

Kinetic Modeling of Quality of Foodstuffs

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ABSTRACT: The present study discusses the possibilities to study relevant quality aspects of food, such as color, nutrient content, and safety, in a quantitative way via mathematical models. These quality parameters are governed by chemical, biochemical, microbial, and physical changes. It is argued that the modeling of such quality aspects is in fact kinetic modeling. Therefore, attention is paid to chemical kinetics, and its possibilities and limitations are discussed when applied to changes occurring in foods. The discussion is illustrated with examples from the literature. A major difficulty is that principles from chemical kinetics are strictly speaking only valid for simple elementary reactions, and foods are all but simple. Interactions in the food matrix and variability are 2 complicating factors. It is discussed how this difficulty can be tackled, and research priorities are suggested to come to better models in food science, and thereby to a better control of food quality.

I. INTRODUCTION

Food quality is obviously an important issue. Quality in a very broad sense means satisfying the expectation of the consumer; in other words, quality experience delivered by a food should match quality expectations of a consumer. This study concentrates on kinetic modeling. The study deals with for mathematical models that describe the fate of quality indicators as a function of conditions in the food chain. Examples of such indicators could be color, presence or absence of certain flavor compounds, presence or absence of certain microorganisms, texture, vitamins, protein composition, and so on. Building mathematical models with which we can simulate such quality indicators requires knowledge of food science and nutrition, as well as of modeling. First, it is essential to know what to model and for what purpose. It makes a difference whether a model is used to gain scientific insight in food properties, or whether it will be used to predict quality upon manufacturing a food. There are various reactions affecting quality of food: [table-1,2]

1. Oxidation reactions
2. Biochemical reactions
3. Catalytic reactions
4. Enzymatic reactions
5. Fermentation
6. Physical reactions

Table 1—. Overview of reactions in foods affecting quality

Example	Type	Consequences
Nonenzymatic browning	Chemical reaction (Maillard reaction)	Color, taste and aroma, nutritive value, formation of toxicologically suspect compounds (acrylamide)
Fat oxidation	Chemical reaction	Loss of essential fatty acids, rancid flavor, formation of toxicologically suspect compounds
Fat oxidation	Biochemical reaction (lipoxygenase)	Off-flavors, mainly due to formation of aldehydes and ketones
Hydrolysis	Chemical reaction	Changes in flavor, vitamin content
Lipolysis	Biochemical reaction (lipase)	Formation of free fatty acids, rancid taste
Proteolysis	Biochemical reaction (proteases)	Formation of amino acids and peptides, bitter taste, flavor compounds, changes in texture
Enzymatic browning	Biochemical reaction of polyphenols	Browning

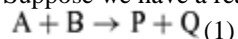
Example	Type	Consequences
Separation	Physical reaction	Sedimentation, creaming
Gelation	Combination of chemical and physical reaction	Gel formation, texture changes

Table 2—. Reactions of key components in foods

Component	Reaction	Consequences
Proteins	Denaturation	Gelation, precipitation, solubility, inactivation of antinutritional factors (ANFs)
	Hydrolysis	Formation of peptides and amino acids, texture changes
	Deamidation	Loss of charge and change in reactivity
	Maillard reaction	Crosslinking, loss of nutritional value, browning
Lipids	Oxidation	Loss of essential fatty acids, rancidity
	Fat hardening	Formation of trans fatty acids
	Hydrolysis (usually enzymatically)	Formation of free fatty acids, leading to a soapy off-flavor
Mono- and disaccharides	Maillard reaction	Nonenzymatic browning.
	Caramelization	Taste and flavor changes
	Hydrolysis	Sugar inversion
Polysaccharides	Hydrolysis (enzymatically during ripening, chemically during cooking)	Softening of tissue, texture changes
	Physical interaction with other components	Gelation, phase separation
	Gelatinization and retrogradation of starch	Staling of bread
Polyphenols	Enzymatic polymerization	Browning
	Interaction with proteins	Crosslinking, gelation
Vitamins	Oxidation	Loss of nutritional value

II. MODELING CHEMICAL REACTIONS

Suppose we have a reaction between 2 molecules A and B, which yield 2 products P and Q:



The rate r is then defined as:

$$r = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[P]}{dt} = \frac{d[Q]}{dt} = k[A][B] \quad (2)$$

The proportionality constant k is the so-called rate constant. For molecules to react, they must first come together, and this happens via diffusion. If the encounter frequency is rate limiting, a reaction is called diffusion limited, which implies that the reaction itself takes place very rapidly. This is the case for acid-base reactions and radical reactions, for instance. The bimolecular rate constant for such a case is:

$$k_{\text{dif}} = \frac{8 \cdot 10^3 RT}{3\eta} \quad (\text{dm}^3/\text{mol/s}) \quad (3)$$

