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Preservation engineering assets developed from an oxidation predictive model

Abstract: A previously developed model which effectively predicts the probability of olive oil reaching the end of its shelf-life within a certain time frame was tested for its response when the convective diffusion of oxygen through packaging material is taken in account. Darcy's Law was used to correlate the packaging permeability with the oxygen flow through the packaging materials. Mass transport within the food-packaging system was considered transient and the relative one-dimensional differential equations along with appropriate initial and boundary conditions were numerically solved. When the Peclet (Pe) number was used to validate the significance of the oxygen transport mechanism through packaging, the model results confirmed the Arrhenius type dependency of diffusion, where the slope of the line per material actually indicated their $-Ea/R$. Furthermore, Pe could not be correlated to the hexanal produced in samples stored under light. Photo-oxidation has a significant role in the oxidative degradation of olive oil confirmed by the shelf-assessing test. The validity of our model for the oxygen diffusion driven systems, was also confirmed, for that reason the predictive boundaries were set. Results safely indicated the significance of applying a self-assessing process to confirm the packaging selection process for oxygen sensitive food via this model.

Keywords: modeling, olive oil, oxidation, packaging, preservation, food systems

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1 Introduction

Storage conditions, predominantly temperature and light, strongly define the rate of olive oil oxidation. The oxidation mechanism involves the formation of hydroperoxides and their subsequent decomposition towards a complex mixture of oxidation descriptive compounds [1].

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 predicting the shelf-life of packaged olive oil has been discussed extensively elsewhere [2]. Suggested new package designs having considered the role of oxygen, the geometrical and structural characteristics of the plastic container and the volume of the oil have been proposed [3-9]. Despite the comprehensive experimental work on the oxidation of olive oil, there are only a limited number of valuable mathematical models in the literature which attempt to predict the shelf-life of packaged olive oil. Among them, the following has been studied; the impact of active ingredients, the film permeability, and the mass transfer rate using a reaction-kinetics based model [10], while a two-dimensional model for the oxidation process of olive oil packaged in plastic bottles with certain limitations has been also introduced [11, 12]. Furthermore, the effect of the activation energy threshold on oxidation rates for several storage conditions and packaging materials has been also studied [13], while a numerically solved mathematical description of diffusive-reactive mass transport for the packaged olive oil has been proposed [14]. On the top of that, the above researchers also proposed a deterministically defined stochastical variable, termed P_{safe}, to macroscopically describe the possibility of packaged olive oil versus the optimum shelf life for given storage periods. This model was suggested by the researchers as a trustworthy tool, which could accurately forecast the quality of packaged olive oil.

Since modeling can be a very powerful tool for predicting shelf-life of olive oil, the mathematical models should provide a more reliable and trustworthy relationship between ever increasingly demanding consumers, and the packed olive oil as a system.

A model developing methodology should take into consideration sensitive, accurate and inexpensive degradation "indicators", capable of providing the necessary accuracy for the shelf-life predictions. Modeling should only be further strengthened by incorporating those parameters influencing the deteriorative reactions (monitoring of the product), at the maximum levels of details.

The probability P_{safe}, is actually an adequate index for olive oil quality and can potentially describe qualitative alterations regarding variations of storage conditions [14]. Further investigation and incorporation into the P_{safe} model of additional polymer properties, may allow for a valuable quality-predicting methodology for packaged food systems, an appropriate selection of packaging materials, as well as recommendations for the most appropriate storage conditions. Since the presence of oxygen within the oil phase is crucial for the quality degradation via an oxidation process, the permeability of packaging materials is considered a major factor for oil preservation, particularly when products are stored in polymer-made containers. Several research studies can be found on this topic, where it seems to be a common practice to represent the permeability through packaging materials by a simply estimated permeability coefficient [15, 16].

Although, the P_{safe} approach has adequately demonstrated the relationship of degradation with storage conditions over long time, to even further build an experimental design paradigm for the investigation of the various phenomena and their inter- and intra-cohesion, incorporating major packaging material properties would be beneficial.

