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ORIGINAL PAPER

A Phenomenological Model of the Peroxide Value's Rise and Fall During Lipid Oxidation

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Abstract During isothermal lipid oxidation at relatively high temperatures, the peroxide concentration frequently peaks while at relatively low temperatures it only rises slowly. These are two manifestations of a process where formation and degradation happen simultaneously on different time scales. A phenomenological mathematical model, comprising a decay factor superimposed on an accumulation term can describe these scenarios. Each has a characteristic time constant shortened by raising the temperature and a rate constant that increases with it. The model's mathematical structure and the magnitude of its coefficients depend on the particular system. However, regardless of the chosen expressions, if the degradation characteristic time falls within or just beyond the experiment's duration, a peak peroxide value will be observed whose height and shape will primarily depend on the other model's parameters. If this characteristic time is far outside the time of the experiment , no peak will be recorded. The model need not be unique and no detailed knowledge of the oxidation mechanisms is required for its formulation. Consequently it can be derived directly from experimental peroxide value versus time relationships, without the need to monitor the intermediate reactions by specialized instrumental methods such as DSC. Through the formation term adjustment, the model can also account for the temperature dependent lag in the rise of the peroxide value and/or the appearance of its peak.

Keywords Peroxide value · Non-linear kinetics · Oxidation · Mathematical modeling · Oils and fats

Introduction

There are complex chemical reactions where synthesis and degradation occur simultaneously [1] and lipid oxidation, as monitored by the peroxide value (or TBA) versus time relationship, is a case in point [2–6]. The result can be a peak peroxide value whose magnitude depends on the process's temperature history. Since peroxides are unstable chemical compounds produced by highly reactive free radicals, they tend to disintegrate after their formation, especially at elevated temperatures. However, their degradation is accelerated at the same time so that their formation rate increases too, creating a competition between the two processes. Traditionally, the kinetics of peroxides synthesis and elimination in lipids has been modeled by addressing each of the underlying reaction steps separately [6], assuming that all the intermediate reactions follow the first or other fixed order reaction kinetics, each having its characteristic rate constant [7]. The temperature dependence of these rate constants has been assumed to obey the Arrhenius equation and hence that each step of the reaction has a fixed 'energy of activation' [8–11]. To determine the intermediate reactions and follow their rates, one has to employ not only standard

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chemical methods but also special instrumental ones such as DSC or even NMR [12]. This approach, however, rarely results in tabulated model parameters that explicitly indicate when a peak peroxide value will be observed let alone its height and shape. This suggests that the interactive array of chemical reactions that produce the peroxides cannot always be characterized effectively by a set of rate constants. There are also reasons to question the usefulness of the Arrhenius equation as a model of the temperature role in such reactions [13]. For example, according to the Arrhenius model, a reaction's rate constant under non-isothermal conditions must be a function of the momentary temperature only and therefore totally unaffected by the system's state and thermal history. Thus, because there is no time in its equation, this model implies that heating oil for several hours, or even days, would have no effect on the underlying oxidation reactions' exponential rates at any storage temperature thereafter. Obviously, incorporating different temperature histories into the model's equation will predict different *concentrations*. But at every same temperature afterwards, the exponential rate would have to be exactly the same, regardless of the system's actual state, because by the model's definition it is a function of temperature only. Also, the rate constants experimental determination requires that all, or at least the most important of the reaction's steps and pathways are fully known. However, identification and quantification of the intermediate stages, as previously stated, usually require advanced analytical and instrumental methods that might not be always available to an industrial oil chemist. Also, different assumptions regarding the reaction mechanism could result in kinetic models that are mutually exclusive [14].

A way to avoid the above and other conceptual problems with the traditional modeling approach is to treat the oxidation reaction in its entirety, i.e., as a manifestation of two superimposed general processes; one of formation, or synthesis, and the other of degradation, or extinction. The details of each are deliberately ignored and it is taken for granted that the relative role of the specific mechanisms can shift with temperature in a manner that need not be fully known. All that counts is that both processes contribute to the reaction's evolution simultaneously. The general concept has been previously described in relation to acrylamide formation and degradation in foods at high temperatures [14] and to microbial growth patterns in a closed habitat accompanied by mortality [15, 16]. Lipid oxidation, acrylamide synthesis and microbial growth are obviously very different processes. However, they and other totally unrelated systems have two things in common: they are all multistage processes that evolve along several possible alternative and interactive pathways and they all have an observed peak at certain temperatures but not at others.

The objective of this communication is to demonstrate that the kinetics of the simultaneous formation and degradation of peroxides in lipids, like that of other systems that exhibit such features, can be described, at least qualitatively, by the same general type of kinetic model. In other words, the goal is to propose a manner in which the progress of oil oxidation can be characterized in a way that does not require experimental determination of all the intermediate reactions and their exact kinetics. At this point, a word of clarification is in order. All the previous statements and what follows only refer to the kinetics of the peroxide formation and degradation chemistry. Therefore, factors such as oxygen solubility, diffusion or heat transfer, will not be addressed, except for when they might explain certain scatter patterns in the peroxide value determinations. Obviously, these factors play a significant and crucial role in lipid oxidation and, consequently, any comprehensive model of the phenomenon would have to take them into account. However, the underlying chemical process kinetics, the specific topic of this work, would have to be described mathematically in order to be an integral part of any such model.

Theoretical Background

Isothermal Peroxides Formation with a Diminishing Rate

Consider an ideal hypothetical complicated lipid oxidation process where the initial peroxide value is low or zero. If all the peroxides formed could remain intact, then with time, the peroxide value, assumed to represent the total amount of peroxides, would approach, asymptotically, a value determined by the appropriate reactants' availability. We do not know the underlying reaction mechanisms in any detail but can still assume that if unimpeded, the rate at which the peroxides are synthesized could be initially relatively high and then progressively diminish as the available reactants are consumed or transformed into chemical species that do not participate in the original reaction [17, 18].

