Shelf-life Assessment of Food Undergoing Oxidation–A Review

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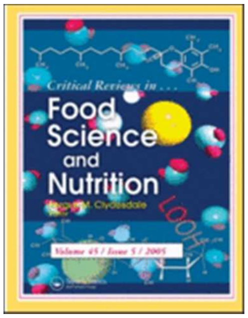

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Abstract

Oxidation is the most common event leading to the end of shelf life of microbiologically stable foods. Thus, a reliable shelf life assessment is crucial to verify how long the product will last before it becomes oxidized to an unacceptable level to the consumers.

Shelf life assessment strategies of foods and beverages suffering oxidation are critically discussed focusing on definition of the acceptability limit, as well as the choice of the proper oxidative indicators, and methodologies for shelf life testing. Testing methodologies for shelf life determination under actual and accelerated storage conditions are considered, highlighting possible uncertainties, pitfalls and future research needs.

Keywords: shelf life, oxidation, acceptability limit, kinetic modelling, accelerated test

Shelf life assessment process

Shelf life is an important feature of all foods, including raw materials, ingredients and semi-manufactured products. Every product has its own shelf life and all the subjects involved in the food chain should be aware of it. In general terms, shelf life can be defined as a finite length of time after production, during which the food product retains a required level of quality under well-defined storage conditions (Nicoli, 2012). This quality level discriminates products which are still acceptable for consumption from those no longer acceptable. Shelf life assessment of foods has always represented an exciting challenge for food scientists, but it is also a vital process for food companies to maintain their brand reputation on the market. To get reliable shelf life data, the adoption of a systematic approach is necessary.

A shelf life study can be divided into three fundamental steps, as schematically shown in Figure 1. The preliminary steps imply the identification of the most critical chemical, physical or biological event leading to the product quality depletion followed by the definition of the relevant acceptability limit. The next step is the evaluation of the changes of the selected quality indicator as a function of time under storage conditions mimicking the foreseeable storage conditions (real-time shelf-life testing) or under environmental conditions able to accelerate deteriorative reactions (accelerated shelf life testing - ASLT). Finally, data should be modelled to obtain a shelf life estimation or prediction, respectively.

Real time shelf life testing is a procedure theoretically applicable for shelf life estimation of any food category. However, it becomes profitable in case of perishable foods, for which quality decay occurs in rather short time. On the contrary, the prediction of long term shelf life is traditionally obtained by accelerating shelf life experiments performing tests under environmental conditions able to speed up quality deterioration. This is the case of many microbiologically stable foods, such as ambient stable and frozen products. In these wide food category, quality depletion during storage is in most cases attributable to oxidation reactions. Table 1 is a list of foods whose shelf life is expected to be limited by oxidative reaction development.

Quality and safety issue in shelf life studies of food undergoing oxidation

Oxidation in foods is a complex set of reactions involving firstly molecules belonging to the lipid family and oxygen and leading to the formation of a number of radical and highly reactive species. When lipid oxidation takes place in foods during storage, it causes the formation of undesirable flavour and/or colour, making foods less acceptable or totally unacceptable to consumers determining the end of their life on shelves. Beside quality depletion, oxidative reactions cause the loss of biological activity of lipophilic bioactives (e.g. carotenoids, α-tocopherol, phytosterols, and polyunsaturated fatty acids) that can be naturally present or voluntarily incorporated into a food. Surprisingly, despite the growing number of new functional foods claiming on the label -after FDA and EFSA approval- their beneficial effects, there are few evidences of their oxidative status during product shelf-life.

At last but not least, oxidative reactions can cause the formation of toxic compounds. For instance, the oxidation of polyunsaturated fatty acids results in significant generation of dietary advanced lipid oxidation end-products (ALEs), which are cytotoxic and genotoxic compounds (Kanner, 2007; Awada et al., 2012). On the basis of these considerations, a shelf life study of food undergoing oxidation is not only a quality issue but also a safety one due to the development of oxidation toxicants in foods.

In this context it can be noted that the unique compulsory indication relevant to the development of oxidation in foods is that of olive oils (Commision Directive 1991/2568/EC). Based on this directive, olive oils are subdivided in different categories according to their quality requirements, such as oxidation indices (e.g. peroxide value, acidity, conjugated dienes) and sensory attributes. Even if not compulsory, recommendations on the oxidation/rancidity level corresponding to a certain quality standard for other fats and oils could also be found in the relevant Official Codex Standards. However, these indications only refer to bulk oils whereas no advices for complex and processed food systems are available. Moreover, compulsory acceptability limits can derive from voluntary label claims, such as the concentration of bioactive molecules included in the formulation.

