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Research Article

A study on the use of empirical models to predict the formation of acrylamide in potato crisps

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The formation of acrylamide in potato crisps was fitted by empirical mathematical models. Potato slices were fried under the same experimental conditions for different times. Besides the content of precursors in the raw potato slices, acrylamide and water content in the potato crisps were quantified after predetermined times (2–6 min). The temperature developments in the surrounding oil and outer cell layer of the potato slices were monitored, giving more insight in the frying process and making future comparisons between studies possible. The pattern found for the formation of acrylamide, which was similar to earlier studies, was fitted to three empirical models. Statistical methods were used to compare the performance of the models, with the "Logistic-Exponential" and "Empirical" model performing equally well. The obtained model parameters were in the range of earlier reported studies, although this comparison is not unequivocal as the experimental conditions differed between studies. The precision of parameter estimates was problematic; this should be improved by better experimental design. Nevertheless, the approach of this study will make it possible to truly compare acrylamide formation patterns and model parameters in the future, with the ability to develop a tool to predict acrylamide formation in potato crisps.

Keywords: Acrylamide / Empirical modeling / Kinetic modeling / Maillard reaction / Potato crisps

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1 Introduction

During the last decades, consumers and the food industry have been confronted with the discovery of several food-borne toxicants, *i. e.*, potential carcinogens that are not naturally present in foods, but may have developed during preservation or cooking. Well-known examples of these food-borne toxicants are nitrosamines, heterocyclic amines and polycyclic aromatic hydrocarbons [1–3]. The latest addition to this list of food-borne toxicants is acrylamide. Acrylamide, classified by the International Agency for Research on Cancer (IARC) as "probably carcinogenic to humans", was found to be present in heat-treated carbohydrate-rich foods [4, 5]. This discovery led to worldwide concern due to the presence of acrylamide in products with a high level of consumption such as French fries, potato crisps, coffee, and bread. Although the amounts of acrylamide in some of these products are low, they can contribute significantly to the overall intake of acrylamide [6]. The intake of acrylamide depends consequently on the consumption pattern and the acrylamide levels in foods.

Acrylamide levels in food and the reaction pathways leading to its formation have been widely investigated. Most investigations point towards the Maillard reaction as the source of acrylamide in heated food [7–9]. Some studies suggest that there are different pathways next to the Maillard reaction [10–12], but these seem to be of less importance in the overall formation of acrylamide.

The kinetics and mechanisms of acrylamide formation are mostly studied in aqueous or dry model systems. The advantage of this approach is that relevant information is obtained about the actual mechanism of the reaction, especially when the technique of multiresponse modeling is applied to the various Maillard reaction pathways that lead, among others, to the formation of acrylamide [13]. These fundamental mechanistic studies cannot, however, be applied easily to

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Abbreviations: **AIC**, Akaike information criterion; **dm,** dry matter real food systems. To predict the formation of acrylamide in real foods with these mechanistic models, it needs to be taken into account that reactants cannot meet each other readily and that there maybe temperature and concentration gradients. Hence, mass and heat transfer models need to be incorporated as well. On the other hand, studies [14–16] on the influence of different processing conditions on the formation of acrylamide in food do not often include the kinetics of acrylamide formation. Recently, an empirical modeling approach was suggested that would get round these difficulties [17]. That is to say, the confounding effects of heat and mass transfer effects are taken up in empirical constants. It would also allow incorporating isothermal and non-isothermal kinetics in a relatively easy way. The objectives of this study were therefore to investigate the kinetics of acrylamide formation in real foods, namely fried potato crisps, under well-controlled conditions and to apply the empirical mathematical approach suggested by Corradini and Peleg [17] to study the kinetics of acrylamide formation in potato crisps. Furthermore, we have evaluated these models statistically and compared them as far as possible with the results from other studies. Although these empirical models will not give much insight in the mechanism behind the formation of acrylamide, as opposed to our mechanistic models [13], empirical models can be quite useful in developing tools to control or reduce acrylamide in potato crisps in the short term.

2 Materials and methods

2.1 Preparation of crisps and frying conditions

Potatoes (*Solanum tuberosum* L.) of the variety Bintje grown in the south of Sweden were harvested in September 2005, and stored at 6°C from December 2005 until April 2006.

