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Shelf-life Modeling of Bakery Products by Using Oxidation Indices

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The aim of this work was to develop a shelf-life prediction model of lipid-containing bakery products. To this purpose (i) the temperature dependence of the oxidation rate of bakery products was modeled, taking into account the changes in lipid physical state; (ii) the acceptance limits were assessed by sensory analysis; and (iii) the relationship between chemical oxidation index and acceptance limit was evaluated. Results highlight that the peroxide number, the changes of which are linearly related to consumer acceptability, is a representative index of the quality depletion of biscuits during their shelf life. In addition, the evolution of peroxides can be predicted by a modified Arrhenius equation accounting for the changes in the physical state of biscuit fat. Knowledge of the relationship between peroxides and sensory acceptability together with the temperature dependence of peroxide formation allows a mathematical model to be set up to simply and quickly calculate the shelf life of biscuits.

KEYWORDS: Biscuits; acceptance; oxidation; shelf-life modeling

INTRODUCTION

The lipid oxidation reactions occurring during the storage of bakery products are the main deteriorative event affecting their quality. Because lipid oxidation proceeds fairly slowly at room temperature, the shelf-life evaluation of lipid-containing bakery products is a time-consuming process that is difficult to fit to industrial needs. The most common way to save time is the application of accelerated shelf-life tests (ASLT). Different accelerative factors could be employed in ASLT (i.e., temperature, light, moisture). Generally, temperature being the most critical environmental factor affecting the reaction rate, this parameter is usually chosen to accelerate the oxidation process (*1*−*3*). Hence, by measuring the rate of the quality index changes at at least three different temperatures, the reaction rate at a desired temperature can be extrapolated by the application of the well-known Arrhenius equation.

The working assumptions to successfully predict the shelf life by applying ASLT are (i) no deviations from the Arrhenius equation in the working temperature range and (ii) a clear relationship between the selected index and the consumer acceptability.

In the case of lipid and lipid-containing foods undergoing oxidation, both factors could be critical depending on the selected working conditions chosen for the ASLT. In fact, if phase transitions occur in the temperature range studied, a nonlinearity in the Arrhenius plot of oxidation rate can be expected (*4*−*7*). In particular, the occurrence of lipid crystallization leads to a positive deviation in the Arrhenius plot, indicating that oxidation proceeds at rates higher than those predicted on the basis of the Arrhenius equation. In such cases, a modified Arrhenius equation can be used to predict the temperature dependence of oxidation even in partially crystallized lipid matrices.

$$k = k_0 \Delta K \, e^{-E_a/RT} \tag{1}$$

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 activation energy (J mol^{-1}), k_0 is the pre-exponential factor of frequency factor, and ΔK is a corrective factor included in the Arrhenius equation to take into account the influence of variables, other than temperature, which significantly affect the reaction rate in the partially crystallized matrix. Depending on the matrix, ΔK was differently defined, being proportional to the compositional changes following transition. In the case of lipid oxidation, the change in reactant concentrations in the liquid phase surrounding fat crystals was found to be the most critical parameter accounting for deviation from Arrhenius behavior. This information suggests that similar deviations could be expected also in lipid-containing foods, causing overestimation of the shelf life.

With regard to the relationship between the chemical index selected to follow the quality loss and consumer acceptability, it is well-known that oxidative reactions lead to the formation of off-flavor volatile compounds, accounting for the consumers' rejection of the product (*8*−*13*). Consequently, a consumer panel would be the most appropriate tool to determine when a food reaches the end of its life by sniffing the product. However, this approach is very expensive and difficult to perform routinely because it is not easy to assemble a consumer panel for multiple

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measurements during shelf life. The best working way for routine shelf-life evaluation should be the identification of a quality index, related to the sensorial acceptability, which could be measured by using a quick and simple analytical method. From an industrial point of view, one of the widest used oxidation indices is the peroxide value (PV), because its evaluation is very easy also with the laboratory equipment owned by small and medium companies. In addition, it should be considered that, even if hydroperoxides are not volatile, they are well-known precursors of volatile secondary oxidation products which are sensorially perceivable. For this reason, the possibility to correlate the peroxide value with the sensory acceptance limits appears to be interesting in order to find methodologies for a rapid prediction of the product shelf life through quality assurance management.

On the basis of these observations, the aims of the present work were (i) to model the temperature dependence of the oxidation rate of bakery products by taking into account the changes in lipid physical state, (ii) to assess the acceptance limit by sensory analysis and relate it with peroxide value, and (iii) to develop a shelf-life prediction model of lipid-containing bakery products.