Shelf life test vs stability test

As extensively revised in many books and papers, the rate of lipid oxidation in foods during storage depends on intrinsic food characteristics, packaging related factors and environmental factors (Table 2). The complex interplay among these factors determines the oxidation rate and thus product shelf life. It is noteworthy that a shelf-life study is addressed to finished packed products. This means that the possible strategies (i.e. formulation, packaging) that can be applied as tools to reduce the development of oxidative reactions during storage have to be defined before shelf life assessment. Thus, in principle compositional and packaging variables can be considered constant during a shelf life study. When these factors are voluntarily varied with the goal to understand the effect of such changes on quality decay, a stability test rather than a shelf life study is required. Stability tests are generally set up to evaluate the susceptibility of a sample to oxidation with the aim to predict the deteriorative reaction kinetics as a function of different variables. On the contrary, a shelf life study has the objective to correctly estimate the product shelf life under expected storage conditions. In other words, while a stability study is addressed to measure oxidation rate; a shelf life study aims to estimate the time limit for the consumption of a food product. Although a wide number of studies dealing with food oxidative stability as a function of different environmental factors is available in the literature, results are difficult to be interpreted in terms of shelf life data because of the great variability in the test conditions adopted as well as the lack of acceptability limits.

Shelf life assessment steps

Definition of critical indicator and relevant acceptability limit

The extent of lipid oxidation in foods could be monitored during storage by using different indicators, measured by different methodologies. In Table 3 the most widely applied methodologies to continuously monitor lipid oxidation during food life are summarized. To this regard it should be noted that, even if instrumental analysis is very powerful, the application of sensory analysis cannot be disregarded since the spoilage of foods undergoing oxidation is early appreciable by the consumer senses.

Although different quality indicators may change simultaneously in food during storage, the most critical index should be chosen to effectively face a shelf life study in terms of cost and time. The first and simplistic criterion of choice among possible indicators is its earliness. However, this issue is more complex and requires additional considerations of the links between the critical indicator and the acceptability limit. The latter is the quality level discriminating acceptable products from unacceptable ones (Manzocco, 2012).

As previously stated, compulsory shelf life indicators and relevant limits coming from national or international regulations are rare. When not available, the acceptability limit can be freely chosen according to quality industry policy. In many cases the identification of the acceptability limit can be rationally made by using information on food product stability acquired from previous company experience, literature data, and competitor data. Such procedures are obviously fraught with the risk of critical overestimation or disadvantageous underestimation of the shelf life. This hazard is much more probable in the case of new foods, for which no previous experience is available.

A further possible approach to define the acceptability limit is based on the application of sensory analysis, since sensory perception is often the earliest indicator of product failure in food undergoing oxidation. The company management may decide that the product reaches the acceptability limit when it is recognized as significantly different from the fresh one by applying discriminant sensory analysis (i.e. paired comparison, triangular, duo-trio or A-no-A tests).

Differently, descriptive sensory analysis carried out with expert panels could be applied to describe the evolution of sensory attributes potentially responsible for consumer rejection. Although providing extensive information about the changes of quality attributes, results achieved with an expert panel could be not related with consumer's decision. For this reason, the hazard should not be focused on the properties of the product undergoing oxidation, rather on the attitude of consumer to accept or reject it (Hough et al., 2006).

Consumer sensory dissatisfaction can be identified using survival analysis methodology (Hough and Garitta, 2012). Following this methodology, the product is analysed during storage by asking the consumers a response of acceptability/unacceptability and data are elaborated by survival analysis obtaining a risk function of consumer rejection of the product over storage time. The application of survival analysis for the estimation of consumer dissatisfaction of foods undergoing oxidation has been applied on minced meat (Hough et al., 2006), on roasted and ground coffee (Cardelli and Labuza, 2001), on sunflower oil (Ramirez et al., 2001) and on biscuits and bread sticks (Calligaris et al., 2007a and 2008). When applying this methodology, the food company can choose to be exposed to more or less risk of product failure by selecting, as an acceptability limit, the proper percentage of consumers rejecting the product. In other words, the acceptability limit becomes the maximum percentage of consumers that the company can tolerate to dissatisfy. In most shelf life studies a medium risk level (50% consumer rejection) is chosen as a reasonable acceptability limit but it has been suggested that lower percentages of consumer rejection could be much more reliable.

Despite being powerful and accurate, survival analysis of consumer data is a time consuming and expensive process because it requires a wide testing plan assembling consumer panels. To overcome these pitfalls and find out methods that can be applied in the daily management of the shelf life issue, food operators could define internal quality levels, described by proper instrumental or sensory quality indicators, accounting for the risk of consumer rejection. It means that instrumental or sensory attributes, whose evolution is correlated to sensory dissatisfaction expressed by consumers, should be identified and used to monitor the evolution of product quality changes during storage. Once the risk function is obtained and the percentage of consumers rejecting the product is selected as acceptability limit, this value is used to identify the corresponding limit expressed by the analytical indicator. In this way, further *routine* shelf life studies can be done by monitoring only the instrumental indicator. For instance, a good correlation among peroxide number and consumer rejection was found in biscuits and bread-sticks (Calligaris et al., 2007a and 2008).

Testing and data modelling

After the identification of the appropriate oxidative indicator and the relevant acceptability limit, it is necessary to estimate the length of time needed to reach such a critical value. This step, generally defined as shelf life testing, implies the monitoring of the changes of the oxidative indicator during food storage under well-defined storage conditions. Data obtained are then modelled to obtain proper parameters describing/predicting the oxidation kinetics.

To get shelf life data, two different strategies can be pursued; namely real-time and accelerated shelf life testing.