R is the gas constant (J/mol/K), T absolute temperature (K), η the viscosity of the solution (Pa s). If we take Eq. 3 as the measure for the fastest bimolecular reaction possible, it is found that for $\eta = 1$ mPas (viscosity of water at 20 °C) $k_{\text{dif}} \cdot 10^9 = 6.6$ dm³/mol/s and at 100 °C $k_{\text{dif}} = 3 \times 10^{10}$ dm³/mol/s. These should be roughly the upper limits for *bimolecular* reaction rate constants in aqueous solutions at the temperature indicated. The effect of temperature on the encounter rate is incorporated via the effect of temperature on the viscosity of the solvent.

In most cases, however, the actual reaction step will be rate limiting rather than the encounter rate. Instead of using Eq. 2 we move to the most simple equation possible, the so-called general rate law, which is for a single reactant at concentration c :

$$r = -\frac{dc}{dt} = kc^n \quad (4)$$

This differential equation is thus in the form of a power law expression, where n is the so-called order of the reaction. The equation reflects the dependence of rate r on concentration for just 1 component; k is again the reaction rate constant. The unit for k for a reaction having order n is (dm³/mol) ^{$n-1$} /s. Equation 4 can be integrated with respect to time to obtain the course of the concentration as a function of time:

$$c^{1-n} = c_0^{1-n} + (n-1)kt \quad \text{for } n \neq 1 \quad ((5a))$$

$$c = c_0 \exp(-kt) \quad \text{for } n = 1 \quad ((5b))$$

c_0 is the initial concentration at $t=0$.

Figure 1 shows a decomposition reaction for dimensionless scales and varying order, using **Eq. 5a** and **5b**.

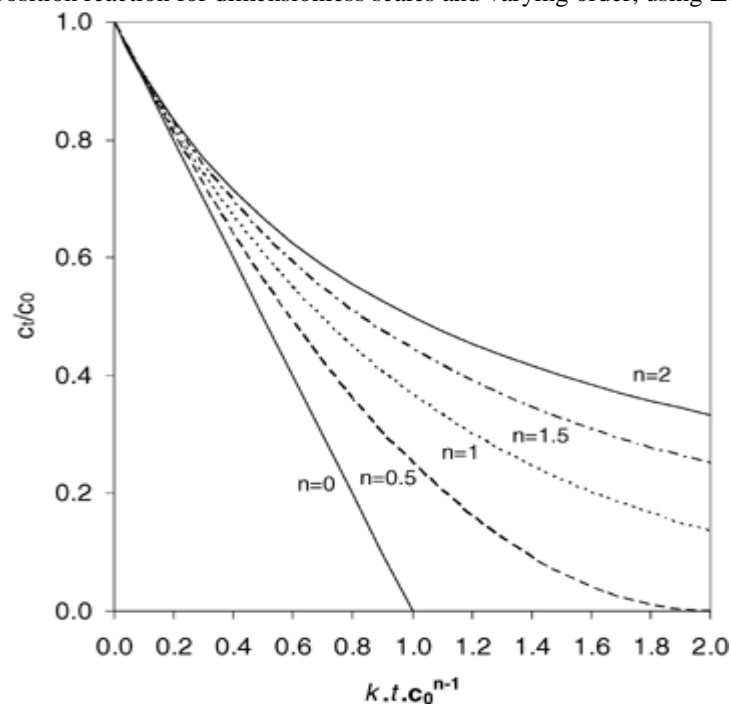


Figure 1

Decomposition of a component for a reaction having the same initial concentration and rate constant but a varying order n .

Quality changes are usually modeled by means of a zero-, 1st-, or 2nd-order reaction, From Eq. 5a it follows that for $n=0$ for a decomposition reaction:

$$-\frac{dc}{dt} = k \quad (6)$$

Integration leads to:

$$c = c_0 - kt \quad (7)$$

Zero-order reactions are rather frequently reported for changes in foods, especially for formation reactions when the amount of product formed is only a small fraction of the amount of precursors present, or for decomposition reactions where only a small amount of product is formed from a reactant. The reactant is then in such large excess that its concentration remains effectively constant throughout the observation period, and hence the rate appears to be independent of the concentration. A frequently reported example of a zero-order reaction is the formation of brown color in foods . see Figure 2. Color is the quality indicator here.