2 Theory

Consider a typical bottle containing virgin olive oil. When the packaging material is not dense (e.g. glass), oxygen may pass through it and diffuse into the oil phase. In most cases the packaging material is usually plastic (e.g. PET or PVC), representing mass transport which is equivalent to that of a typical solid porous material. While other phenomena usually occurring in polymeric structures are neglected here, this assumption can be considered sufficient as negligible changes in the porous structure are expected due to the rather low temperatures where packaged oil is stored.

A detailed mathematical description of such a problem can be found elsewhere [14, 17]. In brief, via the various sequential steps of oxidation, fatty acids (RH) being in bulk phase (oil) as the constituents of triglycerides, produce

hyperoxides (ROOH) through the following reactions with triplet-O_2 (auto-oxidation) and/or highly energized singlet-$O_2^{\,\circ}$ (photo-oxidation) oxygen species present:

$$O_2 \xrightarrow[hv]{k_a} O_2^{\,\circ} \tag{1a}$$

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

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

where k_a, k_b and k_c are the reaction constants influenced by temperature, estimated in detail elsewhere [18]. Reactions (1a) and (1b) require external energy to proceed and they may take place only in the presence of light, therefore, it is clear that the effect of storage conditions must be crucial. The various hyperoxides produced by the various free fatty acids are eventually transformed to a comparative number of different corresponding off-flavor compounds. Although many compounds may be produced during this process, it was hexanal that has been suggested as a trustworthy oxidation indicator [1], mainly due to its origination from essential and abounded in the oil, unsaturated fatty acids.

As far as the oil is quiescent, the mass transport of the species within the oil phase is either diffusion- or reaction- driven. This process can be described by a set of differential mass-transport equations including diffusion of oxygen and hexanal in the oil and reaction terms. This set has to be integrated with the appropriate initial and boundary conditions that assure axial symmetry, constant initial concentration etc. It has to be stressed that sorption phenomena may occur in the interface between packaging material and the oil phase, usually described by a boundary condition expressing a Langmuir-type isotherm [14]. Regarding the oil-package system, the penetration of oxygen through the packaging material has been considered as not only diffusion-driven, i.e. the driving force is not supposed to be only the concentration difference between the inner of the bottle and the environment. Although valid, such an approach does neglect the convection due to the pressure difference between the same points. Therefore, we have included here a novel approach by describing oxygen transport through the packaging material by the convective - diffusion equation:

$$\frac{\partial C_{O_2}}{\partial t} = D_{O_2,wall} \frac{\partial^2 C_{O_2}}{\partial x^2} + u \frac{\partial C_{O_2}}{\partial x} \tag{3}$$

where, $D_{O_2,wall}$ denotes diffusion coefficient of the oxygen through the packaging material. By u is denoted oxygen velocity defined through permeability by the Darcy law

$$u = -\frac{K}{\mu}\frac{\Delta P}{L_W} \qquad (4)$$

where, K is the permeability, μ is the viscosity of oxygen and L_w is the thickness of the packaging material, assumed significantly lower than the bottle radius. The remaining equations, initial and boundary conditions as well as parameters are as in the previously presented model [14, 18].

By considering hexanal as the most critical indicator for the quality of the oil, as indicated in the literature [19-21], the above equation measures the spatial distribution of hexanal concentration over time. This concentration is spatially averaged to produce a unique uniform quantity, characteristic for the whole oil mass in a bottle, at any specific time.

It is now straightforward to define the probability for the olive oil to reach the end of its shelf life during a certain time period, based on the hexanal concentration profiles. This probability, P_{safe}, is based on representing the areas by integrals, and could be expressed as the ratio of the particular integrals [14]:

$$P_{safe} = 1 - \frac{\int_{t_1}^{12}\langle C_{hexanal}\rangle(t)dt}{\int_{0}^{12}\langle C_{hexanal}\rangle(t)dt} \qquad (5)$$

where time is in months, *12* represents the duration of one year and t_1 is the time when the hexanal concentration approximates a critical threshold which might be set as the upper quality acceptance limit, while brackets denote spatial averaging. This mechanism actually initially represents the transient spatial distribution of hexanal concentration with its time dependent but spatially averaged value, in order to obtain one concentration value per time interval. Following that, the values may be integrated over a pre-defined specific time interval, so as to produce the probability P_{safe}. The whole concept has been presented in detail elsewhere [14].