Crisps were prepared as described by Viklund *et al*. [18]. Briefly, potatoes (6–10 cm of diameter and weighing around 100–250 g) were washed and divided into halves lengthwise. One half of each potato was used for analysis of acrylamide precursors, and the other half was cut into 1.5 mm slices that were deep fried in rapeseed oil in three net cages placed on top of each other. Thermocouples (type K, 0.1 mm) were connected to a computer and used to monitor the temperature of the oil and potato crisps. One thermocouple was placed in each net cage to measure the oil temperature within the cage, one thermocouple was placed at the bottom of the oil bath, one as close as possible to the surface of a potato slice and one thermocouple was fixed to a potato slice with the tip of the thermocouple placed in the outer cell layer. The oil was preheated to 180°C. The potato slices were fried for 2, 3, 4, 5 and 6 min. When the potato slices were submerged in the oil bath, the oil temperature decreased rapidly. When the oil reached 160°C after about 1.5–2.0 min, the thermostat setting was changed and the temperature was kept constant at 160°C for the rest of the experiment. After frying, the crisps were cooled to room temperature on paper, and stored in plastic bags at –18°C until analysis.

2.2 Chemical analyses

The dry matter contents of the tubers and crisps were determined as described by Viklund *et al*. [18]. The tubers were analyzed with regard to asparagine using HPLC and a fluorescence detector, and for glucose, fructose and sucrose using GC and a flame ionization detector [19]. The acrylamide content in the crisps was analyzed using LC-MS/MS [18].

2.3 Empirical mathematical models

It is recognized that acrylamide is not only formed but also degraded during heat treatments above 160°C [13, 20–22]. Therefore, models are needed that can handle this phenomenon. Corradini and Peleg [17] proposed three empirical models to describe the formation and degradation of acrylamide. These three models can be divided in two semi-empirical models “Logistic-Fermi” and “Logistic-Exponential”, and one total empirical model “Empirical”. The semi-empirical models have characteristic time parameters for the inflection points in the formation or degradation of acrylamide and steepness parameters around these inflection points. The total empirical model has abstract parameters and is simpler in appearance. The simplicity of this model, as opposed to the semi-empirical models, could lead to less computational problems in the estimation of parameters [17].

The Logistic-Fermi model (Eq. 1) describes the formation of acrylamide by a logistic function and the degradation by a Fermi-type function:

$$C(t) = \left[\frac{a(T)}{1+\exp\{k_1(T)[t_{c1}(T)-t]\}} - \frac{a(T)}{1+\exp[k_1(T)t_{c1}(T)]}\right] \cdot \frac{1}{1+\exp\{k_2(T)[t-t_{c2}(T)]\}} \tag{1}$$

where $C(t)$ is the concentration of acrylamide, $t_{c1}(T)$ and $t_{c2}(T)$ are temperature-dependent time characteristics for the inflection points in the formation (t_{c1}) and degradation (t_{c2}) of acrylamide, $k_1(T)$ and $k_2(T)$ are temperature-dependent steepness parameters around the inflection points for the formation (k_1) and degradation (k_2) of acrylamide and $a(T)$ serves as a temperature-dependent “scale factor” for the acrylamide concentration.

The Logistic-Exponential model (Eq. 2) differs from the Logistic-Fermi model in the part that describes the degradation of acrylamide. The Logistic-Fermi function predicts that at prolonged heating times the acrylamide concentration will become zero. However, the Logistic-Exponential function with its exponential term for the degradation predicts a residual acrylamide concentration at prolonged heating times:

$$C(t) = \left[\frac{a(T)}{1+\exp\{k_1(T)[t_{c1}(T)-t]\}} - \frac{a(T)}{1+\exp[k_1(T)t_{c1}(T)]}\right] \cdot \exp\left(-\frac{t}{\tau}\right) \quad (2)$$

where τ is a characteristic time.

The Empirical model is expressed as:

$$C(t) = \frac{a \cdot t^n}{b + t^m} \quad (3)$$

where a, b, m and n are temperature-dependent constants.

2.4 Parameter estimation and statistical methods

The semi-empirical models "Logistic-Fermi" and "Logistic-Exponential" and the total empirical model "Empirical", proposed by Corradini and Peleg [17], were fitted to the obtained experimental data for the acrylamide formation using the software program Mathcad® version 13.1 (PTC, Needham, MA, USA).

For the estimation of the model parameters, the command "Minerr" was used to minimize the sum of squares. This command makes use of nonlinear regression and to determine the search direction in the iterative process the software used Quasi-Newton methods. The SD of the model parameters were estimated by linear approximation using the variance-covariance matrix and mean squares. The Akaike information criterion (AIC) was used in the model discrimination to investigate statistical differences between models. The AIC gives a penalty for models that have more parameters [23]. This is useful because a model with more parameters fits better in general but leads to more imprecision in parameter estimates. The general equation for the AIC is:

$$AIC = n \cdot \ln\left(\frac{SS}{n}\right)^2 + 2(p+1) \quad (4)$$

where n is the number of data points and p the number of estimated parameters. The number of data points (n) was relatively small compared to the number of estimated parameters (p) ($n/p < 40$) for all cases, therefore the corrected AIC, AIC_c, was used:

$$AIC_c = AIC + 2(p+1)\left(\frac{p+2}{n-p}\right) \quad (5)$$

The model with the lowest Δ_{AIC}, the difference between the AIC values with the lowest value as reference, performs the best.

