Przybylski, & Eskin, 1999), while trans-2-hexenal, and trans, cis, trans-2,4,7-decatrienal and 1-octen-3-one were reported by Min and Bradley (1992) in oxidized soybean oil. According to Warner et al. (1978) and Przybylski and Eskin (1995) flavor compounds that could be used as oxidation indicators were hexanal, pentane, and 2,4-decadienal. Kanavouras et al. (2004b) also separated and identified flavor compounds from olive oil samples packaged in various storage conditions (glass/PET/PVC bottles) for one year exposed mainly to fluorescent light and elevated temperatures. Based on the abundance and evolution of individual flavor compounds, it was suggested that hexanal, 2-pentyl furan, (E)-2-heptenal, nonanal, and (E)-2-decenal were the compounds that most clearly described the oxidation. Frankel (1985) reported that trans, cis-2,4-decadienal was the most significant compound in determining the oxidized flavor of oil followed by trans, trans-2,4-decadienal, trans, cis-2,4-heptadienal, 1-octen-3-ol, butanal, and hexanal.

The transition to Column 2 implies spatial averaging to eliminate the dependence of hexanal concentration on its position in space. A predictive mathematical model was introduced to describe the mass transport from and to the oil phase through various packaging materials under several temperature and light availability conditions (Coutelieris & Kanavouras, 2005). Using results from a study of flavor compound, found during storage of packaged olive oil, to develop a mathematical model (Kanavouras et al., 2004b), showed the evolution rate constants for hexanal clearly increased with temperature, while auto-oxidation reactions appeared to be less sensitive to changes in temperature.

Finally, the incorporation of all species (Column 3) enforces the definition and use of a more accurate quality index, namely P_{safe}, due to the greater complexity of the system and the use of stochastic mathematical descriptions. The latter expresses the probability of the olive oil to reach the end of its shelf-life in a given time period, equivalent to the ratio of areas below and above an arbitrarily defined quality threshold. This quality threshold depends on a certain acceptable value for hexanal concentration, considered an upper limit for quality acceptance. Therefore, P_{safe} is actually expressed as the ratio of the time-integrals for the spatially averaged hexanal concentration (outcome of Column 2).

5. Discussion

The extended presentation of the proposed approach on oxidation studies for packed olive oil was based on a matrix classifying the existing knowledge. Within that matrix, each level-column represent a specific oxidation consideration. In general, the progressive move from Level-1 to Level-3 parallels the phenomena description complexity increment. The first Level refers only to one object/variable as a major representative describing the

system. Following a conservation law and/or a relative mass/ energy balance, only one mathematical equation seems adequate to describe what takes place in the system. A single factor might be well selected to describe the macroscopic behavior of the system, on the basis of one specific relationship between the variables selected and the outcome quantity produced. In brief, the first Level column of the matrix refers to one variable involved in one algebraic, differential or integral equation that was produced by applying one fundamental principle in the system, while one quantity is selected to describe the system macroscopically. This Level produces a rather primitive ideal outcome, which can represent the system only roughly.

The mid, second Level was produced by the transition from one-dimensional events to multi-dimensional ones, with finite dimension. This vector-space dimension might represent the amount of variables selected to describe the system (matter) or details about the phenomena occurring (energy/relationships) or both. In any case, by applying the corresponding fundamental principles on the system – parameters and reactivity-, a system of differential or algebraic equations can be produced, while a single one factor is still selected to describe the system macroscopically. Although a single macroscopic outcome was defined, the difference from the first Level may be significant, since this second Level includes the interactions of more variables and parameters and is, therefore, more accurate in satisfying the approach more efficiently.

Finally, the third Level describes the system in infinite dimensions that signify an infinite number of variables. Since it is not possible to define a system of equations with infinite size, they must be treated with stochastic and/or asymptotic techniques. The selection of one macroscopic quantity has to satisfy the following two requirements, (1) describe adequately the system's behavior (despite the problems arisen due to infinite dimensions), and also (2) consider the impact of all parameters (although not necessarily known in full details) on the descriptive phenomenological perception.