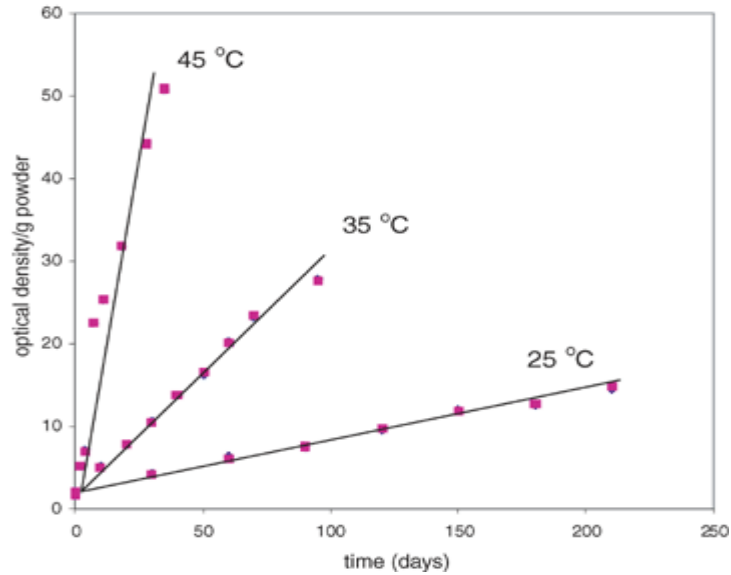


Figure 2

Example of a zero-order reaction reported for the nonenzymatic browning of whey powder .

The kinetics of Maillard-type browning is rather intricate, and it is just fortuitous that a zero-order reaction equation fits.

First-order reactions are also frequently reported for reactions in foods. The equations for a degradation reaction for $n=1$ are:

$$-\frac{dc}{dt} = kc \quad (8)$$

Integration leads to:

$$c = c_0 \exp(-kt) \quad (9)$$

(see also Eq. 5b). Frequently, the logarithmic form is used instead of the exponential equation:

$$\ln c = \ln c_0 - kt \quad (10)$$

The nonlinear Eq. 9 is thus transformed into the linear Eq. 10. An example of a food-related 1st-order reaction is shown in Figure 3.

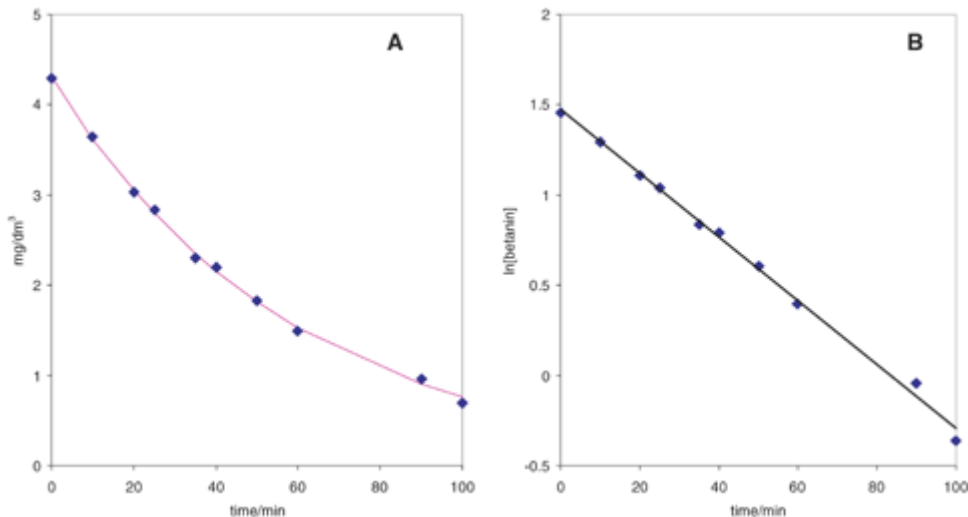


Figure 3

Example of a 1st-order reaction for the degradation of betanin at 75 °C. (A) Untransformed concentration and the fit according to a 1st-order reaction, **Eq. 9** and (B) log-transformed data fitted by a linear line according to **Eq. 10**. The equation for a 2nd-order reaction, $n=2$, is:

$$-\frac{dc}{dt} = kc^2 \quad (11)$$

Integration leads to:

$$c = \frac{c_0}{1 + c_0 kt} \quad (12)$$

In its linearized form it reads:

$$\frac{1}{c} = \frac{1}{c_0} + kt \quad (13)$$

Second-order reactions are sometimes reported for changes of amino acids involved in the Maillard reaction.