Real-time shelf life testing

During real-time shelf life testing, experiments are performed under storage conditions that reasonably foresee the situation expected on the market shelf. The basic requirement to perform a reliable real-time shelf life test is that the environmental factors during storage are kept constant. It is appropriate to store the product under its normal storage conditions controlling not only temperature but also keeping constant other environmental conditions, e.g. humidity and light, since they are likely to significantly impact the shelf life of food undergoing oxidation. Since temperature oscillation is very frequent during food storage, it could be profitable to perform the shelf life test under the worst situation that one could expect during storage. In addition, if the package is a see-through container, the light exposure suffered by the product on the shelf could become a critical factor in determining its shelf life. For this reason, the light intensity commonly found on the market shelves (600-800 lux) should be also considered when planning the shelf life test.

Data describing the changes of the oxidative indicator under conditions simulating actual storage are submitted to modelling according to the fundamental kinetic principles or by exploiting descriptive mathematical models. According to the well-known fundamental kinetic principles, the rate of changes of an oxidative indicator (I_{ox}) can be calculated by integrating the general kinetic equation:

$$\int_{I_{ox_o}}^{I_{ox}} \frac{dI_{ox}}{I_{ox}^{n}} = \int_{o}^{t} k\,dt \qquad (1)$$

where *k* is the rate constant and *n* the reaction order. The general rate law can be integrated to obtain the equations of the pseudo zero, first, second or *n* order. Since oxidation reactions are highly complex and a huge number of factors might affect the reaction rate, it should be stressed that the evolution of any oxidation indicator versus time can be frequently the result of different reactions taking place simultaneously or consecutively. Thus, the reaction order *n* does not give any indications on the true reaction mechanisms involved and *k* is therefore considered as an “apparent” rate constant.

Once the reaction rate constant has been calculated, the shelf life can be computed by solving the integrated forms of equation 1 as a function of time:

$$SL = \frac{1}{k}\int_{Io}^{I_{\lim}} \frac{dI}{I^{n}} \qquad (2)$$

where I_o is the value of the critical indicator just after food production, I_{lim} is the critical indicator value corresponding to the previously defined acceptability limit.

Papers dealing with this well recognized procedure have produced huge amounts of data on the oxidation rates of several foods in different environmental conditions. Zero and first order are frequently applied to describe the changes of oxidation indicators (Table 4).

Unfortunately, due to the complex pathway of oxidative reactions, the application of a defined universal model may be precluded. The evolution of peroxide index as a function of storage time is a case in point since it is expected to follow the typical bell-shaped curve. After an induction period, during which very low peroxide value changes are expected, the progressive increase of peroxide value occurs until a maximum is reached, indicating that the oxidative reactions approach to the termination step.

In terms of shelf life assessment two strategies could be applied depending on the level of peroxide value chosen as acceptability limit: i) first detectable changes approach that is when the shelf-life is defined as the time at which an increase of peroxide value is measured; ii) fixed change level approach that is when a selected value of peroxide is chosen as acceptability limit.

When the first approach is used, the computation of the induction period length allows by itself the shelf life definition. Contrarily, when a fixed limit is defined, it is necessary to engage a modelling step. Assuming that all intermediate reactions follow fixed order reaction kinetics, each having its characteristic apparent rate constant, it is possible to model the exponential increase phase by considering this part of the curve separately from the others. Zero order kinetic is frequently applied in this step. Alternatively, the entire evolution of the peroxide value during the overall product life can be modelled by identifying the empirical mathematical model best fitting the peroxide value curves. Different mathematical models have been applied in literature. For instance, Aragao et al. (2009) proposed a phenomenological mathematical model, comprising a decay factor superimposed on an accumulation term, to describe peroxide changes during lipid oxidation. Additional models (i.e. sigmoidal model, Weibull distribution function, and logistic model) are also frequently used (Özilgen and Özilgen, 1990; Cunha et al., 1998; Corradini and Peleg, 2007; Calligaris et al., 2008; Imai et al., 2008; Odriozola-Serrano et al., 2009). These strategies can be also applied to oxidation indexes other than the peroxide value.

Accelerated shelf life testing

As aforementioned, oxidation advances fairy slowly under actual storage conditions. For this reason, shelf life testing can be performed under environmental conditions that speed up oxidative reactions and the results extrapolated to conditions usually experienced by the product. This procedure is worldwide called accelerated shelf life test (ASLT) (Labuza and Schmidl, 1985).

Temperature as accelerating factor. Among all environmental factors that may be used to accelerate oxidative reactions, temperature is certainly the most widely used. This is not only due to the fact that temperature is one of the most critical factors affecting reaction kinetics in food, but also to the availability of a theoretical basis for the development of a mathematical description of the temperature sensitivity of quality loss rates. Indeed, the Arrhenius equation (3) (Arrhenius, 1901), developed theoretically on the molecular basis for reversible chemical reactions, has been shown to hold empirically for a wide range of complex chemical, physical and sensory changes occurring in foods (Labuza and Riboh, 1982):

$$k = k_o \cdot e^{-\frac{E_a}{RT}} \qquad (3)$$

in which k is the reaction rate constant; R is the molar gas constant (8.31 J K^{-1} mol^{-1}), T is the absolute temperature (K); E_a is the apparent activation energy (J mol^{-1}) and k_o is the so called pre-exponential factor. If the Arrhenius behaviour is fulfilled, the reaction rate at a desired temperature can be extrapolated by measuring the rate of quality depletion at least at three different temperatures.