A schematic view of such hypothetical scenarios is given in Fig. 1 (top-left). The one at the top can be expressed mathematically by:

$$Y_{\mathrm{f}}(t) = \mathrm{PV}_{\mathrm{init}} + [a(T) - \mathrm{PV}_{\mathrm{init}}]\left\{1 - \exp\left[-\frac{t}{t_{\mathrm{cf}}(T)}\right]\right\} \qquad (1)$$

where $\mathrm{PV}_{\mathrm{init}}$ is the initial peroxide value, $Y_{\mathrm{f}}(t)$ and $a(T)$ are, respectively, its momentary and temperature dependent asymptotic levels if the formed peroxides could remain intact, and $t_{\mathrm{cf}}(T)$ a characteristic temperature dependent time constant (according to this model, when $t = 0$,

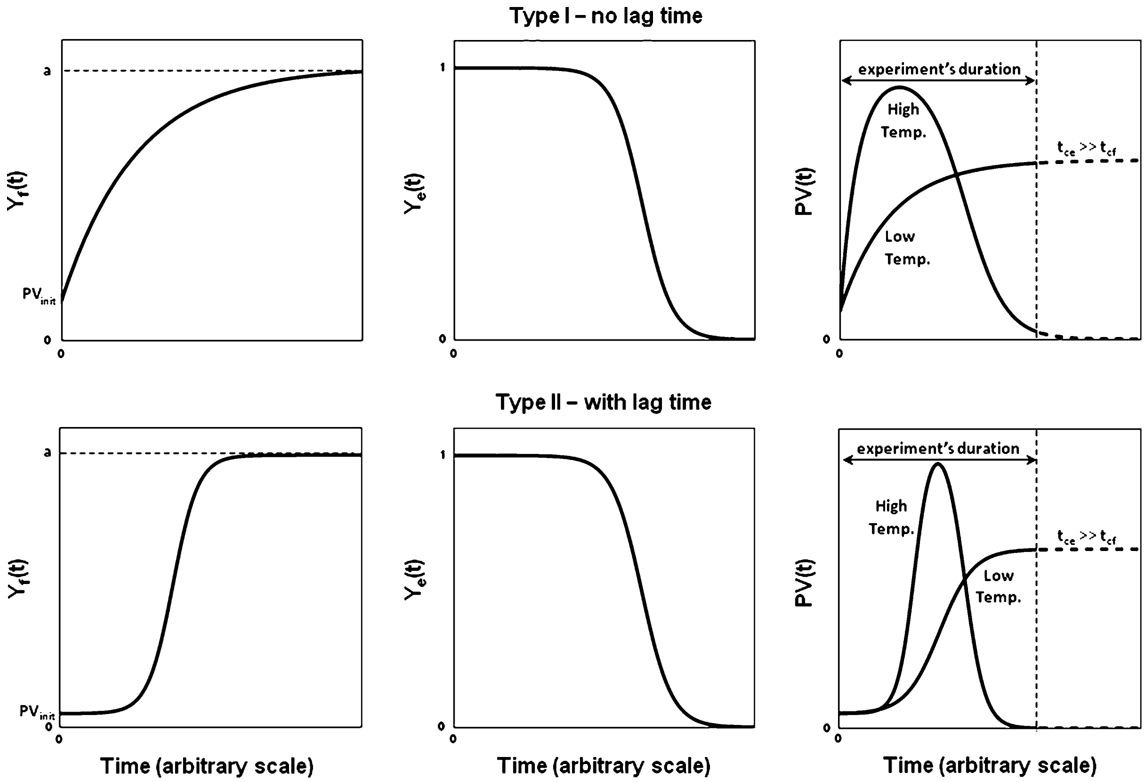


Fig. 1 Schematic view of how to construct a kinetic model of isothermal lipid oxidation curve without and with a lag time (*top* and *bottom*, respectively)

$Y_f(t) = PV_{init}$ and when $t \rightarrow \infty$, $Y_f(t) \rightarrow a(T)$. $t_{cf}(T)$ marks the time where $1 - 1/e$ ($\sim$63%) of the hypothetical net rise is reached).

We have chosen the above model solely because of its relative simplicity and that its parameters have an intuitive meaning. Other models can be just as appropriate. Some might even have better fit to a given set of experimental data but this is not germane to our discussion. For example, a model such as $Y_f(t) = PV_{init}\mathrm{Exp}\{[t/t_{cf}(T)]^{m(T)}\}$, with $m < 1$ would almost certainly also fit oxidation curves of the kind shown in Fig. 1, top. We will show, see below, that the same general approach can be applied to oxidation patterns that show a 'lag time' or 'induction period' [19] and hence that the highest rate of formation need not be the initial, as shown in Fig. 1 (bottom-left). In principle at least, the concept can also be applicable to processes that if unimpeded, would accelerate with time as in a chain reaction. This is to say until the reactants are exhausted and the reaction levels off. Such a scenario will only require that Eq. 1 be replaced by an alternative mathematical expression and a different term to specify the process's time scale.

Since peroxides are inherently highly reactive and hence chemically unstable, they would tend to degrade in a manner, which would also be temperature dependent. This means that while certain lipid molecules or their fragments continue to oxidize, some of the already existing peroxides may disintegrate. Because, however, the underlying disintegration mechanism is not known in detail either, the overall result can be described by a variety of empirical decay factors. The one we have chosen for the discussion is a shifted Fermi term depicted in Fig. 1, middle. It is a mirror image of the classic logistic function and can be expressed by:

$$Y_e(t) = \frac{1}{1 + \exp\{k(T)[t - t_{ce}(T)]\}} + 1 - \frac{1}{1 + \exp\{-k(T)t_{ce}(T)\}} \tag{2}$$

where $Y_e(t)$ is the extinction factor and $k(T)$ and $t_{ce}(T)$ are temperature dependent parameters. Notice that at $t = 0$, $Y_e(t) = 1.0$, when $t \ll t_{ce}(T)$, $Y_e(t) \approx 1$ and when $t \gg t_{ce}(T)$, $Y_e(t) \approx 0$. As shown in the figure, the transition produced by this 'sigmoid term' occurs around $t_{ce}(T)$, which represents the extinction process's characteristic time. The decay's steepness is controlled by $k(T)$; the higher the $k(T)$, the faster is the degradation, if and when it occurs.