To these purposes, biscuits with 20% (w/w) of fat were chosen as the target product. The oxidation kinetics and the acceptance limits were evaluated as a function of temperature from −18 to 45 °C. The oxidative stability was measured following the changes of peroxides, whereas consumer acceptance limits were detected by applying survival analysis concepts.

MATERIALS AND METHODS

Freshly made commercial biscuits containing 20% (w/w) of fat were purchased at an Italian factory. The packaging material was metalized oriented polypropylene (OPP) film. Original packages containing 250 g of biscuits were stored at −18, 20, 30, 37, and 45 °C. At selected lengths of time the samples were kept out and analyzed for peroxide number.

During the storage time no changes in dry matter were observed, confirming the moisture barrier properties of the packaging material.

Analytical Determination. *Fat Separation.* Biscuit fat was obtained by solid−liquid extraction using diethyl ether/petroleum ether (Carlo Erba, Milano, Italy) mixtures (1:1 v/v). In particular, ground biscuits and solvent mixture in the ratio of 1:2.5 w/v were stirred at room temperature for 1 h. After filtration through filter paper (Whatman no. 1), the fat was separated from the solvent by evaporation (Heidolph Instruments, model 4001, Milano, Italy).

Fatty Acid (FA) Content and Peroxide Value (PV). The PV and the FA composition (FA) of the oil samples were determined according to the European Official Methods of Analysis (*14*).

Total solid content determinations were carried out according to AOAC methods (*15*).

Calorimetric analyses were made using a TA4000 differential scanning calorimeter (Mettler-Toledo, Greifensee, Switzerland) connected to Starever 8.10 software (Mettler-Toledo). Heat flow calibration was achieved using indium (heat of fusion = 28.45 J/g). Temperature calibration was carried out using hexane (mp = −93.5 °C), water (mp= 0.0 °C), and indium (mp = 156.6 °C). Samples were prepared by carefully weighing 10−15 mg of the fat extracted from the biscuits in 160 μL aluminum DSC pans, closed without hermetic sealing. An empty pan was used as a reference. Samples were heated under nitrogen flow (0.5 mL/min) at 60 °C for 15 min to destroy crystallization memory, cooled to −80 °C, and then heated from −80 to 60 °C. The scanning rate was 2 °C/min. The start and the end of melting transition were taken as on-set (T_{on}) and off-set (T_{off}) points of transition, which are the points at which the extrapolated baseline intersects the extrapolated tangent of the calorimetric peak in the transition state. Results were normalized to account for the weight variation of the samples. Total peak enthalpy was obtained by integration. The program STAR ever. 8.10 (Mettler-Toledo) was used to plot and analyze the thermal data.

The liquid fraction (LF), defined as the percentage of the liquid mass of oil at selected temperatures, was calculated from the melting thermogram. LF calculation is based on the assumption that at −80 °C the lipid mass, after annealing, is totally crystallized (LF = 0) and that at 60 °C it is totally liquid (LF = 100). This means that the total peak enthalpy was assumed as the melting enthalpy of the total lipid mass. By the partial integration of the curves at different temperatures we obtain the enthalpy of the mass melted at the selected temperature and, finally, by comparison with the total peak enthalpy, the liquid fraction.

At each temperature the concentration factor of the liquid phase (C) was defined as the ratio between the liquid fraction originally present in the sample (LF_o) and the liquid fraction at selected temperature (LF_T) (*5*, *6*):

$$C = \frac{LF_0}{LF_T} \tag{2}$$

Sensory Analysis. The end of the shelf life of biscuits stored at 20, 30, 37, and 45 °C was determined through sensory analysis by applying the survival analysis (*16*−*20*). This method has been developed to evaluate times until an event of interest, often called survival time, taking into account the presence of censored data (*19*). A group of 70 panelists was considered, approximately 50% males and 50% females with ages ranging from 20 to 45 years. Consumers were screened according to the criterion that they usually consumed biscuits. Biscuit samples considered for sensory analysis were stored at the selected temperature for a maximum of 130 days. At selected lengths of time the samples were kept out and frozen. Because lipid oxidation proceeds also at frozen temperatures, prior to the analysis the samples used for sensorial tests were analyzed for PV. Results indicated that after 130 days of storage at −18 °C, PV slightly increased from 0.24 ± 0.01 to 2.92 ± 0.05 mequiv of O_2/kg_{fat}. Before the sensory test, samples were thawed and allowed to equilibrate at room temperature for at least 6 h. Aliquots of 10 g of biscuits were placed into 100-mL capacity plastic containers and sealed with a pressure cap.

