

The concept of single-step approximation and the non-Arrhenian kinetics in modelling the processes occurring in foods

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Summary

Modelling enables to depict physico-chemical processes taking place in foods during their production and storage. In order to describe the kinetics of processes occurring in food at non-isothermal conditions in general, the concept of single-step approximation appears to be a simple and powerful tool. In the paper, the main attributes of this concept are presented and the model-fitting and model-free (isoconversional) methods are outlined. Application of the non-Arrhenian temperature functions in the single-step approximation is suggested and justified. The following case studies are presented: (i) Kinetics of acrylamide elimination; (ii) F -, E - and C -values used for the evaluation of thermal stress in sterilised food; (iii) Induction periods and the thermooxidative stability of edible oils; (iv) Thermooxidative stability of dried milk. It is demonstrated that the non-Arrhenian temperature functions provide more trustworthy estimations of the shelf-life of food products in the extrapolation of high-temperature stability tests to ambient temperature; the Arrhenius extrapolation mostly overestimates the shelf-life predicted.

Keywords

modelling; single-step approximation; non-Arrhenian kinetics; acrylamide elimination; thermooxidative stability

Modelling is a useful tool to depict physico-chemical processes taking place in foods during their production and/or storage; hence, it should be an inherent part of food safety analysis. Food is a complex condensed-phase matrix and also the processes occurring in food are mostly complex and multi-step, involving not only the reaction steps, but also mass and heat transfers. Full and exact kinetic description of such a complex process would be very difficult or even impossible since a detailed mechanism of the process, or parameters occurring in related kinetic equations, could be unavailable. Consequently, modelling of such processes, based on the detailed knowledge of the mechanism, is hardly feasible. A way out of the entangled situation may represent the employment of methods based on the single-step approximation. In this paper, the model-fitting and model-free methods with possible employment of non-Arrhenian temperature functions are presented.

THEORETICAL PART

Single-step approximation

Mechanisms of the processes in condensed phase are very often unknown or too complicated to be characterized by a simple kinetic model. They tend to occur in multiple steps that have different rates. In order to describe their kinetics, methods based on the single-step approximation are frequently used [1, 2].

It is recognized that the rate of the processes in condensed state generally depend on temperature and conversion. The single-step approximation employs the assumption that this dependence can be expressed as a product of two separable functions independent of each other, the first one, $k(T)$, depending solely on the temperature T and the other one, $f(\alpha)$, depending solely on the conversion of the process, α . The rate of the complex multi-step condensed-state process thus can be formally described as [1–3]:

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$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

Eq.(1) is mostly called the general rate equation. Indeed, it resembles a single-step equation, even though it is a representation of the kinetics of a complex condensed-phase process. In general, each reaction step should be described by its own differential equation so that the kinetics of a complex process should be described by a set of rate equations. The single-step approximation thus resides in substituting the set of kinetic equations by the sole single-step equation [1–3].

Conversion and temperature functions

The conversion function in Eq.(1) is mostly considered to reflect the mechanism of the process and the temperature function is considered to be the rate constant. It has been discussed in [2] that this interpretation of both functions is wrong. Since Eq.(1) is a formulation of the single-step approximation, the functions $k(T)$ and $f(\alpha)$ represent, in general, just the temperature and conversion components of the kinetic hypersurface [2].

Obviously due to the prevailing interpretation of $k(T)$ as the rate constant, it is almost universally postulated that the temperature function is expressed by the Arrhenius equation

$$k(T) = A \exp\left[-\frac{E}{RT}\right] \quad (2)$$

where A and E are considered the pre-exponential factor and the activation energy, respectively, T is the absolute temperature and R stands for the gas constant. In reference [2] it has been justified that, since $k(T)$ is not the rate constant, there is no reason to be confined to the Arrhenius relationship and use of two non-Arrhenian temperature functions was suggested:

$$k(T) = AT^m \quad (3)$$

$$k(T) = Ae^{DT} \quad (4)$$

where A , m and D are parameters.