Subsequently, a road-map towards the systemic mathematical description can be achieved with a set of transition rules as well as the necessary definitions for filling the matrix satisfactorily (Table 1). Such a road-map should provide a structured, engineering-based, tool that may support decisions on future research. The present work indicates that such a goal may only be obtained through this matrix and the proposed filling methods. Moreover, open points, such as original knowledge or existing knowledge "gaps" in understanding, which restrict a proper and adequate compliance of theory to mathematics, may be revealed through the empirical experience (field/lab observations). Apparently, the aforementioned process may also reveal the experimental set-up in order to answer and/or address any inconsistencies and allow for the most "economical" experimentation via a highly efficient plan.

From the mathematical point of view, there are three columns in the matrix because this is the least number of points that might be linearly independent, in terms of Linear Algebra and, therefore, allow for the construction of a three-dimensional vector space (Coutelieris & Kanavouras, 2017). In terms of engineering, each filled column represents the impact of each systemic descriptor on the selected macroscopic outcome.

In order to achieve Table 1, we needed to start from a description of the general necessities of any system to function (Table 2). Furthermore, to quantify the necessities via mathematics, we proposed Table 3 (Coutelieris & Kanavouras, 2017; Kanavouras & Coutelieris, 2017).

The above described overall concept is summarized in Table 3.

The "system descriptor" in Table 3 contains the principle components of the system, as described by "Categories" in Table 2. The first Level represents a simple, one-dimensional description of the

Table 2
The classification matrix.

Categories	Levels		
Matter	One	Many	All
Energy	Reality	Disallowance	Restrictions
Relationships	Inter-dependent	Reasons	Intra-dependent
Outcome	Potential	Existence	Necessity

Table 3
The translation of Table 2 to the language of mathematics.

System descriptor	Level 1	Level 2	Level 3
Dimension	One	Finite	Infinite
Mathematical treatment	Equation	System of Equations	Asymptotic
Macroscopic quantity	One (produced by the solution of the equation)	One (produced by the solution of the system)	One (appropriately selected)

hypothesis; the second corresponds to a next level transition in a multi-dimensional space, while the third Level depicts the influence and the cohesions in an infinite, multi-dimensional vector space.

Regarding the macroscopic description of the phenomenon/-a, occurring as part of the systemic behavior under certain conditions, both Level 1 and Level 2 denote the selection of one representative factor/quantity, but they clearly differ in the amount of parameters the influence of which has to be taken into account. So, the factor/quantity of the Level 1 represents, inevitably, the effect of just one parameter. For the factor/quantity of the Level 2, a finite number of parameters is assumed to affect the systemic outcome, while for the Level 3 an infinite amount of parameters, as well as their impact, are incorporated.

We considered it was equally important to define the following rules regarding the matrix content completion. Consideration and application of these rules will eventually allow the transition functionality to be defined, from the Level 1 to the Level 3. The key rules for filling the matrix are:

- Rule 1: transition from a description of a system to a model is able if, and only if, all the cells of Table 3 are appropriately filled according to a given hypothesis
- Rule2: a system may allow for more than one transition pathway from description to model, as the content of the cells in Table 3 are not necessarily unique.
- Rule 3: For cells in Table 3 that may contain more than one value, the selected macroscopic quantity has to be different, in accordance to the selected parameters.

Although all of the potential different quantities in a cell are equivalent among each other, it is possible to translate each one of them interchangeably to another through mathematical transformations. The critical assessment procedures confirm whether this system satisfies the rules acknowledged previously. More precisely, Rule 1 is obviously satisfied. Rule 2 also is valid for this system, as far as multiple options for filling the cells are available. For instance, if a different outcome was selected as quality indicator instead of hexanal, different but analogous conclusion should be derived, each adequately describing the quality of the oil. Finally, Rule 3 is also satisfied, as indicated schematically in the following Eq. (8), where the selected outcome is shown in its transformation from Level 1 to Level 3:

$$C_{hexanal}(t) \xrightarrow[\text{in space}]{\text{integration}} \langle C_{hexanal}(t) \rangle \xrightarrow[\text{in time}]{\text{integration}} P_{safe} \qquad (8)$$

Inverting the mathematical operations in Eq. (8) is obviously allows Levels to proceed backwards, ending to Level 1, i.e. from a complicated system to a simpler outcome.