Each consumer received six samples corresponding to six random storage times. Panelists were asked to sniff the samples and report whether they were acceptable or unacceptable. The CensorReg procedures from S-PLUS (Insightful Corp., Seattle, WA; ver. 7) were used according to the protocol of Hough et al. (*16*, *18*). Censoring was defined as follows: at a given storage time t two possible answers could be given by the panelists. (a) The sample was perceived as acceptable, indicating that it would be rejected beyond time t; thus, the data are right censored. (b) The sample was perceived as unacceptable, indicating that the panelist would start rejecting the product before time t; thus, the data are left censored.

Data were fitted by maximizing the likelihood function for six standard distributions (smallest extreme value, Weibull; normal, lognormal, logistic, loglogistic). The likelihood function is a mathematical expression that describes the joint probability of obtaining the data actually observed on the subjects on the study as a function of the unknown parameters of the distribution being considered. The Weibull distribution parameters and the storage time corresponding to different percentages of consumers rejecting the product [$F(t)$ = 10, 30, 50, 70, and 90% quantile) were thus estimated.

Kinetic Data Analysis. Pseudo zero-order rate constants of peroxide (k) formation were calculated by linear regression of at least six points from the initial part of the curves. No lag phase was detected. The effect of temperature on the rate of lipid oxidation was evaluated by means of the Arrhenius equation

$$k = k_0 \, e^{(-E_a/RT)} \tag{3}$$

where 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 activation energy (J mol^{-1}), and k_0 is the pre-exponential factor of the frequency factor. To make a better estimate of the apparent activation energy a one-step nonlinear regression was applied to all data by using the

Table 1. Qualitative Characteristics and Fatty Acid Composition of Fat Extracted from the Biscuits Considered in This Research

fatty acid	%
$C_{16:0}$	41.36 ± 0.56
$C_{16:1}$	0.22 ± 0.01
$C_{18:0}$	3.86 ± 0.28
$C_{18:1}$	39.31 ± 0.61
$C_{18:2}$	14.61 ± 0.48

reparametrized Arrhenius equation, in which was inserted a reference temperature chosen in the middle of the temperature range considered in the experimental plan (*21*):

$$k = k_{\mathrm{ref}}\, \mathrm{e}^{-E_a/R(1/T-1/T_{\mathrm{ref}})} \tag{4}$$

As reference temperature was used 286.5 K.

Moreover, the temperature dependence of peroxide formation rate was evaluated by applying the reparametrized modified Arrhenius equation (eq 1)

$$K = K_{\mathrm{ref}}\Delta K\, \mathrm{e}^{-E_a/R(1/T-1/T_{\mathrm{ref}})} \tag{5}$$

where ΔK is the corrective factor and T_{ref} is the reference temperature (286.5 K).

Data Analysis. The results reported in this work are the average of at least three determinations, and the coefficients of variation, calculated as the percentage ratio between the standard deviation and the mean value, were <5% for PV determinations.

Linear and nonlinear regression analysis by least-squares regression was performed by S-PLUS (Insightful Corp.;ver. 7) and the goodness of fit evaluated on the basis of statistical parameters of fitting (R^2, p, standard error) and residual analysis. Fitting by maximizing the likelihood function on survival data was also performed by S-PLUS (Insightful Corp., ver. 7, 2004).

RESULTS AND DISCUSSION

Chemical and Physical Properties of Biscuit Fat. Table 1 reports the fatty acid (FA) composition of the fat separated from the biscuits considered in the present research. The FA content suggests that the fat used for the production of the biscuits can be associated with a palm oil derivative.

These results were confirmed by DSC analysis (**Figure 1**). In fact, in agreement with Tan and Che Man (*22*, *23*), three main exothermic peaks (*1*−*3*) were detected during cooling: peak 1 can be reasonably attributed to the crystallization of highly saturated triacylglycerol (TAG) crystals, whereas peaks 2 and 3 can be attributed to the phase transition of the lipid fractions progressively richer in unsaturated TAGs. Upon further heating, melting progressively happens and the endothermic peaks appear not completely separated. In the temperatures range between −27 and 40 °C, two major endotherm regions were detected corresponding to the endothermic transition of olein (lower temperature peak) and stearin (higher temperature peak). By integration of DSC melting data, the liquid fraction (LF) of fat as a function of temperature was calculated. **Table 2** shows the liquid fraction and the corresponding concentration factor as a function of temperature. It should be kept in mind that the concentration factor *C*, defined according to eq 2, indicated how many times compounds involved in the oxidative process (i.e., unsaturated TAGs, metals, O_2) concentrated in the liquid phase as a consequence of crystallization. A *C* value equal to 1 indicates that, at the given temperature, crystallization did not occur and sample concentration remained unchanged. By contrast, *C* values higher than 1 indicate that the oil partially crystallized at the given temperature, leading to a *C*-times increase in the concentration of the liquid phase.