The Arrhenius equation has been successfully used to estimate the temperature dependence of oxidation rate for bulk fats and oils as well as bioactive compounds and complex foods. A number data can be found in the literature relevant to the application of the Arrhenius equation to describe the temperature dependence of oxidative reactions by using different oxidation indices (Table 5). E_a values for different oxidative indicators greatly vary from 9 up to about 200 kJ mol^{-1}. This can be attributed to differences in compositional and environmental factors taken into account in the studies.

Possible pitfalls in the use of temperature as accelerating factor. The successful application of the Arrhenius model requires that food is able to withstand the increase in temperature without leading to dramatic development of phenomena other than the event responsible for product unacceptability at usual storage temperatures. Although the Arrhenius equation is frequently applied, unfortunately many pitfalls could arise in practice leading to deviations from the Arrhenius equation potentially causing errors in shelf life prediction. As shown in Figure 2, in some circumstances an abrupt change in the temperature dependence of the reaction rate can be observed causing positive or negative deviations from the Arrhenius behaviour. The choice of the temperature interval for ASLT is crucial to avoid deviations from linearity of the Arrhenius equation. Different factors can be responsible for deviations from the Arrhenius behaviour of the temperature dependence of oxidation rate:

- Changes in reaction pathway. For complex reactions, such as oxidation, the overall reaction rate is directly dependent on the slowest step which is obviously the rate-determining one. As temperature changes, different activation energies and pre-exponential terms for these steps can lead to non-Arrhenius behaviour. Moreover, a switch in the rate determining steps or a shift in the reaction pathway can occur. When a pathway dominates at lower temperatures while another dominates at higher temperature, the prediction based on high temperature behaviour could underestimate or overestimate the instability. As stated by Frankel (2005) for food lipids, the use of temperatures higher than 100 °C in ASLT is questionable, because samples develop excessive levels of rancidity, which are not relevant to what happens under normal storage conditions. The more polyunsaturated the oils, the lower the temperatures that should be used to test their oxidative stability; for instance, vegetable oils should be tested at temperatures lower than 60 °C while fish oils only below 40 °C (Frankel, 2005).

- Changes in pro-oxidant and antioxidant concentration. As temperature increases, the eventual thermal degradation of minor compounds with pro- or antioxidant activity could become critical since they can modify the temperature dependence of the overall oxidation rate of lipids. In addition, in multi-component foods, in which lipids, carbohydrates and proteins could react generating novel compounds, additional complications could arise. A case in point is the development of Maillard reaction that could lead, depending on the reaction step involved, the formation of compounds with pro-oxidant or antioxidant capacity These substances could greatly affect the kinetics of oxidation (Zamora and Hidalgo, 2007; Echavarria et al., 2012).
- Changes in gas solubility. As well-known from the thermodynamic laws, the solubility of gasses in solvents decreases with increasing temperature. This is the case of oxygen in food matrices. When the main driving force involved in the alterative reaction is the oxygen availability, deviations from the Arrhenius equation can be observed. For example, the rate of peroxide formation in oil-in-water emulsions stored at -30 °C resulted higher than that expected on the basis of the Arrhenius equation (Calligaris et al., 2007b). The latter was fulfilled at temperatures from 60 to -18 °C. It was hypothesized that at -30 °C the role of oxygen concentration becomes critical in affecting the formation of primary oxidation products. Similarly, oxygen concentration was found to be critical in determining the rate of carotenoid bleaching in tomato derivatives stored at temperatures below 0 °C (Manzocco et al., 2006).
- Changes in physical structure. Physical structure modifications occurring in the temperature range considered for ASLT may be responsible for unexpected changes in the temperature dependence of oxidation rate (Parker and Ring, 1995; Calligaris et al., 2004, 2006; 2007b and 2008; Manzocco et al., 2006). Deviations from the Arrhenius behaviour may be the result of the occurrence of a cascade of temperature-dependent events, such as reactant concentration (i.e. unsaturated TAGs, O_2, antioxidants and pro-oxidants) and changes in

physico-chemical properties (i.e. reactant solubility, pH, ionic strength, water activity, viscosity) in the liquid phases surrounding crystals (Parker and Ring 1995; Champion et al., 1997). These compositional modifications could counterbalance and/or even oppose the direct effect of temperature on the reaction rate, giving reason to the observed deviations. Examples of Arrhenius deviations of peroxide formation rate as a function of the reciprocal of temperature are reported in Figure 3.

Due to the huge number of pitfalls potentially arising during ASLT of products undergoing oxidation, the extrapolation of oxidation rates at usual storage temperatures from accelerated data shall be performed only within the temperature range experimentally proven to conform to the Arrhenius model. In other words, the Arrhenius methodology requires being adapted to the specific circumstances of the product being considered.