6. Conclusions

The broadly recognized issues of controlling packed olive oil oxidation through existing knowledge and efficiently planning new research drew the attention for this work. Originating from the fundamental problem of identifying the potential lack of knowledge, we have tried to establish a methodology for structured background ("category X level" matrix) existing knowledge, and a deeper and more detailed insight of oxidation phenomena. This work has progressed through knowledge integration to implementation of a four by three classification matrix, where each cell corresponds to a specific situation/parameter.

Furthermore, the proposed process requires the definition of rules and conditions under which it may be used. Transition through columns of the matrix could be posed adequately using three specific rules that, in the authors' opinions, are valid for controlling a system described as suggested in this work, such as the oxidation of packed olive oil.

Since this was highly compatible and meaningful for olive oil oxidation, we wish to propose this roadmap as a powerful tool for approaching the preservation hypothesis, identifying research gaps and eventually addressing, through circular feedback, knowledge regarding the phenomena in question. The methodology proposed has been presented extensively to provide context, regarding the knowledge management matrix scheme, as well as for creative potential of managing the relationships among the theoretically evolved situations related to oxidation of olive oil.

In conclusion, this particular description of a system is highly appropriate and satisfactory for capturing potential chemical-physical evolution of oxidation. Transition through the three columns in Table 3, followed the simple rule of dimensions increment: passing from the one-dimensional description (column 1) to a multi- but finite-dimensional space (column 2), finally, a vector space of infinite dimension (column 3). Likewise, the mathematical treatment followed the same trend: from a single equation (column 1) to a system of equations (column 2), while Level 3 asked for a kind of different specific mathematical manipulations (asymptotic procedure, generalized integrations, etc.) in order to satisfy the transitions. Since this approach was tested both in adequacy as well as in its mathematical confirmation, the matrix may be considered to capture fully the phenomena of oxidation. Having completed the application of this proposed methodology for olive oil oxidation, we can now comment with high confidence on the validity of our methodology for moving through the Levels in the classification matrix using a mathematical formalism. Thus, the methodology may have applications beyond olive oil oxidation, and be verified in other areas of research as well.

References

Andersson, K. (1998). Influence of reduced oxygen concentrations on lipid oxidation in food during storage [Ph.D thesis]. Chalmers Reproservice, Sweden: Chalmers University of Technology and the Swedish Institute for Food and Biotechnology.

Andersson, K., & Lingnert, H. (1999). Kinetic studies of oxygen dependence during initial lipid oxidation in rapeseed oil. *Journal of Food Science, 64*, 262–266.

Blekas, G., Tsimidou, M., & Boskou, D. (1995). Contribution of α-tocopherol to olive oil stability. *Food Chemistry, 52*, 289–292.

Brimberg, U. I., & Kamal-Eldin, A. (2003). On the kinetics of the autoxidation of fats: Influence of pro-oxidants, antioxidants and synergists. *European Journal of Lipid Science and Technology, 105*, 83–91.

Caponio, F., Bilancia, M. T., Pasqualone, A., Sikorska, E., & Gomes, T. (2005). Influence on the exposure to light on extra virgin olive oil quality during storage. *European Food Research and Technology, 221*, 92–98.

Choe, E., & Min, D. B. (1992). Interaction effects of chlorophyll, β-carotene and tocopherol on the photooxidative stabilities of soybean oil. *Foods and Biotechnology, 1*, 104–110.

Choe, E., & Min, D. B. (2006). Mechanisms and factors for edible oil oxidation. *Comprehensive Reviews in Food Science and Food Safety, 5*, 169–186.

Coutelieris, F. A., & Kanavouras, A. (2005). Use of the activation energy concept to estimate packaged olive oil quality reduction. *Journal of the American Oil Chemists Society, 82*, 119–123.