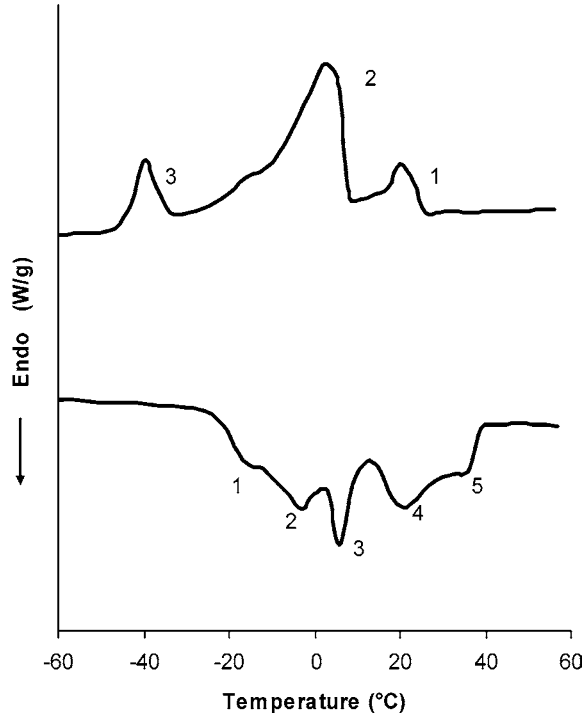

Figure 1. Cooling and melting thermogram of fat extracted from biscuits.

Table 2. Liquid Fraction (LF) and Corresponding Concentration Factor (*C*) of Oil Samples as a Function of Temperature

T (°C)	LF (% w/w)	concn factor (*C*)
−18	3.2	31.10
20	73.4	1.36
30	90.6	1.10
37	98.5	1.01
45	100	1.00

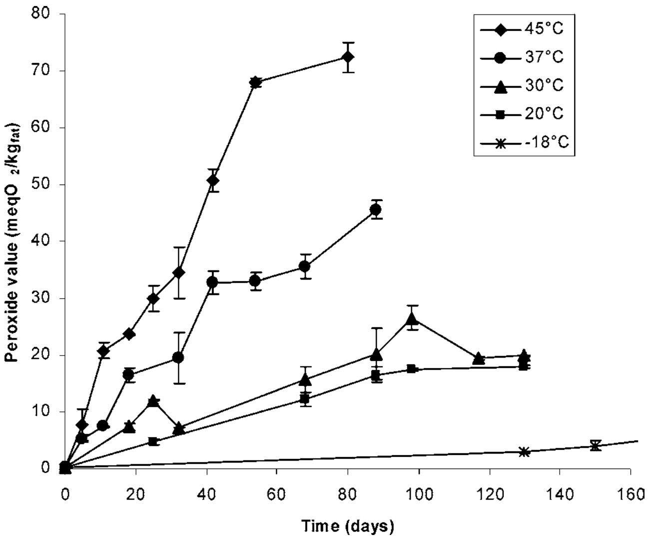

Figure 2. Changes in peroxide value of biscuits stored at different temperatures.

Oxidation Kinetics. Figure 2 shows the changes in peroxide value (PV) of biscuits stored at −18, 20, 30, 37, and 45 °C. As expected, PVs increased during storage, and this enhancement was faster as temperature increased. The pseudo zero rate constants (*k*) of peroxide formation are reported in **Table 3**.