This extinction pattern has its own time scale characteristic, given by $t_{ce}(T)$ when Eq. 2 is used to specify the extinction factor. Again, although the extinction factor can be defined in various ways, e.g.,

$Y_e(t) = \exp\{-[t/t_c(T)]^{n(T)}\}$, where $n(T) > 1$, or $1 - (1 + \tanh\{k[t - t_c(T)]\})/2$, the chosen expression must include the characteristic time scale marker, $t_c(T)$.

When, under isothermal conditions, formation and extinction occur simultaneously, the momentary isothermal concentration will be determined by the product:

$$\mathrm{PV}(t) = Y_f(t) \times Y_e(t). \tag{3}$$

When Eq. 1 describes the formation component and Eq. 3 the extinction, the momentary peroxide value, PV(t), would be:

$$\mathrm{PV}(t) = \mathrm{PV}_{\mathrm{init}} + [a(T) - \mathrm{PV}_{\mathrm{init}}]\left\{1 - \exp\left[-\frac{t}{t_{cf}(T)}\right]\right\} \times \left\{\frac{1}{1+\exp\{k(T)[t - t_{ce}(T)]\}} - 1 + \frac{1}{1+\exp\{k(T)t_{ce}(T)\}}\right\} \tag{4}$$

Despite its cumbersome appearance, Eq. 4 is just an algebraic expression. Once written, it can be used to generate and examine hypothetical 'oxidation curves' by substituting its parameters $\mathrm{PV}_{\mathrm{init}}$, $a(T)$, $t_{cf}(T)$, $k(T)$ and $t_{ce}(T)$ with numeric values. It can also be used as a regression model for estimating these parameters from experimental oxidation data, see below.

As shown in Fig. 1, the overall shape of the PV(t) versus time curve primarily depends on the gap between t_{ce} and t_{cf} and its relation to the experiment's duration. We will disregard the scenario where $t_{ce}(T) \ll t_{cf}(T)$, in which case whatever amount of already existing peroxides will readily disappear. When t_{ce} is much longer that t_{cf} and exceeds the experiment's duration by far, PV(t) will have the general shape of $Y_f(t)$, i.e., no peak will be recorded. However, if the two characteristic times are of comparable magnitude and t_{ce} falls within the experiment's duration or just outside it, then a peak peroxide value will be clearly observed as also shown in the figure. The peak's location, height, width and degree of symmetry will depend on both the gap between the formation and extinction time constants, $t_{ce}(T) - t_{cf}(T)$, and the absolute and relative magnitudes of the other parameters, namely $a(T)$ and $k(T)$ in the above example. The same will happen if an alternative pair of models is used to describe $Y_f(t)$ and $Y_e(t)$, see Fig. 1, bottom as an example.

Since oxidation reactions are accelerated by temperature, one would expect that elevating the temperature will shorten both $t_{cf}(T)$ and $t_{ce}(T)$, albeit not necessarily at the same pace. Thus, at low temperatures, where $t_{ce}(T)$ can well exceed the time scale of the experiment, PV(t) might appear as rising monotonically. In contrast, at higher temperatures, $t_{ce}(T)$ might fall within or close to the experiment duration and a peak peroxide value would appear. The peak's location, shape and height, as already stated, would depend on the particular combination of the parameters at hand as shown schematically in Fig. 2.

Oxidation with a 'Lag' or 'Induction' Time

Several reports show, see below, that noticeable oxidation did not start right away but after a delay [19, 20]. Such an oxidation pattern is shown schematically in Fig. 1, bottom. During the 'lag' or 'induction' time, the newly created free radicals are probably too few to produce a noticeable amount of peroxides and at least some of them might be annihilated by mutual interactions. Another possibility is that during the 'lag time' a substantial fraction of the peroxide molecules disintegrate before they can initiate a new oxidation cycle. Yet, it is also possible that there is a continuous but initially very slow build-up of the free radicals and peroxides at this stage, which is just too small to be detected. But once the free radicals formation has

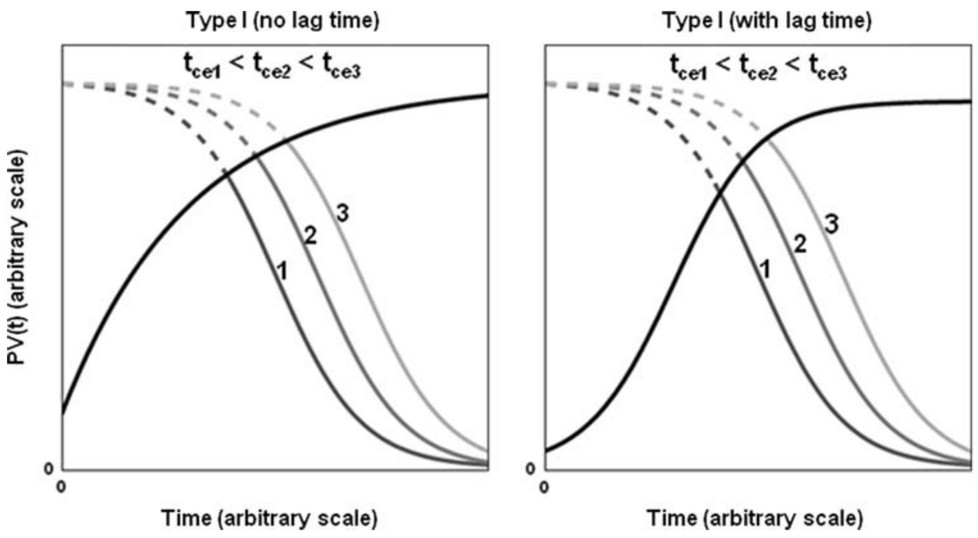


Fig. 2 Schematic view of how of the peroxides' characteristic extinction time, t_{ce}, affects a typical oxidation curve's shape