Coutelieris, F. A., & Kanavouras, A. (2006). Experimental and theoretical investigation of packaged olive oil: Development of a quality indicator based on mathematical predictions. *Journal of Food Engineering, 73*, 85–92.

Coutelieris, F. A. & Kanavouras, A. (2017) Addressing theoretical & practical aspects on knowledge classification, Applied for Engineers. Under review.

Dachtler, M., Van dePut, H. M., Stijn, F. V., Beindorff, C. M., & Fritsche, J. (2003). On-line LC-NMR-MS characterization of sesame oil extracts and assessment of their antioxidant activity. *European Journal of Lipid Science and Technology, 105*, 488–496.

de Leonardis, A., & Macciola, V. (1998). Evaluation of the self-life of virgin olive oils. *Rivista Italiana delle Sostanze Grasse, 75*, 391–397.

Del Nobile, M. A., Ambrosino, M. L., Sacchi, R., & Masi, P. (2003a). Design of plastic bottles for packaging of virgin olive oil. *Journal of Food Science, 68*, 170–175.

Del Nobile, M. A., Bove, S., La Notte, E., & Sacchi, R. (2003b). Influence of packaging geometry and material properties on the oxidation kinetic of bottles virgin olive oil. *Journal of Food Engineering, 57*, 189–197.

Frankel, E. N. (1985). Chemistry of autoxidation: Mechanism, products and flavor significance. In D. B. Min & T. H. Smouse (Eds.), *Flavor chemistry of fats and oils* (pp. 1–34). Champaign, Ill.: American Oil Chemists' Society.

Guillen, M. D., & Cabo, N. (2002). Fourier transform infrared spectra data versus peroxide and anisidine values to determine oxidative stability of edible oils. *Food Chemistry, 77*, 503–510.

Ho, C.-T., Smagula, M. S., & Chang, S. S. (1978). The synthesis of 2-(1-Pentenyl) furan and its relationship to the reversion flavor of soybean oil. *Journal of the American Oil Chemists' Society, 55*(2), 233–237.

Kanavouras, A. & Coutelieris, F. A. (2017). On the Mathematics about Similarity of Physical Phenomena. Under review.

Kanavouras, A., & Coutelieris, F. A. (2006). Shelf-life predictions for packaged olive oil based on simulations. *Food Chemistry, 96*(1), 48–55.

Kanavouras, A., Hernandez-Münoz, P., & Coutelieris, F. A. (2004a). Shelf life predictions for packaged olive oil using flavor compounds as markers. *European Food Research and Technology, 219*(2), 190–198.

Kanavouras, A., Hernandez-Munoz, P., Coutelieris, F., & Selke, S. (2004b). Oxidation derived flavor compounds as quality indicators for packaged olive oil. *Journal of the American Oil Chemists Society, 81*, 251–257.

Karel, M. (1992). Kinetics of lipid oxidation. In H. G. Schwarzberg & R. W. Hartel (Eds.), *Physical chemistry of foods* (pp. 651–668). New York: Marcel Dekker.

Kaya, A., Tekin, A. R., & Oner, M. D. (1993). Oxidative stability of sunflower and olive oil: Comparison between a modified active oxygen method and long term storage. *Lebensmittel-Wissenschaft & Technologie, 26*, 464–468.

Kiritsakis, A., Kanavouras, A., & Kiritsakis, K. (2002). Chemical analysis, control and packaging issues of olive oil. *European Journal of Lipid Science and Technology, 104*, 328–338.

Korycka-Dahl, M. B., & Richardson, T. (1978). Activated oxygen species and oxidation of food constituents. *Critical Reviews in Food Science and Nutrition, 10*, 209–240.

Labuza, T. P. (1971). Kinetics of lipid oxidation in foods. *Critical Reviews in Food Science and Nutrition, 2*, 355–405.

Lee, E. C., & Min, D. B. (1988). Quenching mechanism of beta-carotene on the chlorophyll-sensitized photooxidation of soybean oil. *Journal of Food Science, 53*, 1894–1895.