Table 3. Pseudo Zero Rate Constant of Peroxide Formation (*k*) of Biscuits Stored at Different Temperatures and Corresponding Regression Parameters

T (°C)	*k* (mequiv of O_2 kg^{-1}_{fat} day^{-1})	SE	intercept	*p*	R^2
−18	0.05	0.006	1.70	$<10^{-4}$	0.99
20	0.18	0.004	0.26	$<10^{-5}$	0.99
30	0.23	0.03	2.17	$<10^{-4}$	0.92
37	0.51	0.04	3.90	$<10^{-5}$	0.94
45	1.10	0.09	3.05	$<10^{-5}$	0.96

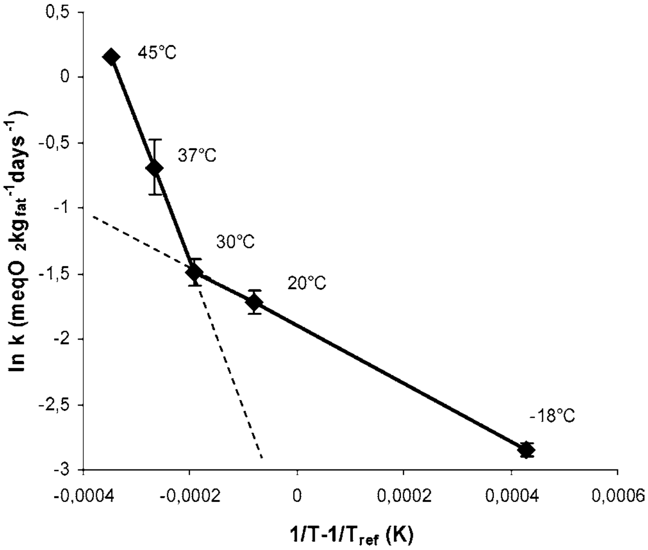

Figure 3. Apparent zero-order rate constants of peroxide formation of biscuits as a function of temperature.

The values of *k* were plotted according to the Arrhenius model (**Figure 3**). Looking at all data in the Arrhenius plot, two different temperature dependences of peroxide formation rate can be identified: one above and one below 30 °C. By applying the Arrhenius model (eq 3) on peroxide data and performing a nonlinear regression analysis ($R^2 = 0.99$, $p < 0.005$), the activation energies above and below 30 °C were obtained: the values were 87.8 ± 0.9 and 18.3 ± 0.2 kJ/mol, respectively. Because the peroxide curve results from a balance between hydroperoxides produced and decomposed, the presence of different activation energies seems to indicate that the formation and decomposition kinetics of peroxides change as a function of temperature.

Considering the Arrhenius equation obtained above 30 °C, the data at 20 and −18 °C could be regarded as positively deviating. In other words, the experimental rate constants at 20 and −18 °C were higher than those estimated by the Arrhenius equation obtained between 30 and 45 °C (**Figure 3**). These results, which are in agreement with those of Calligaris et al. (*4*−*7*), appear to be of great interest considering that (i) a temperature of 20 °C is the most probable biscuit storage condition during their life on the shelf and (ii) a temperature of −18 °C is the storage temperature normally used for control samples during ASLT. Consequently, the observed deviation implies that (i) ASLTs should be carefully applied for bakery shelf-life prediction and (ii) reference samples cannot be obtained by storage at frozen temperatures.

Modeling the Temperature Dependence of the Oxidation Rate. The deviation from the Arrhenius equation previously described was observed at temperatures at which the fat is partially crystallized. In fact, about 27 and 3% (w/w) of biscuit fat was liquid at 20 and −18 °C, respectively (**Table 2**). As indicated by Calligaris et al. (*4*−*7*), the existence of a critical temperature below which the Arrhenius equation is not fulfilled can be attributed to the occurrence of temperature-dependent compositional changes upon crystallization phenomena. In particular, during the progressive separation of fat crystals, the liquid fraction is expected to gradually present an increase in the relative concentration of reactants (i.e., unsaturated TAGs, O_2, antioxidants, and prooxidants) involved in oxidation. These compositional modifications could counterbalance and even oppose the direct effect of temperature on oxidation rate. For this reason a modified Arrhenius equation, taking into account the changes in the physical state of oil, was developed (eq 1).

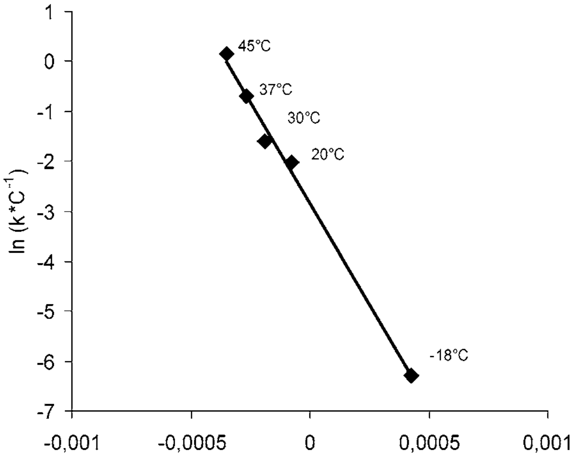

Figure 4. Apparent zero-order rate constants of peroxide formation, expressed as $\ln(k_{PV}C^{-1})$, of biscuits as a function of temperature.