reached a sufficient level, they could start a ‘chain reaction’ causing an exponential rise in the oxidation’s products. Since, as already mentioned, exponential growth cannot be sustained indefinitely, the process’s rate must at some point drop as the concentration of suitable reactants is exhausted. Oxidation curves stemming from such hypothetical chain of events can be described mathematically by a variety of ‘sigmoid’ growth models. The one we have chosen is based on the logistic function:

$$
\begin{aligned}
Y_{\mathrm{f}}(t) &= \mathrm{PV}_{\mathrm{init}} + [a(T) - \mathrm{PV}_{\mathrm{init}}] \\
&\quad \times \left\{ \frac{1}{1+\exp\{k_{\mathrm{f}}(T)[t_{\mathrm{cf}}(T)-t]\}} - \frac{1}{1+\exp[k_{\mathrm{f}}(T)t_{\mathrm{cf}}(T)]} \right\}
\end{aligned} \tag{5}
$$

where again, $a(T)$ is the hypothetical temperature dependent asymptotic PV level had it been allowed to form unimpeded, $k_{\mathrm{cf}}(T)$ a rate parameter representing the steepness of the oxidation curve at the exponential growth region and $t_{\mathrm{cf}}(T)$, the inflection point’s marker, which represents the time scale of the peroxides synthesis (the last term at right side of the equation has been added in order to satisfy the condition that $t = 0$, $Y_{\mathrm{f}}\ (0) = \mathrm{PV}_{\mathrm{init}}$).

As before, the formed peroxides tend to disintegrate, especially at elevated temperatures, and when this happens, an extinction factor ought to be added to the equation. If the extinction factor, $Y_{\mathrm{e}}(T)$ is defined by Eq. 2, as before, its superposition would result in the model:

$$
\begin{aligned}
Y(t) &= Y_{\mathrm{f}}(t)_{\mathrm{e}}(t) \\
&= \mathrm{PV}_{\mathrm{init}} + [a(T) - \mathrm{PV}_{\mathrm{init}}] \\
&\quad \times \left\{ \frac{1}{1+\exp\{k_{\mathrm{f}}(T)[t_{\mathrm{cf}}(T)-t]\}} - \frac{1}{1+\exp[k_{\mathrm{f}}(T)t_{\mathrm{cf}}(T)]} \right\} \\
&\quad \times \left\{ \frac{1}{1+\exp\{k_{\mathrm{e}}(T)[t-t_{\mathrm{ce}}(T)]\}} + 1 \right. \\
&\qquad \left. - \frac{1}{1+\exp[-k_{\mathrm{e}}(T)t_{\mathrm{ce}}(T)]} \right\}
\end{aligned} \tag{6}
$$

Despite its even more complicated appearance, Eq. 6, like Eq. 4, is just an algebraic expression that can be easily used to generate and examine hypothetical ‘oxidation curves’ by assigning numeric values to its parameters. Similarly, it can also be used as a regression model for estimating these parameters from experimental oxidation data, see below.

Here again, the gap between $t_{\mathrm{ce}}(T)$ and $t_{\mathrm{cf}}(T)$ is the main factor that would determine whether a peak peroxide value would be observed during the experiment. The other parameters would determine the peak’s height and shape as demonstrated in Fig. 2. Notice that Eq. 6 has five temperature dependent coefficients instead of the four that Eq. 4 has. This allows Eq. 6 to describe a larger variety of oxidation patterns and transitions between them. For example, when $t_{\mathrm{cf}}(T)$ is very short on the pertinent time scale and $k_{\mathrm{f}}(T)$ relatively small, Eq. 6 can describe oxidation patterns with no discernible lag similar to those previously modeled by Eq. 4. As before, when $t_{\mathrm{cf}}(T)$ is much larger than the experiment’s duration, $k_{\mathrm{f}}(T)$ large and $k_{\mathrm{e}}(T)$ small, then the extinction factor $Y_{\mathrm{e}}(t)$ will be practically one over the whole pertinent range. In such a case, the extinction factor can be dropped from the equation and the oxidation curve would have a noticeable lag time but no peak of the kind described by Eq. 5 as a model.

Non-isothermal Peroxide Formation

According to the conventional theories of oxidation kinetics, as already stated, a reaction rate constant’s temperature dependence is governed by the Arrhenius equation. Thus, once the reaction’s energy of activation has been determined (by a series of isothermal experiments), the reaction’s outcome under non-isothermal conditions could be calculated by analytic or numerical integration of the rate equation over the thermal history of the system. Doing the integration only requires replacing the constant temperature in the original formula, T, by the temperature history, $T(t)$. The same is true for the log-linear or other models of the temperature effect on reaction rates. But the integration over $T(t)$, which is used to predict the progress of reactions characterized by a single history independent rate constant, notably those following a fixed order kinetics, need not apply here. This is because the peroxide concentration versus time relationship does not follow any fixed order kinetics and is governed not by one but by at least four temperature dependent parameters. How exactly these parameters are affected by temperature is not known in advance and ought to be determined experimentally. We can assume that, under non-isothermal (‘dynamic’) conditions, the momentary logarithmic rate of change in the peroxide concentration, PV(t), is the isothermal rate at the momentary temperature, at a time that corresponds to the system’s momentary state. This is a testable hypothesis, which has been confirmed in other processes [21, 22]. Unfortunately, suitable dynamic lipid oxidation data are very scarce and therefore it remains a hypothesis. Even if such data were available, however, development of a dynamic model of lipid oxidation will still not be a simple task. In order to derive a dynamic rate model with Eq. 4 or 6 as the underlying isothermal peroxide value’s rise and fall, two obstacles would be encountered. Like most four- or five-parameter models of its kind, Eq. 4 or 6 has no analytic inverse. This means that one cannot write the time that corresponds to the momentary peroxide value in the form of an explicit algebraic expression (one need to make a clear distinction between the real (process) time t, and t^*, the time that corresponds to the momentary peroxide value at the momentary temperature during the non-isothermal process. This t^* is a function of PV(t) and $T(t)$ and hence of the real time t. For detail see [13]. The problem of a lack of an by expressing the time that corresponds to the momentary peroxide value, t^*, as a numerical solution of an equation, which will be solved iteratively by the computer whenever the model is used for calculation or simulation. The other difficulty arises when the peroxide value has a peak in the pertinent temperature range. In such a case, the oxidation curve has regions where two different (real) times correspond to the same peroxide value. The possible solution to this mathematical problem is a topic, which is outside the scope of this work and hence will not be further discussed. What must be mentioned is that different temperature histories might not only affect the chemical reaction's kinetics but also physical factors such as the reactants' solubility and diffusivity, which too can affect the oxidation rate.