3 Result

For the purpose of solving the equations described previously, a finite-differences scheme was adopted for a spatially discretized grid, in conjunction with a modified 4th-order Runge-Kutta method for integration in time. The above correspond to a mesh consisting of approximately 10000 grid points. An i7 PC with 16 GB RAM memory was used to obtain the numerical approximation. Given the required accuracy of at least 10^{-4} for all the involved quantities, the convergence time was approx. 2 minutes, corresponding to an average number of 750 iterations.

For the sake of validity, the current model was compared to that of [14], when permeability tends to zero (i.e. dense packaging material) and when pressure different is zero, as well. The results found identical, therefore the new model is considered valid for further analysis.

To investigate the significant of convection term [see eq. (2)], the new model was compared to that of [14], where only diffusion through the packaging material has been considered. The quality index chosen is the dimensionless spatially averaged hexanal concentration, which is widely accepted as the main indicator for oil oxidation. Only two storage conditions have been selected: (a) 15 $^{\circ}$C in the dark, and (b) 40 $^{\circ}$C in light. The first has been widely accepted as the most favorable option for optimal olive-oil storage, while the second one represents the worst case, as the oxidation process is strongly supported by both the high temperature and the continuous presence of light. This comparison is presented in Fig. 1.

Regarding Fig. 1, the decrease of hexanal concentration towards the end of time period can be produced by truncation and round-off errors, since the values of the results are of comparable significant digits with the accuracy of the numerical scheme. In general, results showed high similarity and consistency among the two versions of the model, indicating the independence of the reaction kinetics to the additional factor U. This could be attributed to the stronger temperature dependency of the reactions compared to the inherent convection parameters. In short, oxidative degradation of olive oil has cohesion to the energy level of the surroundings where the product is stored, compared to the oxygen presence *per se*. The additional functionality of the model when the velocity was incorporated did not actually affect the reaction rates. Furthermore, the behavior of the model specifies that oxygen transport due to convection is negligible compared to to diffusion, and therefore it is likely that U is not a significant parameter in the system's response to oxidation. This is in general valid for foods packaged under nearly atmospheric pressure, since ΔP tends to zero and, consequently, the convective velocity is negligible. For the cases of packaging under vacuum or in very low pressure, convection becomes a significant mass transport mechanism, even dominating over diffusion. Obviously, this is not the case for packaged olive oil.
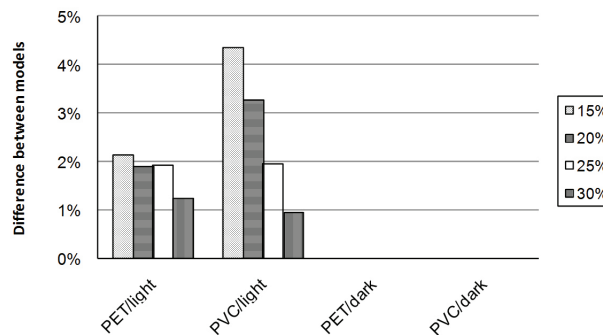
To clarify whether the above result is unsystematic or not, the new version of the model (including convection),

(a)

(b)
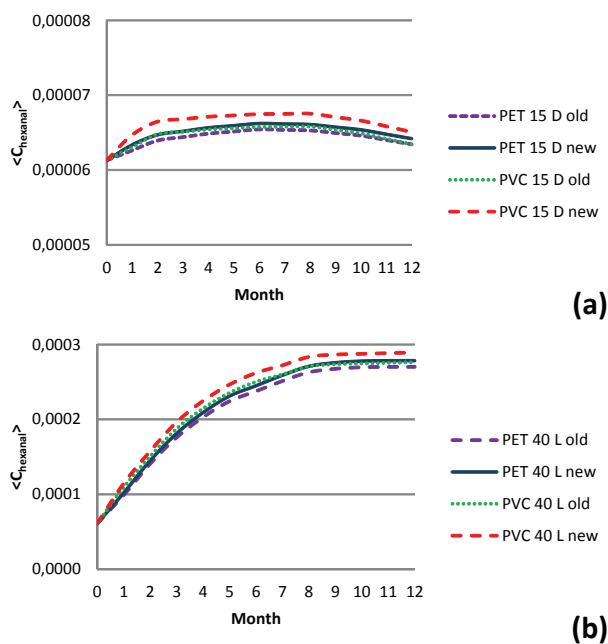
Figure 1: Effect of convection on the hexanal concentration for the "best" (a) and the "worst" (b) case.