To use the modified Arrhenius equation on biscuit oxidation data, it is necessary to quantify the corrective factor Δ*K*. The latter, in a first approximation, could be assimilated to the concentration factor (*C*).

The model of the temperature dependence of biscuits oxidation was thus obtained imposing $\Delta K = C$ in eq 1:

$$(k_{PV}) = (k_0 C_{fat})\, e^{-E_a/RT} \qquad (6)$$

Applying the reparametrized eq 6 (T_{ref} equal to 286.5 K) on *k*, the regression generated satisfactory results ($R^2 = 0.99$, $p < 0.001$) with frequency factor k_0 and activation energy E_a equal to 1.04×10^{14} and 85.05 kJ/mol, respectively.

Figure 4 graphically shows the temperature dependence of the new dependent variable (kC^{-1}) in an Arrhenius plot. The linear relationship between $\ln(kC^{-1})$ and the reciprocal of *T* (K) is evident:

$$\ln(kC^{-1}) = \ln k_0 - \frac{E_a}{RT} \qquad (7)$$

These results clearly indicate that the relative concentration of reactants participating in the oxidative reactions in the liquid phase is, besides temperature, the main variable affecting the oxidation rate not only in bulk oils but also in complex foods such as biscuits.

Sensory Analysis. To apply the model proposed to predict the biscuit shelf life, the missing information is the consumer acceptability limit. Therefore, biscuit samples stored at 20, 30, 37, and 45 °C were analyzed for sensory acceptability during storage. As already mentioned, the survival analysis was used applying six standard distributions (smallest extreme value, Weibull; normal, lognormal, logistic, loglogistic) (*11*, *16*−*19*). Because no statistical tests are available to compare the goodness of fit of different distributions for censored data, as indicated by Hough et al. (*16*), visual assessment of estimation was performed to select the best model among the six standard distributions considered. The Weibull distribution was finally chosen because of its simplicity and good fit to the data. The maximum likelihood estimates the parameters of the Weibull distribution, allowing the storage time corresponding to the desired percentage of consumers rejecting the biscuits to be calculated. According to industrial policy, the food company can choose exposure to more or less risk by selecting, as shelf-life limit, the proper percentage of consumers rejecting the product.

For instance, **Table 4** shows the storage time corresponding to 10 (very low), 30 (low risk), 50 (medium risk), and 70% (high risk) of consumers rejecting the sample, as a function of temperature.

It is noteworthy that this approach allows by itself the estimation of the biscuit shelf life, which is exactly the time needed to reach the chosen percentage of consumers rejecting the product.

Although the approach of survival analysis is very effective and provides company-tailored assessment of product shelf life, it is indeed difficult to perform routinely. For this reason, the identification of the relationship between the evolution of PV and consumer acceptance would be extremely useful. To this purpose, from the pseudo zero rate constants the PV in correspondence with the time at which different percentages (10, 30, 50, and 70%) of the consumers reject the samples was calculated at different temperatures. **Table 5** shows, as an example, the PVs corresponding to 50% sensory rejection, which is a well-accepted limit in shelf-life studies (*16*).

Statistical analysis demonstrated that, at each risk level, the PV limits at different temperatures were not significantly different ($p > 0.05$). These results highlight that PV limit at any percentage of sensory rejection is not temperature dependent. Therefore, for each risk level, a mean value of PV was calculated (**Table 6**). These values can be used as peroxide limits to determine when 10, 30, 50, and 70% of consumers reject the biscuits and, finally, on the basis of industrial policy, to estimate the shelf life of the product.