The Fit of the Model to Isothermal Oxidation Data

Published (and one yet unpublished) sets of experimental lipids oxidation data are presented in Figs. 3, 4, 5. Also shown in the figures is the fit of Eqs. 1, 4, 5 or 6 as the oxidation model. The regression parameters are summarized in Table 1 together with the corresponding mean square error (MSE), which served as a comparative measure of the goodness of fit. Because the central topic of the work is modeling general oxidation patterns rather than those of the particular oils, the statistical aspects of the fit have not been pursued further. Also, since none of the experiments has been originally designed to test the model, the reported temperature levels and the data spacing were not always the most suitable for the analysis. The same can be said of the control of other factors, especially the manner in which the oxygen had been administered.

The first three sets (Figs. 3, 4) show two kinds of curves: with and without peak peroxide value depending on temperature. The same has been observed in a set of conjugated dienes concentration versus time relationships (Fig. 4, bottom). In all these cases, the initial part of the oxidation curves had clear downward concavity, i.e., none has a discernible lag time. The peaked curves of this group were all fitted with Eq. 4 as a model. The monotonic curves, i.e., those who showed no sign of a slope direction reversal were fitted with Eq. 1, which can be considered a special case of the general model (Eq. 4) where $t_{ce} \gg t_{cf}$ or $t_{ce} \to \infty$ and $Y_e(t) \sim 1$.

Oxidation curves with a noticeable lag time are shown in Fig. 5. Except for two that had no peak, they were fitted with Eq. 6 as a model. The 'monotonic' two curves, of the sunflower and Pollock oils, were fitted with Eq. 5 as a model. As before, Eq. 5 could be considered a special case of the general model (Eq. 6) where t_{ce} is well outside the experimental range. Here too, the 'extinction factor' $Y_e(t)$, specified by Eq. 2, was considered as being practically equal to one hence could be dropped from the model's equation.

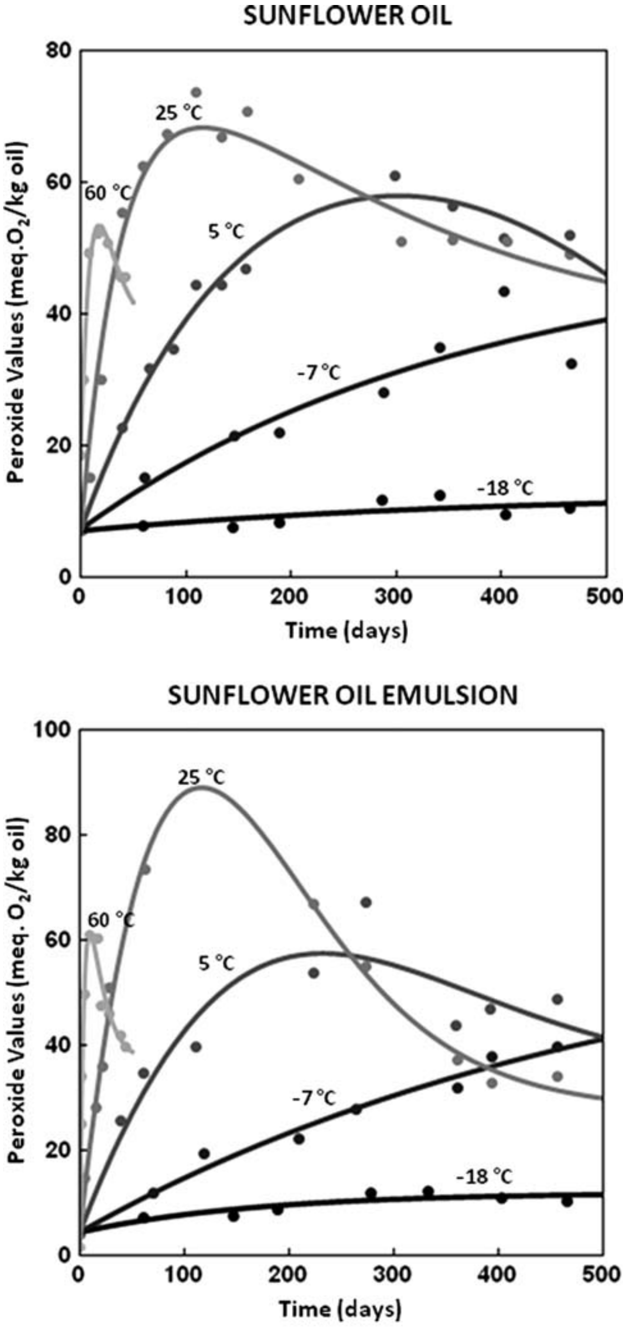


Fig. 3 Isothermal oxidation curves of sunflower oil and oil emulsion, at five temperatures, fitted with Eq. 4 as a model. The original experimental data are from Calligaris et al. [3, 4]

The differences in the examined systems are clearly expressed in their time scales, the overall oxidation levels