In contrast to the almost universally accepted form of the temperature function, there is a wide range of conversion functions applied. Practically every function is connected with a certain idea of reaction mechanism. The conversion functions are reviewed, e.g. in [4]. However, as discussed above, Eq.(1) is not a true kinetic equation, it is just an approximation. Consequently, any couple of the separable functions $k(T)$ and $f(\alpha)$, leading to a satisfactory description of the kinetic data, is suitable to be employed.

Model-fitting methods

Separation of variables in Eq.(1) and subsequent integration leads to the result

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \int_0^t k(T) dt \quad (5)$$

In order to solve Eq.(5), appropriate conversion and temperature functions need to be chosen and the time/temperature regime of heating of the food should be known as well. Experimental data are then fitted to the integrated form of Eq.(5). Mainly for the nonisothermal kinetic data, almost any $f(\alpha)$ can satisfactorily fit data, as it is demonstrated in [5].

The temperature and conversion functions contain adjustable parameters. Their values are adjusted in the procedure of fitting in order to reach the best fit between the experimental and calculated data. The parameters possess no clear physical meaning in general; however, when knowing their values, modelling of the process for any time/temperature regime is feasible.

Isoconversional methods

Isoconversional methods represent probably the most widely employed category of methods based on Eq.(1). Their basic idea is that the kinetic analysis is carried out over a set of kinetic runs at a fixed value of conversion. Under these conditions, the value of conversion function $f(\alpha)$ in Eq.(1) is constant and the reaction rate is a function of temperature only. The isoconversional methods can be crudely divided into two groups, i.e. the isothermal methods and the methods at linear heating [6]. Another division of the isoconversional methods are the differential and integral methods. The differential methods reside in the treatment of the isoconversional reaction rate as a function of time/temperature [6].

The integral isoconversional methods are mostly used since the differential methods suffer from numerical instability [6]. After integration of Eq.(5) and some re-arrangements one can get

$$F(\alpha) - F(0) = \int_0^{t_\alpha} k(T) dt \quad (6)$$

where $F(\alpha)$ is the primitive function of the inverted conversion function, $1/f(\alpha)$. The latter equation can be re-arranged into the form

$$1 = \frac{1}{F(\alpha) - F(0)} \int_0^{t_\alpha} k(T) dt \quad (7)$$

Eq.(7) enables to evaluate the time to attain the conversion α , t_α , for any time/temperature regime.

APPLICATIONS FOR THE KINETICS OF PROCESSES TAKING PLACE IN FOODS

Influence of table salt on the kinetics of acrylamide elimination during heating

In paper [7], acrylamide was applied onto table salt and heated in a glass reaction vessel within the temperature range of 50–210 °C with a constant heating rate of 2 °C·min⁻¹, in order to study the influence of temperature and table salt on the acrylamide elimination. For comparison, pure acrylamide was also heated at the same conditions to 190 °C. During heating, degree of acrylamide conversion in contact with the table salt was about twice comparing to the degree without table salt (Fig. 1), obviously due to polymerization reactions taking place in both studied systems.

For the treatment of experimental data, the temperature function given by Eq. (3) was chosen. This temperature function was employed earlier, for example, for the description of the kinetics of processes in frozen foods [8]. Considering the conversion function, a first-order conversion function was chosen in the form:

$$f(\alpha) = 1 - \alpha \quad (8)$$

Combination of Eq. (1), (3) and (8) gives:

$$\int_0^{\alpha} \frac{d\alpha}{1 - \alpha} = \int_0^t AT^m dt \quad (9)$$

For the linear heating, the dependence of temperature on time can be expressed as

$$T = T_0 + \beta t \quad (10)$$

where T_0 is the starting temperature and β stands for the heating rate. Combining Eq. (9) and (10), one can get after integration and some rearrangement:

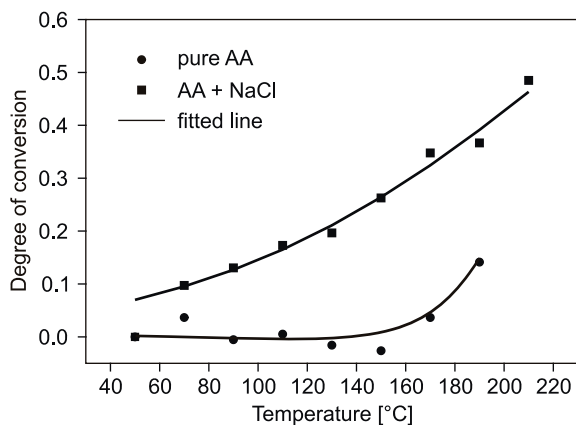


Fig. 1. Degree of acrylamide conversion as a function of temperature, heating rate 2 °C·min⁻¹.

$$\alpha = 1 - \exp \left[- \frac{AT^{m+1}}{\beta(m+1)} \right] \quad (11)$$

In Eq. (11), it is assumed that no process occurs at the beginning of experiment so that the lower temperature integration limit was set $T_0 = 0$ K.

In order to avoid the manipulation with extremely small values of the parameter A , the reduced temperature, ϑ , was defined for the treatment of experimental results:

$$\vartheta = \frac{T}{T_r} \quad (12)$$

where T_r is a reference temperature. Then, Eq. (3) can be rewritten as

$$k = a\vartheta^m \quad (13)$$

where

$$a = AT_r^m \quad (14)$$

Finally, Eq. (11) takes the form

$$\alpha = 1 - \exp \left[- \frac{aT_r\vartheta^{m+1}}{\beta(m+1)} \right] \quad (15)$$

The conversion of acrylamide polymerization is defined as

$$\alpha = \frac{g_0 - g}{g_0} \quad (16)$$

where g_0 and g are the amounts of acrylamide in the reaction vessel at the temperatures T_0 and T , respectively.

The detailed procedure of minimizing the sum of squares between experimental and fitted values of the acrylamide amount is described in [7]. The experimental and fitted degrees of acrylamide conversion are shown in Fig. 1. The adjustable parameters a and m have no mechanistic significance or physical meaning. Knowing their values, however, one can model the kinetics of the process without a deeper insight into its mechanism [2, 3, 6]. It is possible to calculate α at a chosen time for any time-temperature regime.

From Fig. 1 it can be seen that the table salt has a substantial catalytic effect on the acrylamide polymerization. Based on the treatment of experimental results, the parameters characterizing the kinetics of acrylamide polymerization, e.g. the rate of its elimination, have been obtained [7].

F -, E - and C -values

Ball in 1923 introduced the F -value as a unit of measurement for comparing relative sterilizing effects of different thermal procedures with

various time/temperature regimes. The value $F = 1$ corresponds to the sterilizing effect with the duration of 1 min at 121.1 °C [9]. For variable temperature, the F -value can be calculated as [10]

$$F = \int_0^t 10^{\frac{T-T_r}{z}} dt \quad (17)$$

where T_r is the reference temperature (121.1 °C) and z is the z -value.

Comparing Eq. (6) and (17), it can be seen that the both equations are identical if the temperature function is given by Eq. (4) and the value of F in Eq. (6) at time $t = 0$ is $F(0) = 0$. Then, the parameters A and D in Eq. (5) are expressed as

$$A = 10^{\frac{-T_r}{z}} \\ D = \frac{\ln 10}{z} \quad (18)$$

Hence, from the purely formal point of view, the F -value is calculated by an integral isoconversional method, where a non-Arrhenian temperature function in the form of Eq. (4) is applied.

Analogous formulas as Eq. (17) are used for the thermal enzyme inactivation (E -value) and sensory degradation (C -value or cook-value). It is a matter of course that the reference temperatures and z -values are different for the assessment of F , E and C values.