Table 4. Shelf Life of Biscuits, Defined as Storage Time Corresponding to 10, 30, 50, and 70% of Consumers Rejecting the Sample, as a Function of Temperature

consumers rejecting the sample (%)	T (°C)	time (days)		
		95% lower limit	estimated quantile	95% upper limit
10	20	15.3	24.8	40.3
	30	12.2	20.5	34.5
	37	5.2	8.3	13.2
	45	0.9	1.8	3.6
30	20	36.5	48.5	64.4
	30	29.3	39.7	53.9
	37	13.2	17.5	23.2
	45	3.7	5.7	8.7
50	20	57.8	69.9	84.4
	30	46.6	57.1	70.0
	37	21.6	26.4	32.2
	45	7.9	10.7	14.4
70	20	81.9	94.6	109.3
	30	66.1	77.2	89.9
	37	31.4	36.9	43.5
	45	13.9	17.8	22.8

Table 5. Peroxide Values Corresponding to the Acceptance Limits Obtained by Sensorial Analysis as a Function of Storage Temperature

T (°C)	peroxide value at 50% of consumers rejecting the sample (mequiv of O_2 kg^{-1}_{fat})		
	95% lower limit	estimated quantile	95% upper limit
20	10.6	12.8	15.4
30	12.7	15.1	18.1
37	14.8	17.2	20.2
45	11.3	14.8	19.4

Table 6. Mean Peroxide Values at Different Percentages of Consumers Rejecting the Biscuits

consumers rejecting the sample (%)	peroxide value (mequiv of O_2 kg^{-1}_{fat})		
	95% lower limit	estimated	95% upper limit
10	4.9	6.4	8.9
30	8.6	10.9	14.4
50	12.9	15.6	18.1
70	18.4	21.7	25.7

Reporting the PV limits (PV_{lim}) as a function of the percentage of consumers rejecting the sample (F%) (**Table 6**), a linear relationship was found ($R^2 = 0.99$, $p < 0.05$):

$$PV_{lim} = 0.24(F\%) + 3.28 \tag{8}$$

This equation allows the PV that indicates the end of the product shelf life to be defined on the basis of the risk level the industry is willing to run.

Because the formation of peroxides follows a pseudo zero order kinetics, the shelf life of biscuits can be finally predicted accordingly:

$$SL = \frac{PV_{lim} - PV_i}{k_{PV,T}} \tag{9}$$

SL is the shelf life, expressed as days, PV_{lim} is the peroxide value corresponding to the limit of biscuit sensory acceptability chosen on the basis of eq 8, PV_i is the peroxide value at zero storage time, and $k_{PV,T}$ represents the pseudo zero rate constant at the selected temperature.

Because k_{PV} values can be extrapolated from the modified Arrhenius equation (eq 6), the following model could be applied to evaluate the shelf life of biscuits at any temperature of interest between 20 and 45 °C:

$$SL = \frac{(0.24(F\%) + 3.28) - PV_i}{k_0 C \exp^{-(E_a/RT)}} \tag{10}$$

T is the temperature at which shelf life should be assessed, C is the lipid concentration factor reported in **Table 2**, F% is the percentage of consumers rejecting the sample chosen by the industry, and PV_i is the initial peroxide value. Equation 10 represents a simple and rapid mathematical instrument allowing the shelf life of biscuits to be calculated by measuring only the initial PV.

In conclusion, the setup of a rapid procedure to predict the shelf life of shelf-stable products, such as bakery products, requires the possibility to follow the evolution of a quality index by using a simple and quick analytical method. The working assumption to successfully evaluate the shelf life is that the selected index should be related to consumer acceptability. In addition, to save time and perform an ASLT, it is necessary to know the temperature dependence of the kinetics of the selected index changes. The results obtained in this work clearly show that the peroxide number is a representative index of the quality depletion of biscuits during their life on the shelf. In fact, its change was found to be linearly related to consumer acceptability. In addition, the evolution of peroxides during storage can be properly predicted by a modified Arrhenius equation accounting for the changes in the physical state of biscuit fat.

The availability of the mathematical relationship between sensory acceptability and PV together with that of the temperature dependence of peroxide formation can be exploited in developing a useful model allowing the simple and quick calculation of the shelf life of biscuits.

Finally, once the PV limit has been assessed by applying the proper sensory technique, further time-consuming sensory tests can be skipped and the cheaper and faster instrumental analysis of the peroxide formation may be routinely applied to evaluate shelf life in the industry quality control programs. The procedure used to find a predictive shelf-life model of biscuits could be definitely followed also to draw up models for other kinds of bakery products.

LITERATURE CITED

(1) Ragnarsson, J. O.; Labuza, T. P. Accelerated shelf-life testing for oxidative stability in foods—a review. *Food Chem.* **1977**, *2*, 291−308.

(2) Labuza, T. P.; Schmidt, M. K. Accelerated shelf-life test in foods. *Food Technol.* **1985**, *39* (9), 57−64.