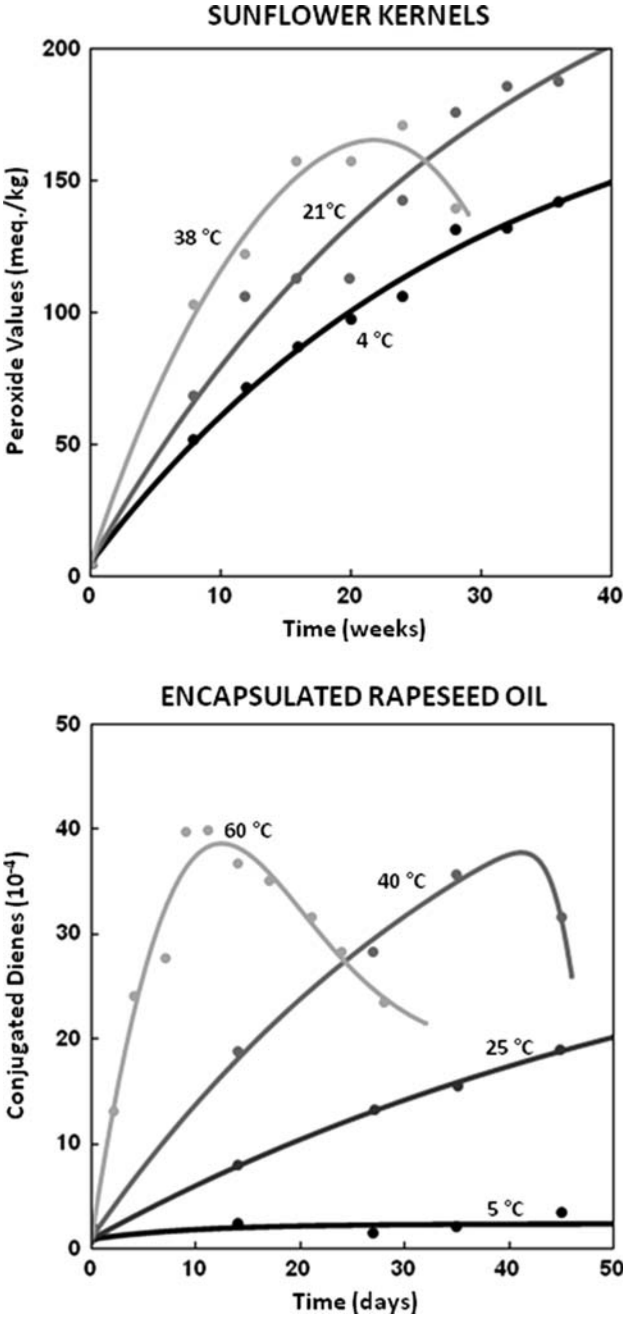


Fig. 4 Isothermal oxidation curves in sunflower kernels, at three temperatures and encapsulated rapeseed oil at four fitted with Eq. 4 as a model. The original experimental data are from Fritsch et al. [23] and Orlien et al. [2], respectively

and the experimental scatter's magnitudes. But the figures also show the two typical qualitative manifestations of the temperature effect on lipids oxidation, i.e., on whether the oxidation curves has a discernible peak or not. They also suggest that the shown oxidation patterns not only can be explained in terms of interplay between two competing 'global' mechanisms but also that they can be expressed mathematically within the framework of what is basically the same general mathematical model. None of the experimental curves that we have examined had been originally intended to serve as a data base for testing the applicability of mathematical kinetic models, and in at least one case, the reported oxidation levels were well above those reached in oils during their normal use or consumption. Also, and unfortunately, most of the published oxidation curves that we could find had been determined at too few temperatures to derive mathematical expressions that would adequately describe the temperature dependence of the isothermal oxidation parameters as defined by the model, e.g., $a(T)$, $t_{cf}(T)$, $k(T)$ and $t_{ce}(T)$ in Eq. 4 or their equivalents in Eq. 6. An example of the trends, based on the data in Fig. 3, is given in Fig. 6 where the plots shown had all been produced with ad hoc empirical models. Despite being derived from a very limited database, shown curves still provide a visual demonstration of how temperature affects the peroxides synthesis and disintegration time scales. Contrary to our initial expectations, finding appropriate data for testing the model and more accurate determination of the oxidation parameter has not been an easy task. In several reports that we had examined, the data scatter was too high to derive any meaningful mathematical model. In others, there had been too few data points to start with, contradictory results or too many obvious outliers. At least some of these imperfections were probably due to factors such as compositional variability, impurities, the sample's age and the effects of other conditions not monitored or reported. Also, since free radicals are strongly involved in lipid oxidation, high sensitivity to local conditions and low reproducibility might be idiosyncratic rather than exceptional. This may explain why the oxidation curves of the same sunflower oil could have very different shapes, see Figs. 3 and 5. Support for this view comes from the potentially dramatic effect that the presence of a small quantity of a pro-oxidant could have on the oxidation pattern as shown in Fig. 5. Interestingly, this effect too could be quantified in terms of the model, see Table 1. Yet, and in spite of all the above, the switch from monotonic increase at low temperatures to a noticeable peak value at high ones has consistently and unmistakably been observed. This suggests that the described models, or similar ones derived from the same premises, indeed capture the essence of the oxidation phenomenon.

Interpretation of the Oxidation Parameters

The oxidation parameters listed in Table 1 were all calculated by non-linear regression using the 'Nonlinear Regress' function of Mathematica 6® (Wolfram Research, Champaign, IL), the software used in this study. Because of the large scatter in some of the data and small number of points