When the Arrhenius equation is not applicable, other models should be identified. Such models may be simply descriptive or built up starting from the understanding of the physicochemical phenomena leading to the Arrhenius deviation. The Williams-Landel-Ferry (WLF) model (1955) has been stated as appropriate to describe the rate-temperature relation for diffusion limited reactions. This approach was used with satisfactory results to model the kinetics of enzymatic browning in dried foods and model systems, flowability of fructose and melted cheese, kinetics of microbial and enzymatic inactivation (Roos, 1995). On the contrary, it resulted quite difficult to find out literature examples on the exploitability of WLF equation to describe the temperature dependence of oxidative reactions. For instance, Giannakourou and Taoukis (2003) reported that both Arrhenius and WLF models are adequate to represent temperature-dependence of ascorbic acid degradation within the rubbery state of a frozen vegetable matrix.

Moreover, a modified Arrhenius equation was successfully applied to describe the temperature dependence of oxidation in different food systems. The common feature of these systems was that phase transitions of lipids or water occurred in the ASLT temperature range. The model proposed included a corrective factor into the Arrhenius equation to take into account the influence of the compositional changes caused by the temperature changes on oxidation rate:

$$k = k_0 \cdot \Delta k \cdot e^{-\frac{E_a}{RT}} \qquad (4)$$

where Δk is the corrective factor. Since at a given temperature the rate at which any reaction develops can be considered as the result of the ratio between driving forces and resistances, Δk can be defined by the identification of the proper forces and resistances responsible for the Arrhenius deviation. The application of this approach requires a deep understanding of the complex phenomena involved and the analytical possibility to quantify the changes occurring in the matrix as a consequence of temperature changes. Table 6 shows examples of factors used to compute Δk in different systems, such as sunflower oil, extra virgin olive oil, emulsions, biscuits, bread sticks and tomato derivatives (Calligaris et al., 2004; 2006; 2007a and b, 2008; Manzocco et al., 2006). The advantage of this approach is the possibility to perform accelerated shelf life tests even in the temperature range precluded due to Arrhenius deviations.

Additional cautions should be taken in performing ASLT base on the accelerating effect of temperature. In fact, it may happen that the use of temperature does not allow the time necessary for the shelf life test to be sufficiently saved, causing the uselessness of the test. Since quality depletion phenomena can be differently accelerated by the increase in temperature, the time saved when performing the shelf life test under temperature accelerated conditions may be considerably different. Table 7 shows the percentage of time which can be saved when the temperature of the shelf life test is increased by 10 °C as a function of the activation energy of the critical phenomena. It is evident that about 50 kJ mol^{-1} activation energy is required to save 50 % of the time needed to perform the shelf life test. From a practical point of view this means that, for oxidative reactions characterized by E_a values lower that 30-40 kJ mol^{-1}, the acceleration obtained by a 10 °C increase could be too low to be of interest in the attempt to save time during shelf life assessment. The worst possible case is when no temperature dependence of the alterative phenomena reaction rate (E_a approaching 0) is observed (Calligaris et al., 2012).

Other acceleration factors

Low values of activation energies based on temperature changes are frequently observed monitoring light induced oxidative reactions. For instance, the oxidation rate of some lipids, pigments and flavors under dark may be slow, even at temperatures higher than the ambient one. By contrast when the product is exposed to the light, oxidation quickly goes on showing, in any case, slight temperature dependence (Kristensen et al., 2001; Manzocco et al., 2008; Manzocco et al., 2012). In these conditions, light can be regarded as unconventional acceleration factor in shelf life studies. Thus, the accelerated shelf life testing can be conducted by exposing the samples to increasing light intensity levels instead of different storage temperatures. The basic requirement for the successful exploitation of light as accelerating factor is the availability of a robust and validated mathematical model correctly predicting the effect of the selected accelerating factor on the reaction rate leading to quality depletion. To our knowledge, there are few examples of the use of light as accelerating factor and thus predictive mathematical models. To this regard, Manzocco et al. (2012) developed a mathematical model predicting the effect of light intensity on oxidation rate of soybean and sunflower oil. The light dependence of the rate constants of peroxide formation (PV) resulted to be well described by a power law equation:

$$k = k_d + E_{l_1} \cdot L^{E_{l_2}} \qquad (4)$$

where L is light intensity (lx), k_d is the reaction rate under dark and E_{l_1} and E_{l_2} are the experimental parameters of the model, namely the electromagnetic energy required to activate the reaction. Similarly to thermal activation energy (E_a) in the Arrhenius equation, these parameters account for the electromagnetic energy required to activate the oxidative reaction.

By keeping constant the temperature during the test, the Authors performed ASLT of oils exploiting the light as accelerating factor and predicted the shelf-life under foreseeable enlighten conditions (i.e. 600-800 lux on market shelves; dark). Considering that peroxide formation (PV) was well described by the zero order reaction order, the shelf life equation used was:

$$SL = \frac{PV_{\lim} - PV_o}{k_d + E_{l_1} \cdot L^{E_{l_2}}} \qquad (5)$$

This equation represents actually a model allowing prediction of shelf life by changing the light intensity at a given temperature *T*. The only independent variables of the proposed model is the light intensity (*L*), which is the enlighten condition experienced by the product on the retail shelves, and the acceptability limit. A similar approach was also efficaciously used to study the stability of carotenoid containing beverages exposed to different light intensity levels (Manzocco et al., 2008). The exploitation of light as accelerating factor appears interesting since it may allow solving the difficult task of predicting shelf life of photosensitive food usually marketed in the presence of light. Further advantages could be the possibility to use light instead of temperature to quickly predict shelf life of foods that cannot withstand high temperature during shelf life testing.