(3) Waterman, K. C.; Adami, R. C. Accelerating testing: prediction of chemical stability of pharmaceuticals. *Int. J. Pharmacol.* **2005**, *293*, 101−125.

(4) Calligaris, S.; Manzocco, L.; Conte, L. S.; Nicoli, M. C. Application of a modified Arrhenius equation for the evaluation of oxidation rate of sunflower oil at sub-zero temperature. *J. Food Sci.* **2004**, *69* (8), E361−366.

(5) Calligaris, S.; Manzocco, L.; Sovrano, S.; Nicoli, M. C. Influence of crystallization on oxidative stability of extra virgin olive oil. *J. Agric. Food Chem.* **2006**, *54*, 529−535.

(6) Calligaris, S.; Manzocco, L.; Nicoli, M. C. Modeling the temperature dependance of oxidation rate in water-in-oil emulsions stored at sub-zero temperatures. *Food Chem.* **2007**, *101*, 1019−1024.

(7) Manzocco, L.; Calligaris, S.; Nicoli, M. C. Modeling bleaching of tomato derivatives at sub-zero temperatures. *J. Agric. Food Chem.* **2006**, *54*, 1302−1308.

(8) Shahidi, F.; Yun, J.; Rubin, L. J.; Wood, D. L. The hexanal content as an indicator of oxidative stability and flavour acceptability in cooked ground pork. *Can. Inst. Food Sci. Technol. J.* **1987**, *20* (2), 104−106.

(9) Fernandez, J.; Perez-Alvarez, J. A.; Fernandez-Lopez, J. A. Thiobarbituric acid test for monitoring lipid oxidation in meat. *Food Chem.* **1997**, *59* (3), 345−353.

(10) Brewer, M. S.; Vega, J. D.; Perkins, E. G. Volatile compounds and sensory characteristics of frying fats. *J. Food Lipids* **1999**, *6* (1), 47−61.

(11) Grosso, N. R.; Resurreccion, A. V. A. Predicting consumer acceptance ratings of cracker-coated and roasted peanuts from descriptive analysis and hexanal measurements. *J. Food Sci.* **2002**, *67* (4), 1530−1537.

(12) Kanavouras, A.; Hernandez-Munoz, P.; Coutelieris, F.; Selke, S. Oxidation-derivated flavor compounds as quality indicators for packaged olive oil. *J. Am. Oil Chem. Soc.* **2004**, *81* (3), 251−257.

(13) Frankel, E. N. Formation of headspace volatiles by thermal decomposition of oxidized fish oil vs. oxidized vegetables oils. *J. Am. Oil Chem. Soc.* **1993**, *70* (8), 767−772.

(14) European Community, Regulation 2568/91. *Off. J. Eur. Communities* 1991, *L 248*.

(15) AOAC. *Official Methods of Analysis*; Horwitz, E., Ed.; AOAC: Washington, DC, 1980.

(16) Hough, G.; Garitta, L.; Sanchez, R. Determination of consumer acceptability limits to sensory defects using survival analysis. *Food Qual. Pref.* **2004**, *15*, 729−734.

(17) Cardelli, C.; Labuza, T. P. Application of Weibull Hazard Analysis to the determination of the shelf life of roasted and ground coffee. *Lebensm. Wiss. -Technol.* **2001**, *34*, 273−278.

(18) Hough, G.; Lamgohr, K.; Gomez, G.; Curia, A. Survival analysis applied to sensory shelf life of foods. *J. Food Sci.* **2003**, *68*, 359−362.

(19) Anese, M.; Manzocco, L.; Nicoli, M. C. Modeling the secondary shelf-life of ground roasted coffee. *J. Agric. Food Chem.* **2006**, *54*, 5571−5576.

(20) Gomez, G.; Calle, M. L.; Oller, R. *A Walk through Interval-Censored Data*; technical report 2001/16; Department of Statistics and Operations Research, Univ. Politecnica de Catalunya: Barcelona, Spain, 2001.

(21) Van Boekel, M. A. J. S. Statistical aspects of kinetic modeling for food science. *J. Food Sci.* **1996**, *61* (3), 477−486.

(22) Tan, C. P.; Che Man, Y. B. Differential scanning calorimetric analysis of palm oil, palm oil based products and coconut oil: effects of scanning rate variation. *Food Chem.* **2002**, *76*, 89−102.

(23) Tan, C. P.; Che Man Y. B. Differential scanning calorimetric analysis of edible oils: comparison of thermal properties and chemical composition. *J. Am. Oil Chem Soc.* **2000**, *77* (2), 143−155.

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