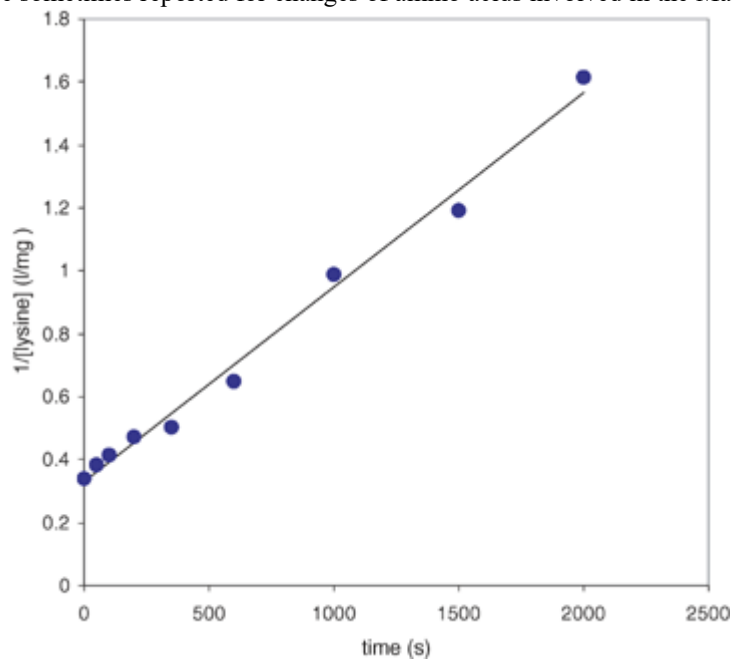


Figure 4

Lysine loss in milk heated at 160 °C plotted as $1/[\text{lysine}]$ compared with time according to a 2nd-order model (drawn line).

Second-order kinetics is reported in the food science literature not as frequently as one might perhaps expect. A likely reason is the following. If we take Eq. 1 and suppose that one of the reactants, say B, is present in excess, it follows that:

$$-\frac{d[A]}{dt} = k[A][B] = k'[A] \quad (14)$$

$$k' = k[B] \quad (15)$$

k' is called a pseudo 1st-order rate constant, which is constant as long as $[B]$ does not change notably. This goes to show that the experimentally observed kinetics of a reaction does not necessarily correspond to the actual mechanism.

Therefore, stochastic models are introduced, such as for a 1st-order model:

$$c = c_0 \exp(-kt) + \varepsilon \quad (16)$$

The symbol ε reflects the error, or uncertainty, involved. In Eq. 16 it is an additive model.

Modeling temperature dependence of chemical reactions

Arrhenius' law was empirically derived to describe the temperature dependence of simple chemical reactions. It has proven to be very worthwhile in chemical kinetics. It relates the rate constant k of a reaction to absolute temperature T :

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad (17)$$

The linearized form is:

$$\ln k = \ln A - \frac{E_a}{RT} \quad (18)$$

in which A is a so-called “pre-exponential factor” (sometimes called the frequency factor), E_a the activation energy, and R and T the gas constant and absolute temperature, respectively. The dimension of A should be the same as that of the rate constant k ; it therefore does not have units of frequency only in the case of a 1st-order reaction. For instance, for a 1st-order reaction this would be:

$$c = c_0 \exp \left[-A \exp \left(-\frac{E_a}{RT} \right) \cdot t \right] \quad (19)$$

It is possible to reparameterize the Arrhenius equation; and it is actually desired from a statistical point of view because of the strong correlation between A and E_a . A very simple reparameterization is to introduce a reference temperature T_{ref} . The basis for this arises from the application of Eq. 17 at 2 temperatures T_1 and T_2 :

$$k_1 = A \exp \left(-\frac{E_a}{RT_1} \right)$$

$$k_2 = A \exp \left(-\frac{E_a}{RT_2} \right)$$

If one arbitrarily chooses a reference temperature, say $T_2 = T_{\text{ref}}$, one can combine these 2 equations, assuming that the pre-exponential factor and E_a do not depend on temperature:

$$\frac{k}{k_{\text{ref}}} = \exp \left[-\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_{\text{ref}}} \right) \right] \quad (20)$$

The actual result of this is that the pre-exponential factor A is replaced by a rate constant at some reference temperature k_{ref} . The reference temperature should preferably be chosen in the middle of the studied temperature regime.

III. CONCLUSIONS

It can be concluded that most of the work is done on model systems rather than on foods. This is quite understandable in view of the complexity of foods. Nevertheless, there is a pitfall here, namely, that large mistakes can be made if we translate the outcomes for model systems directly to foods. There could be synergistic and antagonistic factors present in foods that completely change the kinetics of a reaction, or even the reaction mechanism. Also, many reactions occur simultaneously and they interfere with each other. This is an area that requires more attention in the future. We anticipate that this is one of the big challenges for food science in the near future.

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