Marquez-Ruiz, G., Martin-Polvillo, M., & Dobarganes, M. C. (1996). Quantitation of oxidized triglyceride monomers and dimers as a useful measurement for early and advanced stages of oxidation. *Grasass y Aceites, 47*, 48–53.

Méndez, A. I., & Falqué, E. (2007). Effect of storage time and container type on the quality of extra-virgin olive oil. *Food Control, 18*, 521–529.

Min, D. B., & Bradley, G. D. (1992). Fats and oils: Flavors. In Y. H. Hui (Ed.), *Wiley encyclopedia of food science and technology* (pp. 828–832). New York: John Wiley & Sons.

Min, D. B., Callison, A. L., & Lee, H. O. (2003). Singlet oxygen oxidation for 2-pentylfuran and 2-pentenyfuran formation in soybean oil. *Journal of Food Science, 68*(4), 1175–1178.

Min, D. B., & Wen, J. (1983). Effects of dissolved free oxygen on the volatile compounds of oil. *Journal of Food Science, 48*, 1429–1430.

Mistry, B. S., & Min, D. B. (1988). Prooxidant effects of monoglycerides and diglycerides in soybean oil. *Journal of Food Science, 53*, 1896–1897.

Osborne, H. T., & Akoh, C. C. (2003). Effects of natural antioxidants on iron-catalyzed lipid oxidation of structured lipid-based emulsions. *Journal of the American Oil Chemists Society, 80*, 847–852.

Przybylski, T., & Eskin, N. A. M. (1988). A comparative study on the effectiveness of nitrogen or carbon dioxide flushing in preventing oxidation during the heating of oil. *Journal of the American Oil Chemists Society, 65*, 629–633.

Przybylski, R., & Eskin, N. A. M. (1995). Methods to measure volatile compounds and the flavor significance of volatile compounds. In K. Warner & N. A. M. Eskin (Eds.), *Methods to assess quality and stability of oils and fat-containing foods* (pp. 107–133). Champaign, Ill.: American Oil Chemists' Society.

Przybylski, R., Malcolmson, L. J., Eskin, N. A. M., Durance-Tod, S., Mickle, J. & Carr, R. A. (1993). *Lebensmittel-Wissenschaft & Technologie*, 26, 205–209.

Rahmani, M., & Csallany, A. S. (1998). Role of minor constituents in the photooxidation of virgin olive oil. *Journal of the American Oil Chemists Society, 75*, 837–843.

Ramezan, R. (2004). The effect stability of packaging materials and refined sunflower oil storage condition on the oxidative. *Food Science Technology Research, 10*(3), 350–354.

Sattar, A., DeMan, J. M., & Alexander, J. C. (1976). Effect of wavelength on light-induced quality deterioration of edible oils and fats. *Canadian Institute of Food Science and Technology Journal, 9*, 108–113.

Smagula, M. S., Ho, C. T., & Chang, S. S. (1979). The synthesis of 2-(2-pentenyl) furans and their relationship to the reversion flavor of soybean oil. *Journal of the American Oil Chemists Society, 56*, 516–519.

St. Angelo, A. J. (1996). Lipid oxidation in foods. *Critical Reviews in Food Science and Nutrition, 36*, 175–224.

Steenson, D. F. M., Lee, J. H., & Min, D. B. (2002). Solid-phase microextraction of volatile soybean oil and corn oil compounds. *Journal of Food Science, 67*, 71–76.

Vaisey-Genser, M., Malcomson, L. J., Przybylski, R. & Eskin, N. A. M. (1999). Consumer acceptance of stored canola oils in canola. 12th Project report research on canola, seed, oil meal. Canada Canola Council. Canada. pp. 189–202.

Velasco, J., & Dobarganes, C. (2002). Oxidative stability of virgin olive oil. *European Journal of Lipid Science and Technology, 104*, 661–676.

Warner, K., Evans, C. D., List, G. R., Dupuy, H. P., Wadsworth, J. I., & Goheen, G. E. (1978). Flavor score correlation with pentanal and hexanal contents of vegetable oil. *Journal of the American Oil Chemists Society, 55*, 252–256.