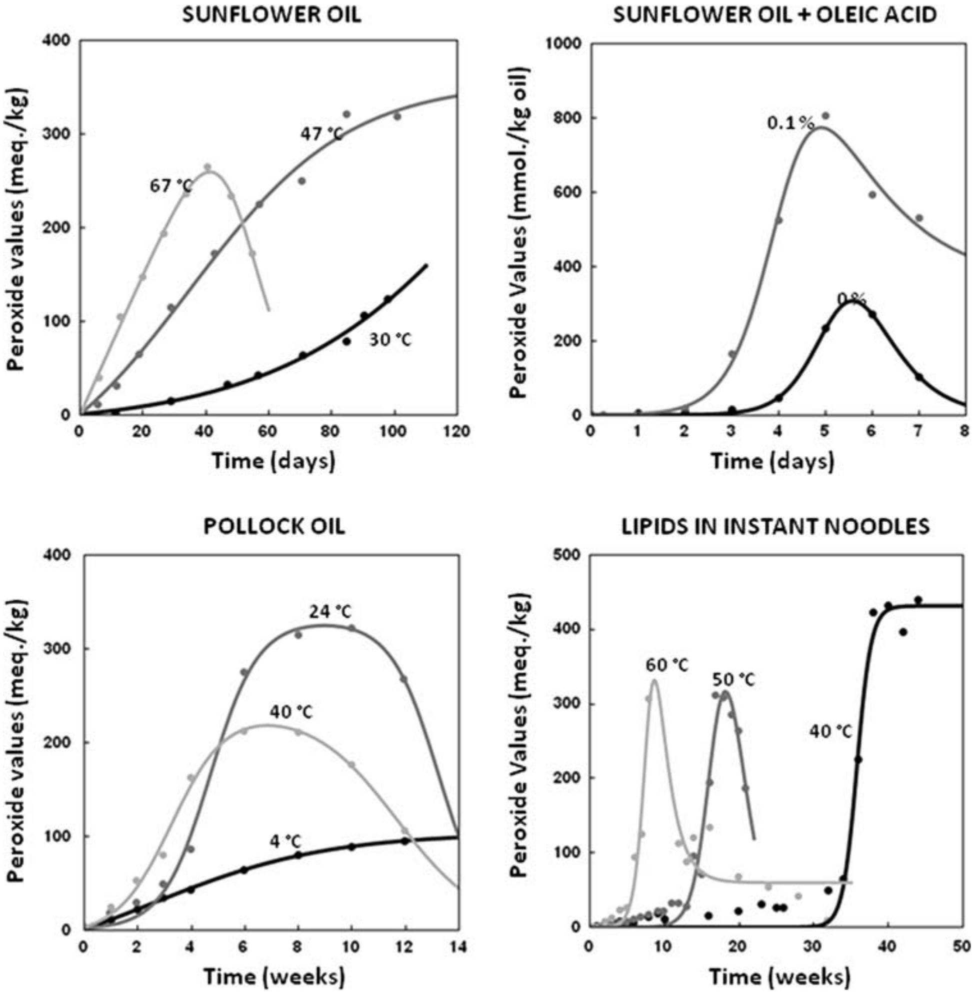


Fig. 5 Isothermal oxidation curves of sunflower oil at three temperatures and ambient temperature with and without a pro-oxidant, Pollock oil at three temperatures and lipids in instant noodles fitted with Eq. 6 as a model. The original experimental data are from Capistre et al. [24], Waraho and Decker (unpublished data), Sathivel et al. [25] and Gotoh et al. [26], respectively

or replicates, some of the tabulated parameters should be considered as rough estimates at best. Moreover, only few, if any, of the experiments described in the original publications had been with fresh samples of oils from different sources. Thus how representative they may also be a matter of debate. For this reason, the statistical confidence margins that the Mathematica® program also produces are not reported in the table. Yet, despite some of the records obvious limitations, even a glance at the parameters, will reveal the overall peroxides peak level reached in the value of a(T), the time scales of the underlying processes in the days or weeks, see $t_{cf}(T)$ and $t_{ce}(T)$, and their relation to the experiment time which determines whether a peak will appear or not. In most kinetic studies, the process's progress is reported in terms of a characteristic rate or rates which have reciprocal time units. Although a characteristic time and rate can be the two sides of the same coin only the former can reveal the existence of a concentration peak appearance and its approximate location directly. This can be done by comparison of the two 't_c's' during the experiment duration. Also, lipid oxidation, unless deliberately accelerated, is a very slow process. Consequently, the rates involved are extremely low. Thus if reported as such, their value would have little intuitive meaning, except for to the specialist (see the values of k in the table). In contrast, differences in the characteristic times, t_{cf} and t_{ce}, be they expressed in hours or days, weeks or months, would be clear, even to the uninitiated. All the above pertains to characteristic times calculated by any alternative model derived from the same principles and as far as the rate models are concerned, regardless of the number of intermediate reactions that are considered.

Concluding Remarks

Two competing chemical processes are involved in lipid oxidation: peroxides synthesis and their degradation. Each has a different characteristic time whose temperature dependence has a profound effect on the observed oxidation pattern. Whether the peroxide value (or other oxidation measures) will peak or not at a given temperature

Table 1 Lipid oxidation parameters derived from published data shown in Figs. 3, 4, 5 and fitted with Eqs. 4 and 6 as models

Equation 4 as a model

Lipid	Temp. (°C)	a (mequiv O_2/kg oil)	t_{cf} (days)	k (days^{-1})	t_{ce} (days)	MSE	Experiment duration (days)	Data source
Sunflower oil	−18	12.8	380	–	–	1.91	455	[3]
	−7	50.3	371	–	–	17.4		
	5	74.7	151	0.007	569	5.07		
	25	84.6	42	0.005	53	15.8		
	60	89.1	12	0.063	5.3	6.17		
Sunflower oil emulsion	−18	12	170	–	–	1.13	455	[4]
	−7	64.7	531	–	–	3.58		
	5	171	315	0.007	189	37.9		
	25	161	84	0.011	138	6.85		
	60	81.9	3.8	0.081	2.4	25.7		
Sunflower kernels	(°C)	(mequiv/kg oil)	(weeks)	(weeks^{-1})	(weeks)		(weeks)	[16]
	4	200	30	–	–	16.0	36	
	21	276	31	–	–	121		
	38	245	16	0.21	32	82		
Encap. rapeseed oil	(°C)	[CD (10^{-4})]	(days)	(days^{-1})	(days)		(days)	[2]
	5	2.4	10	–	–	0.50	45	
	25	36.8	65	–	–	0.06		
	40	60.9	42	0.69	47	2.35		
	60	130	20	0.14	12	6.42		