3 Results and discussion

3.1 Temperature development in the potato crisps

The set-up used in these experiments has been described comprehensively by Viklund *et al.* [18]. The laboratory frying conditions mimicked industrial processing and gave reproducible results regarding color, water content and acrylamide levels with no significant differences between duplicate batches [18]. The temperature profile during frying plays an important role in the production of potato crisps. Figure 1A shows the temperature profile of the oil at the bottom of the fryer and the temperature of the oil within the three net cages. The profile is in line with the tempera-

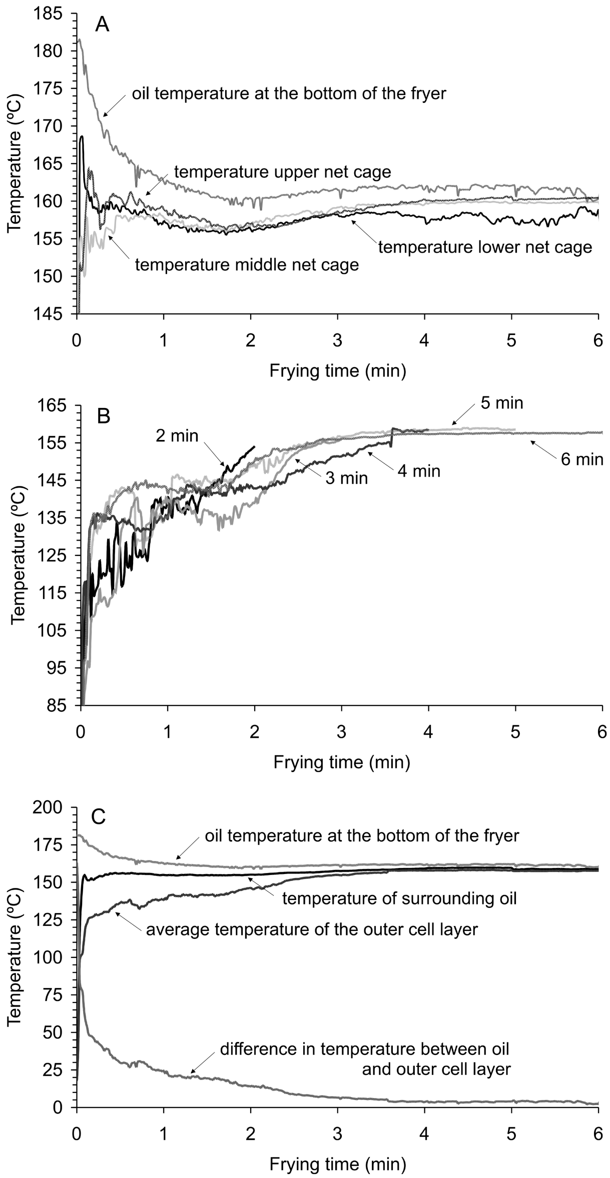

Figure 1. (A) Temperature profiles during frying of potato crisps of the oil at the bottom of the fryer, the lower, middle and upper net cage. (B) Temperature profiles during frying of potato crisps on or close to the surface of a potato crisp during frying for the different frying experiments. (C) Average temperature profile during frying of potato crisps of the outer cell layer of a potato crisp during frying compared to the oil temperature in the oil bath, the oil surrounding the crisp and the difference between the oil and the outer cell layer.