Theoretically, the aforementioned approach can be applied also by using other environmental factors able to accelerate the oxidation. Since the oxidative reactions are strongly dependent on oxygen concentration, this parameter could represent a potentially exploitable accelerating factor to develop proper shelf life assessment methodologies and relevant predictive models. However, to our knowledge, until now little effort has been made on this topic. This is an open research field which will certainly require more attention from researchers in the future.

Conclusion

Shelf life assessment of food undergoing oxidation has always represented a challenge for food scientists and industry managers. Actual literature information provides limited help to solve the problem of shelf-life determination, which can only be faced by adopting rigorous, systematic, and well-designed shelf-life assessment. The most urgent open issues appear to be i) the identification of acceptability limits and ii) the possibility to reduce testing time as much as possible without losing in predictive capability. The former issue could be faced by implementing rational procedures merging consumer and marketing aspects and thus supporting the decision process leading to the identification of the acceptability limit. The second problem for food industries facing the oxidation development during food storage is linked to the need to apply accelerated shelf-life tests that can effectively speed up the shelf life assessment process. However, the generation of predictive models for product suffering oxidative reactions could be an arduous task due to the huge number of environmental and compositional factors affecting the oxidation rate.

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Figure caption

Figure 1. Fundamental steps in shelf life assessment process

Figure 2. Schematic representation of possible positive and negative deviations from the Arrhenius equation

Figure 3. Example of Arrhenius deviations of zero order rate constant of peroxide formation as a function of temperature in biscuits and bread-sticks (modified from Calligaris et al., 2007a; 2008)

Table 1. Foods whose quality depletion during storage is mainly attributed to oxidative reaction development.

Food category	Examples
Ambient stable	Oils and fats
	Dried and freeze-dried foods and ingredients
	Coffee products
	Bakery products
	Breakfast cereals
	Canned products
	Fried snacks
	Soft drinks containing colorants and flavours
	Functional foods containing lipophilic bioactives
Frozen	Ready meals (e.g. pasta, lasagna, pizza)
	Meat and fish
	Fried foods
	Blanched fruit and vegetables

Table 2. Main food characteristics, environmental and packaging related factors affecting oxidative reactions in foods.

Food characteristics	**Environmental factors**	**Packaging related factors**
Fatty acid unsaturation degree	Oxygen partial pressure	Packaging barrier properties to moisture, light and oxygen
Redox potential	Temperature	
Presence of antioxidants and pro-oxidants	Relative humidity	
Surface area	Light	Active packaging
Food component physical state		

546 Table 3. Oxidative reaction indicators and relevant analytical methodologies

Indicator	Methodology
Peroxide value	Titration, spectroscopic methods
Conjugated dienes (CD)	Spectroscopic methods
Acidity	Titration
Volatile carbonyl compounds	GC-MS
Anisidine value	Spectroscopic methods
Thiobarbituric acid index (TBA)	Spectroscopic methods
Hydrocarbons and fluorescent products	Fluorescent spectroscopy
Sensory attributes (off flavour, off odours)	Discriminant and descriptive methods, consumer acceptance
Colour	Colour analysis, image analysis, spectrophotometry
Selected compound concentration	HPLC, GC-MS

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Table 4. Apparent zero and first reaction orders used to describe the evolution of oxidation indices (modified from Manzocco et al., 2010)

Apparent reaction order	Index	Product	Reference
Zero	Peroxide value	Potato chips	Houhoula and Oreopolou, 2004
		Biscuits	Calligaris et al., 2007
		Extra virgin olive oil	Calligaris et al., 2006; Mancebo-Campos et al., 2008
		Salmon oil	Huang and Sathivel, 2008
		Perilla oil	Shim and Lee, 2011
		Soybean oil	Manzocco et al., 2012
	K232	Extra virgin olive oil	Mancebo-Campos et al., 2008
First	Vitamin C degradation	Frozen vegetables	Giannakourou and Taoukis, 2003
		Orange juice	Polyedra et al., 2003; Tiwari et al., 2009
		Fresh-cut strawberries	Odriozola-Serrano et al., 2009
	K270	Extra virgin olive oil	Gutierrez and Fernandez, 2002; Mancebo-Campos et al., 2008
	Oxygen consumption	Soybean oil	Colakoglu, 2007
	Free fatty acids	California almond	Lin et al., 2012

Table 5. Temperature range of application of Arrhenius equation to estimate oxidation of different foods by using different indices