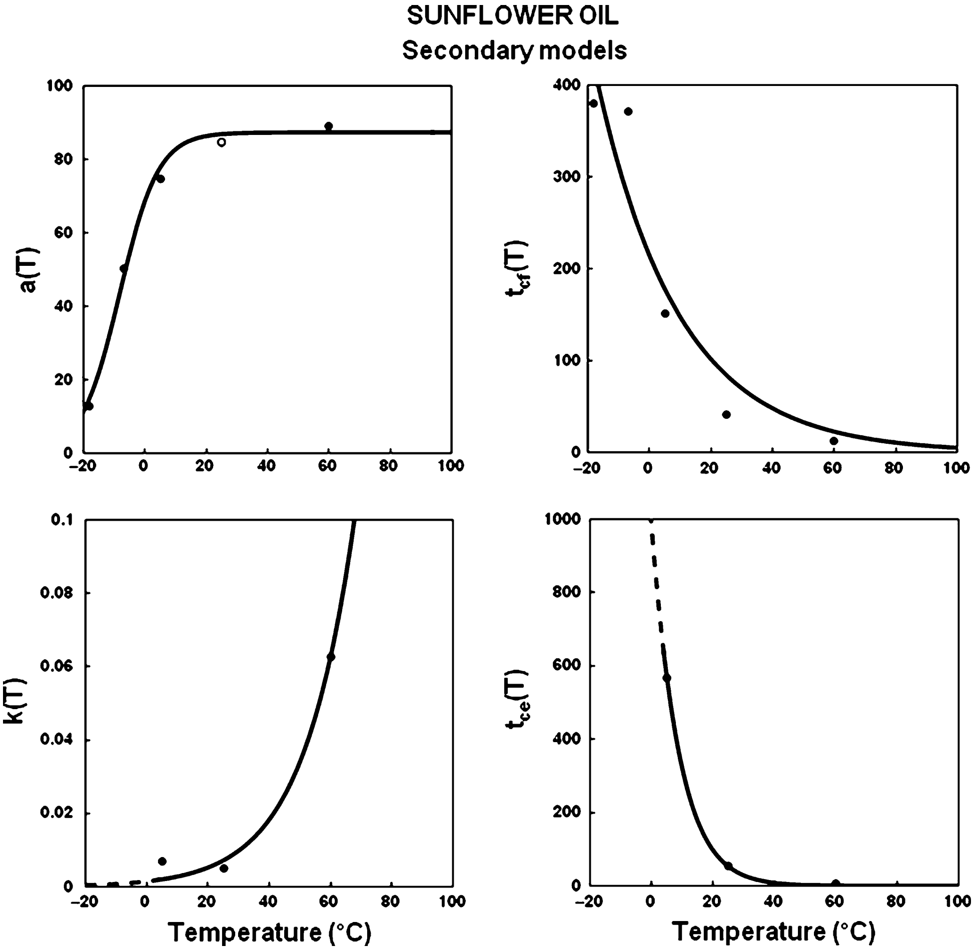
Equation 6 as a model

Lipid	Temp. (°C)	a (mequiv/kg)	k_f (weeks^{-1})	t_{cf} (weeks)	k_e (weeks^{-1})	t_{ce} (weeks)	MSE	Exp. duration (weeks)	Data source
Fat and oil in instant noodles	40	432	1.1	36	–	–	434	44	[19]
	50	497	0.8	16	0.61	20	451		
	60	1,935	1.4	8	0.56	6.2	1,019		
Pollock oil	(°C)	(mequiv/kg)	(weeks^{-1})	(weeks)	(weeks^{-1})	(weeks)		(weeks)	
	4	151	0.3	2.5	–	–	0.94	12	[18]
	24	332	1.1	4.7	1.12	13	194		
	40	244	1.0	3.3	0.63	12	113		
Sunflower oil	(°C)	(mequiv/kg)	(days^{-1})	(days)	(days^{-1})	(days)		(days)	
	30	700	0.026	153	–	–	20	100	[17]
	47	446	0.040	35	–	–	135		
	67	550	0.057	14	0.16	55	43		
Sunflower oil + oleic acid	Oleic acid conc. (%)	(mmol/kg)	(days^{-1})	(days)	(days^{-1})	(days)		(days)	
	0	903	2.2	5.2	1.4	5.6	38	7	Waraho and Decker
	0.1	2,950	2.1	4.1	0.7	20	451		

The actual data and fitted curves are shown in Figs. 3, 4, 5

primarily depends on the gap between the two time scales and their relation to the experiment's duration. The peroxide value peak's height, its overall shape and time of appearance, would depend on the absolute and relative magnitudes of all the oxidation kinetic parameters. Phenomenological empirical models constructed as the product of a formation and extinction terms can be used to describe isothermal oxidation curves with and without lag. The terms choice should be guided by mathematical convenience and their parameters' intuitive meaning. In principle, if and when the model parameters' temperature dependence could be determined experimentally, then the model would be able to predict the temperatures at which a peak peroxide value would be observed and the peak's

Fig. 6 Temperature dependence of sunflower oil's oxidation parameters when described by Eq. 4 as a model, fitted with ad hoc empirical models. The isothermal curves from which the plots have been derived are shown in Fig. 1, top



shape. But even without knowledge of the parameters exact temperature dependence, even their casual examination in a tabulated form can indicate where a peak is likely or unlikely to be observed, information that is extremely difficult to extract from a set of conventional rate constants. In principle, the concept should be applicable to both low and high temperatures. The difference will be manifested in the absolute and relative magnitudes of the model's parameters. It is also possible that the temperature elevation will result in the elimination of the 'lag' or 'induction' phase. As explained, the elimination or appearance of a 'lag time' can be accounted for in terms of Eq. 6 coefficients. The same can be said about quantifying the effects of other factors that affect the oxidation pattern, notably the presence of pro or antioxidants. Constructing the oxidation model does not require detailed let alone full knowledge of the underlying mechanisms at the molecular level. Such knowledge is very important, of course, and essential if one wants to control the oxidation reaction or slow it down through chemical and other means. Therefore, the model described in this work, or any alternative phenomenological model of its kind, is not intended to replace classic kinetic models. The phenomenological models can only quantify the overall manifestation of events at the molecular level in the shape of the oxidation curve. With such models, this can be done in a convenient mathematical manner and in terms of parameters, such as characteristic times, that have an intuitive meaning.

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