Figure 2: Comparison of two approaches in terms of P_{safe}, for several storage conditions and 4 different quality thresholds.

was assessed for its fitting to the P_{safe} values, in other words, would it be of any significance on the shelf-life predictions, obtained with the previous version (Fig. 2). The difference between predictions with and without the convection term is presented for two packaging materials (namely, poly(ethylene terephthalate)-PET and poly(vinyl chloride)-PVC) and two storage conditions (storage in continuous light and storage in continuous dark). Furthermore, four different quality thresholds have been considered: 15%, 20%, 25% and 30%. Results showed that, based on the risk level the model was asked to provide, P_{safe} with and without the consideration of the convection term that there was less than 5% difference in the predictive possibility that the olive oil would not reach the end of its shelf-life within a certain time frame. Interestingly enough, the olive oil stored in the light conditions had the highest level of difference and the lower possibility-higher risk-of 15% was the least similar. This is because of the domination of photo-oxidation over all the other mass-transport processes, with slightly distinct differences between the two packaging materials tested. Regarding the quality threshold, the model progressively fails as the quality threshold increases, i.e. as the constraints for model's validity become more restricted.

With the focus on the cohesion of the systemic properties to oxidation, the Peclet number was selected to describe the relative strengths of the mass transport processes through the packaging material. Although it

is obvious that oxygen convection is the minor process affecting the olive oil oxidation progression, we supported the use of Pe number for the identification of the potential differences among the performance of packaging materials against oxidation. While this number is very low it may be an indicator allowing a qualitative description among oxygen permeable materials of variable barrier properties. Alternatively, there are other dimensionless numbers indicating the relative strengths of the processes that take place, such as Damköhler numbers, but these processes do not constitute an appropriate indicator for oxygen penetration through packaging materials. Thus, the Pe number may be used as a comparison means and as an independent factor among oxygen barriers. As it will be discussed further below, this may be a satisfactory way to engineer the protective role and functions of packaging materials.

Actually, the number Pe, i.e. the ratio of convection over diffusion, is a very reliable indicator of the role of oxygen transport in the oil mass over its mass transfer through the packaging materials. It is worth mentioning that Pe was selected in order to check the model for its capability to respond according to the physical mass transport mechanisms allowing the presence of oxygen in the system. The results should also indicate the potential of engineering the packaging materials' properties in satisfying the requirements of shelf-life.

The above Fig. 3 presents the Peclet value as a function of temperature for various storage materials and conditions. Generally speaking, the oxidation evolution rate seems to be temperature dependent due to the system interdependency on defining the oxygen availability. Independent of the packaging materials and storage conditions, Pe versus temperature shows remarkably identical behavior of steep curve slops, i.e. higher dependency of Pe to temperatures below 15 °C, rather than above 15 °C. Applying the straight line model to each
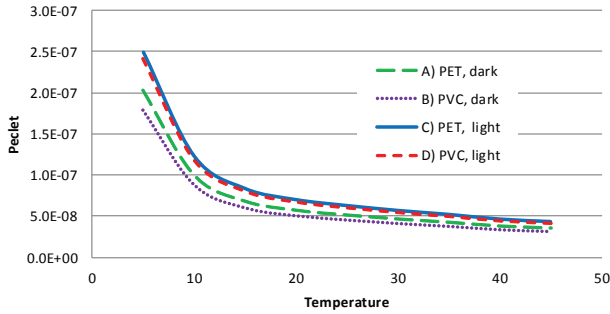
Figure 3: Influence of temperature on Peclet number for various storage materials and conditions.
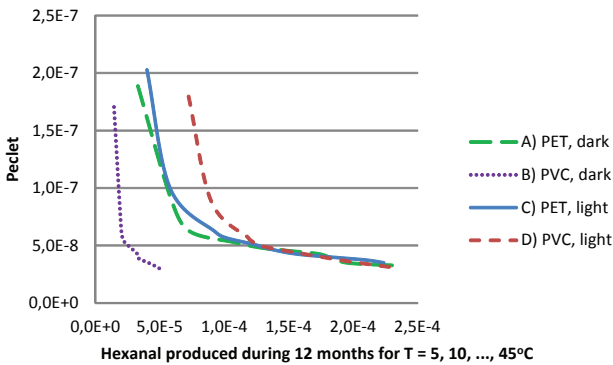