Thermooxidative stability of edible oils

Oxidation in condensed phase exhibits an induction period, in other words, the stage preceding the main process, where seemingly no chemical reaction takes place. At the end of induction period (IP), a sudden change in physical, physico-chemical or sensory properties of the material mostly takes place so that the length of induction period is often considered as a relative measure of material stability. The oxidation is an exothermic process and the reaction heat evolved makes it possible to employ the differential scanning calorimetry (DSC) or differential thermal analysis (DTA) for its study. Thermogravimetry (TG) can be also used since the oxidation is accompanied by a change of the sample mass. All the techniques mentioned, i.e. DSC, DTA and TG, belong to the category of thermoanalytical methods. The end of induction period is determined as the time/temperature of a sudden increase in the rate of the main oxidation stage, i.e. as the oxidation induction time (OIT) in the case of isothermal measurements and the oxidation onset temperature (OOT) in the case of measurements with linear heating [11]. Thermoanalytical methods are generally very

efficient in the study of oxidation stability of edible oils [12], methyl esters of fatty acids [13], pharmaceuticals [14] or other organic matter such as polymers [11]. They can be used also for screening the cereal varieties for antioxidant and radical-scavenging properties [15].

As it has been mentioned above, the induction period is a stage preceding the main oxidation stage. The processes occurring during IP are “invisible” since they are not registered by the experimental technique used. The end of IP is determined indirectly as the time/temperature of a sudden increase in the rate of the main oxidation stage [11]. Assume that Eq. (1) describes also the kinetics of the processes occurring during IP and denote α_i the conversion of the reactions occurring during IP and corresponding to the end of IP. Since the processes occurring during IP are not registered, the value of α_i is unknown. Nonetheless, as for all isoconversional methods, it is assumed that the conversion α_i is always the same irrespective of the temperature regime employed during the ageing stress [11].

The rate of degradation processes under application conditions is usually too slow to be measured. In order to estimate the stability of materials, a sample is mostly subjected to an accelerated test under standardized conditions where heating is the most common means of accelerating the oxidation. The principal goal of stability studies is to extrapolate the kinetic data, obtained from accelerated stability tests, to the application conditions. The prediction of long-term durability by extrapolation is a very difficult task since many fundamental scientific problems in this field remain unsolved. The extrapolation is almost exclusively carried out using the Arrhenius temperature function. However, in a recent paper [1] it has been proven that the Arrhenius function is the worst choice of the temperature function in the case of a complex process. In reference [16] it has been shown that the best estimation of material stability from the accelerated tests is obtained when the extrapolation is based on the temperature function given by Eq. (4). In this case, from Eq. (5) it can be obtained that the temperature dependence of the oxidation induction time is given as

$$t_i = A_i e^{-DT} \quad (19)$$

Eq. (19) represents the dependence of OIT on temperature. For the linear heating, the dependence of the oxidation onset temperatures on heating rate obeys the relationship

$$T_i = \frac{1}{D} \ln(A_i D \beta + 1) \quad (20)$$

where the parameter A_i in Eq.(19) and (20) is given as:

$$A_i = \frac{F(\alpha_i) - F(0)}{A} \quad (21)$$

Using Eq.(19) and (20), the stability of rapeseed and sunflower oils in oxygen in a thin layer at 25 °C was estimated to be 20 and 8 days, respectively [16]. The estimation based on the Arrhenian extrapolation provided the unrealistic values of 2.5 and 0.6 years, respectively.

In paper [17], the oxidative stability of rapeseed and sunflower oils, refined both by the steam deodorization/deacidification and by the deodorization/deacidification in a wiped-film molecular evaporator, has been evaluated. For the evaluation of oxidative stability, the DSC method with linear heating was used. The kinetic parameters A and D describing the length of oxidation induction period were obtained from the experimental data of oxidation onset temperatures versus heating rates applying Eq.(20), and the oxidation induction times were calculated using Eq.(19). The sunflower oil appeared to be less stable than the rapeseed oil in the whole range of temperatures [17].

From the point of view of the oil stability, the efficiency of the refining method can be illustrated more clearly by the protection factor [11]. The protection factor is defined as a ratio of the oxidation induction times of the refined oil and the original unrefined oil. The temperature dependence of the protection factors is shown in Fig. 2. It can be seen that the refining leads to the increase of sunflower oil stability by 2–8 times depending on temperature; the protection factor of vacuum steam refining is about 1.2 times higher than the factor of the molecular distillation in the whole range of temperatures. For the sunflower oil, the protection factors decrease with increasing temperature; on the contrary, the protection factors increase with temperature for the rapeseed oil. Depending on temperature, the protection factor of the oil refined by the vacuum steam refining is 8–13 times higher than for the oil refined by the molecular distillation [17].