Oxidation index	Product	Temperature range (°C)	Reference
Induction period	Perilla oil	25/75	Shim and Lee, 2012
Peroxide value	Sunflower oil	4/60	Calligaris et al., 2004
	Extra virgin olive oil	25/60	Calligaris et al., 2006
	Salmon oil	10/35	Huang and Sathivel, 2008
	Bread sticks	20/45	Calligaris et al., 2008
	Soybean oil	10/30	Manzocco et al., 2012
Coniugated dienes	Almond-based products	5/40	Tazi et al., 2009
TBARS	Almond-based products	5/40	Tazi et al., 2009
Volatiles	Sunflower oil	460	Calligaris et al., 2004a
	Extra virgin olive oil	25/60	Calligaris et al. 2006
	Milk powder	37/55	Thomsen et al., 2005
Free fatty acids	California almonds	4/38	Lin et al., 2012
Carotenoids	Osmo-dehydrofrozen tomatoes	-20/-5	Dermesonlouoglou et al., 2007
	Frozen vegetables	-15/-5	Giannakourou and Taoukis, 2003
Vitamin C	Orange juice	20/45	Manso et al., 2001
	Osmo-dehydrofrozen tomatoes	-20/-5	Dermesonlouoglou et al., 2007
	Frozen pumpkin	-25/-7	Goncalves et al., 2011

554 Table 6. Examples of factors used to effectively compute Δk

Sample	Indicator	Factors affecting Δk
Sunflower oil	Hexanal in the headspace	Liquid fraction of oil
		Viscosity
Extra virgin olive oil	Peroxide value	Liquid fraction of oil
		Polyphenol concentration in liquid phase
Oil-in-water emulsion	Peroxide value	Oxygen concentration
	Hexanal in the headspace	Liquid fraction of oil
		Freeze concentration
		Oil viscosity
Tomato derivatives	Colour (a* value)	Oxygen concentration
		Freeze-concentration
Biscuits	Peroxide value	Liquid fraction of oil
Bread-sticks	Peroxide value	Liquid fraction of oil

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Table 7. Percentage of expected time saved by 10 °C temperature increase as a function of activation energy values.

Activation energy (kJ/mol)	Estimated saved time % by 10 °C increase
10	11
20	21
30	30
40	38
50	45
60	51
70	56
80	61
100	69

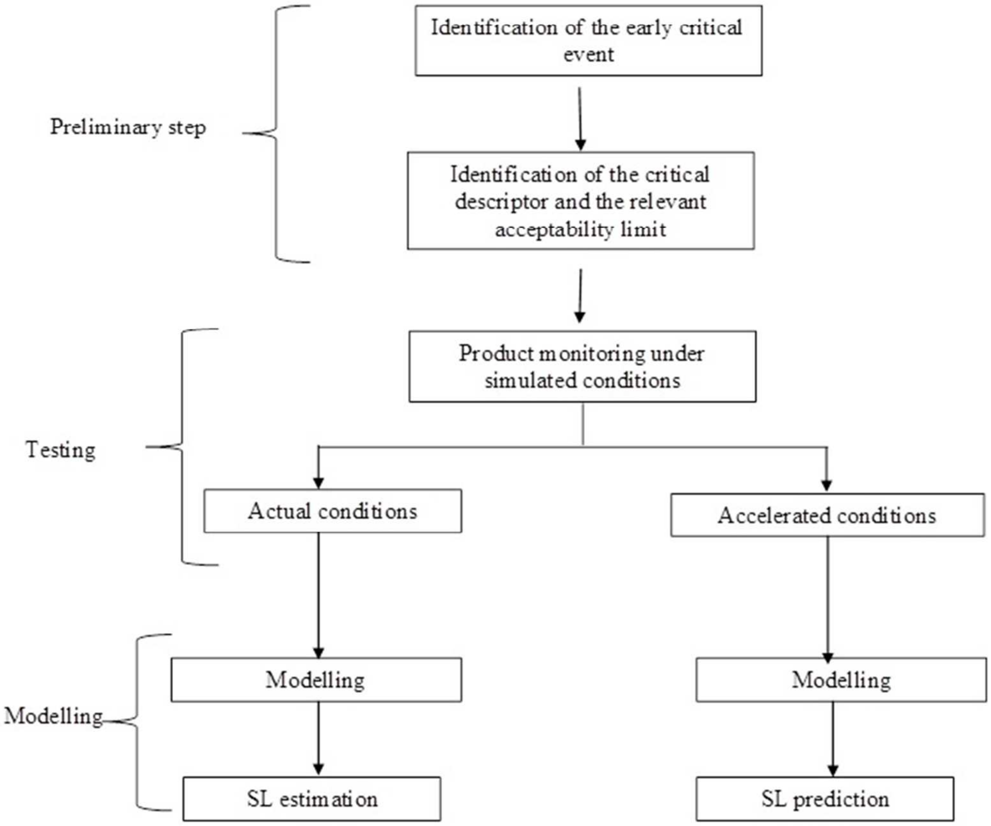

Figure 1. Fundamental steps in shelf life assessment process
178x180mm (96 x 96 DPI)