Figure 4: Peclet number as a function of overall hexanal concentration.

part, below 15 °C or above 15 °C, provided very similar line trends among all materials.

Independent of the packaging materials and light conditions, the lines had an almost identical behavior, indicating that the model was responding similarly for these conditions, meaning that the presence of oxygen was irrelevant of the material but more relevant to the temperature of exposure. This could be an indication of packaging and storage conditions cohesive role on selecting the combination of their properties for particular shelf-life requirements, by engineering both factors for optimum outcome.

As seen in Fig. 3, all curves can be represented by two lines, one before 15 °C and one after this temperature. The results are presented in Table 1. It is also important to underline that the ratio of the slopes before and after 15 °C is actually constant (=19.9) as well as the abscissas ratio (=3.87). This observation further clarifies the Arrhenius type correlation of the Peclet number with temperature through the diffusivity,

$$Pe(T) = \frac{UL_w}{D(T)} = \frac{UL_w}{D_o e^{-\frac{E_A}{RT}}} = \frac{UL_w}{D_o} e^{\left(\frac{E_A}{R}\right)\frac{1}{T}} = \mathrm{K} e^{\Lambda \frac{1}{T}} \qquad (6)$$

where $\mathrm{K} = \frac{UL_w}{D_o} = const.$ and $\Lambda = \frac{E_A}{R} = const.$ Therefore, Pe has to follow a reverse exponential behavior with temperature, which is also observed in Fig. 3.

Finally, it is necessary to correlate the major parameter (Pe) with the most critical macroscopic result (hexanal produced during a 12 months period). This correlation is not straightforward, as far as there is no analytical relation of Pe with temperature as well as concentration with temperature. Therefore, Fig. 4 presents the Pe number plotted against hexanal, for several storage conditions and materials. The significant different behavior among packaging materials and storage conditions is apparent from Figure 4. The two model versions were applied mainly for testing the new version of the model for its capability to correlate the outcome of hexanal to the conditions over which the food-packaging system was exposed at.

As shown above, Pe decreases with concentration because the higher the concentration in the oil's space, the higher the concentration gradient through the packaging material, i.e. the lower the Peclet. Again, the model fails for storage in light because photo-oxidation, which is unattained throughout the Peclet concept, is significantly stronger than oxidation itself. Finally, for storage in dark (where model is valid), PVC seems to be more preferable than PET since it corresponds to lower Pe values, as already discussed.

4 Conclusions

A reliable shelf-life prediction model has been developed and its capability to predict indications on the oxidation system interactions has been tested. The shelf assessment of the model was performed and results were considered for both their predictive validity and confirmation of the model, as well as for identifying the areas interfering with the systemic properties.

Packaging applications have been captured quite well in the model, for the non-light exposure samples, indicating the strong influence of light and the alterations in the food system responses. The model was not capable of predicting these alterations and thus could not allow for managing the system decisions. On the other hand, the model had a very consistent function for samples stored in the dark. It became possible to reveal the strong coherence of the packaging materials diffusivity versus convection of oxygen in the oil and to differentiate the temperature level impacting on the following outcome.

By focusing on mass transport processes, it is found that mass transport is reaction (oxidation) driven, while convection through packaging material is absolutely negligible compared with diffusion. In terms of shelf-light assessment, olive oil seems to respond differently above 15 °C, where diffusion becomes the only driving-force for oxygen presence and, consequently, for the oxidation itself. This is a very interesting conclusion, considering the protective role of packaging materials and importance of barrier properties becoming insignificant compared to temperature.

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