The molecular distillation is a purification method very gentle to the oil; therefore, the lower stability of the oils refined by the molecular distillation is surprising. The reason is that the purification is so efficient that also a part of antioxidants are removed from the oil besides the pungent and pro-oxidative compounds. The removal of tocopherols by the molecular distillation is thus reflected in lower stability of the oils produced in this way [17].

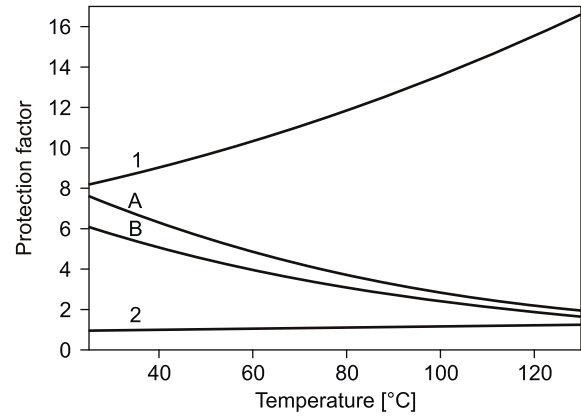


Fig. 2. Protection factors for the sunflower and rapeseed oils.

Description of the samples: A – sunflower oil refined by the steam vacuum distillation; B – sunflower oil refined by the molecular distillation; 1 – rapeseed oil refined by the steam vacuum distillation; 2 – rapeseed oil refined by the molecular distillation.

Thermooxidative stability of dried milk

This problem was first tackled in [18] and the experimental data were re-evaluated in [16] and [19]. In [19], a new method for the prediction of shelf-lives has been described. It is based on the fact that, in the degradation tests carried out under linear heating, the dependence $T_i = f(\beta)$ can be plausibly described by the function

$$T_i = T_\infty (1 - \exp[-\beta^a]) \quad (22)$$

where T_∞ is the isoconversional temperature at an infinite heating rate and a is an exponent. The kinetic parameters T_∞ and a are adjustable and they are obtained from the treatment of experimental dependence $T_i = f(\beta)$. Knowing their values, the temperature dependence of the isoconversional time can be obtained as:

$$t_i(T) = \frac{F(\alpha_i) - F(0)}{k(T)} = (T_\infty - T) a \left(\ln \frac{T_\infty}{T_\infty - T} \right)^{\frac{a-1}{a}} \quad (23)$$

In [18] it has been shown that the kinetic parameters describing oxidation of three types of dried milk from the same source (whole, semi-skimmed and skimmed milk) are practically the same. Using Eq.(19), the thermooxidative stability of dried milk at 25 °C under air was estimated to be 66 days whereas the estimation by applying Eq.(23) provided the value of 79 days. It can be seen that the estimations by Eq.(19) and (23) are practically the same within the error of kinetic parameters. At the same time, the Arrhenian extrapolation provided an absolutely unrealistic value

of almost 10 years [16]. Variations of temperature around the average value lead to the decrease of the shelf-life of milk by 20–40 % [18].

CONCLUSIONS

The single-step approximation is a mathematical tool for describing the kinetics in a simple way represented by Eq.(1), irrespective of the complexity of the overall process. Since the temperature function cannot be interpreted as the rate constant in general, use of non-Arrhenian temperature functions is justified. The non-Arrhenian temperature functions provide more trustworthy estimations of the shelf-life of products in the extrapolation of high-temperature stability tests to ambient temperature; the Arrhenius extrapolation mostly overestimates the predicted shelf-life.

The methods based on the non-Arrhenian functions are used in food science for long time in the evaluation of inactivation of microorganisms and enzymes by heat. The aim of this paper is to encourage the food science community to apply the method based on non-Arrhenian temperature functions for the assessment of food stability, food shelf-life and for the description of kinetics of other complex processes, such as the acrylamide elimination from food.

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