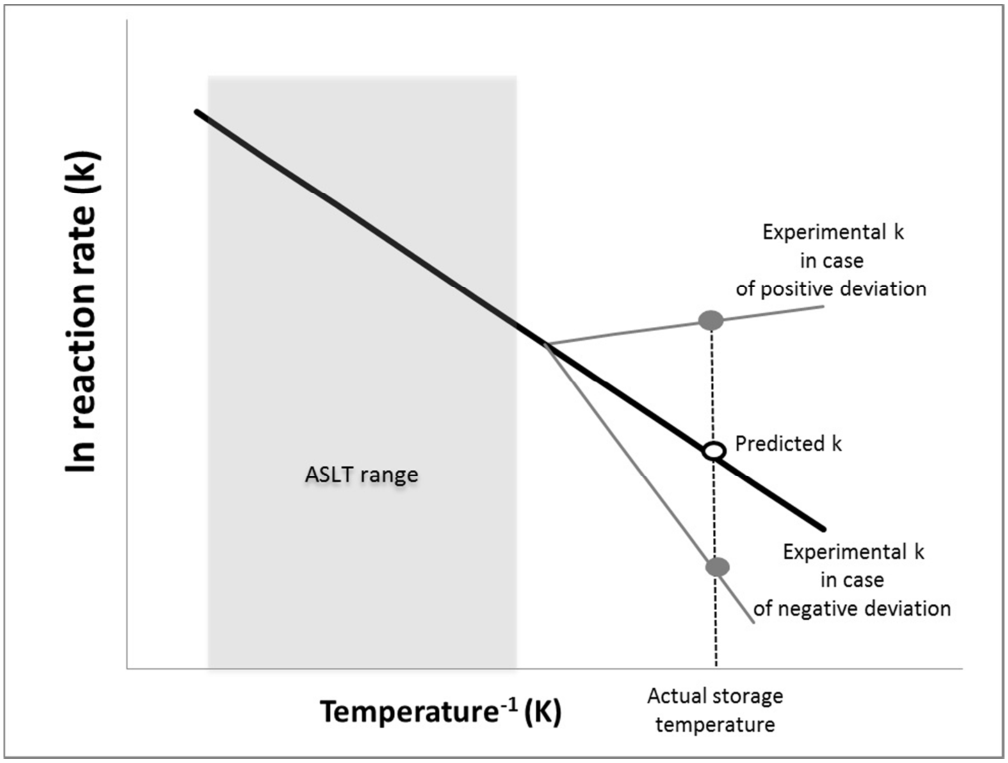

Figure 2. Schematic representation of possible positive and negative deviations from the Arrhenius equation
259x196mm (96 x 96 DPI)

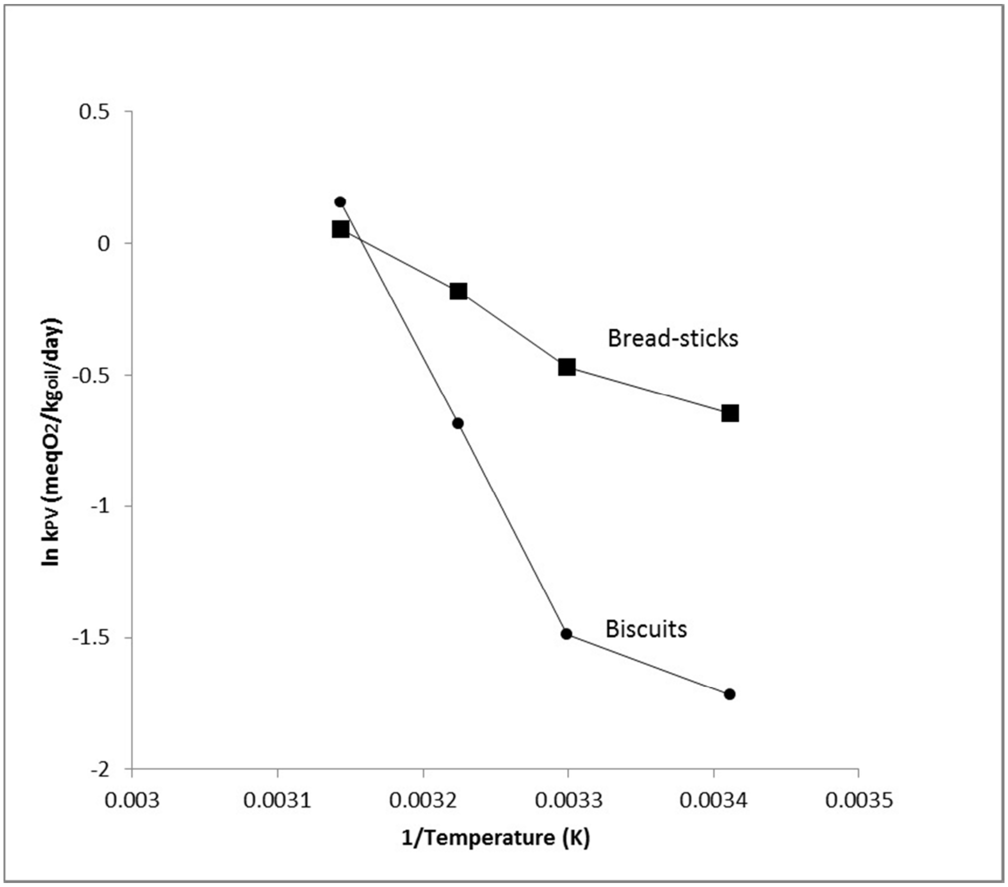

Figure 3. Example of Arrhenius deviations of zero order rate constant of peroxide formation as a function of temperature in biscuits and bread-sticks (modified from Calligaris et al., 2007a; 2008)
227x199mm (96 x 96 DPI)