ture profile commonly found in industry where potato slices are immersed in oil having a starting temperature of around 180–190°C and an end temperature of around 150–175°C [24]. The temperature within the cages was lower than in the rest of the oil bath. Within the first seconds, the temperature fluctuated between 150 and 170°C and after this period stabilized around 160°C. The temperature in the three cages was similar. Figure 1B shows the temperature profile obtained by the thermocouple that was fixed to a potato slice with the tip placed in the outer cell layer. The results of this temperature measurement differed between experiments. It was reported earlier by Yildiz *et al.* [25] that obtaining a reliable temperature at the surface of potato slices is difficult and could lead to potential errors. They proposed another way of determining the surface temperature by establishing the heat transfer coefficient based on measurements of time-dependent temperature and moisture content of potato slices. However, this approach could also lead to potential errors in the estimation, as the thermophysical properties of the potato slices were assumed constant throughout the potato [25]. In our approach, we tried to fix the tip of thermocouple into the outer cell layer to gain insight in the actual temperatures in this region. The observed differences in the measurements could be the result of the depth of the tip within the outer cell layer, but the temperature profiles could also be influenced by the changes that occur at the outer cell layer. Costa *et al.* [26] have illustrated the structural changes and shrinkage of potato slices during frying, which could lead to changes in the placement of the tip. The tip could be exposed to the oil instead of measuring the temperature within the potato cell layer. Another factor that could influence the temperature measurements in the cell layer is the release of water vapor from deeper parts of the potato slice. Because of the difficulties to obtain accurate temperature measurements in the outer cell layer, we have averaged the temperature profile to estimate the temperature in the part of the potato slice where the crust is formed, see Fig. 1C. Within the first seconds, the temperature increased to 120°C, and from 10 to 35 s, the temperature increased to 140°C. This rapid temperature increase was followed by a slight decrease to 135°C, which could be caused by release of water vapor. After 45 s, the temperature steadily increased to 160°C at about 210 s; from this moment on the temperature remained stable at 160°C. Within the first 2 min of frying, the temperatures of the oil and the outer cell layer differed substantially, after 2 min, the temperature of the slices and the oil was almost constant at 160°C. Although the temperature measurements are perhaps not as reliable as one would like, these measurements do give insight in the temperature development during the frying process of potato crisps. With this knowledge, one could truly compare the formation patterns of acrylamide with the results from studies where the temperature profile during frying of potato crisps has also been studied. Currently, these details are seldom

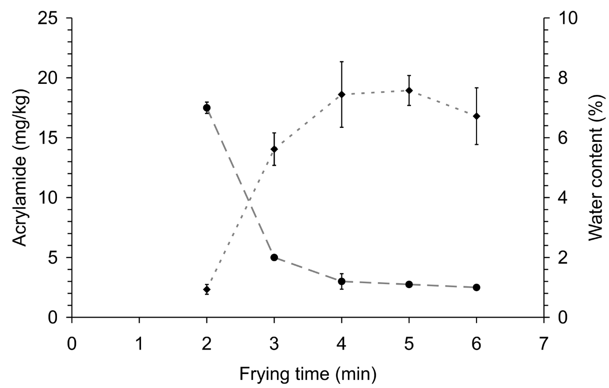

Figure 2. Average acrylamide concentration (♦) and water content (•) *versus* frying time in potato slices (1.5 mm) fried for 2–6 min. Error bars indicate SD (acrylamide concentration: n = 4; water content: n = 2). Initial water content at t = 0 was around 75%.

mentioned or even studied for potato crisps [14–16, 27] making comparison of published results difficult and could lead to wrong conclusions. Gökmen *et al.* [28], however, have reported these details for the frying of French fries, creating the opportunity to compare the results of acrylamide formation in French fries, as this study does for the formation of acrylamide in potato crisps.

3.2 Chemical analysis

As explained in the introduction, the aim of this study was to investigate the use of empirical models; therefore, the results from the chemical analysis are described briefly to provide information about the precursor and water content, so that the results from modeling can be put into context with other studies. The fresh potatoes were analyzed for their sugar and asparagine content (n = 2). The fructose, glucose and sucrose concentration were 10.4 ± 0.11 mg/g dry matter (dm), 15.4 ± 0.26 mg/g dm and 5.9 ± 0.17 mg/g dm, respectively. The asparagine concentration was 11.7 ± 0.47 mg/g dm. It has to be mentioned that the variety Bintje is not a potato normally used for the production of potato crisps due to its high sugar content. The sugar content also increases during storage and declines in April-May [19].

Figure 2 shows the acrylamide and water content for potato slices fried for 2, 3, 4, 5 and 6 min. Due to the high concentration of precursors, the acrylamide concentration was high compared to acrylamide levels reported in literature [5, 10]. Between 2 and 4 min, the concentration of acrylamide increased rapidly from 2.3 mg/kg dm to 18.6 mg/kg dm and stabilized between 4 and 6 min. At 6 min, the concentration of acrylamide was slightly lower than that at 4 and 5 min, probably reflecting the earlier mentioned breakdown of acrylamide [13, 21, 22]. The initial water content of the raw potato slices was around 75% and decreased with frying time from 7% at 2 min to 1% at 4 min and remained around 1% from 4 to 6 min. During the

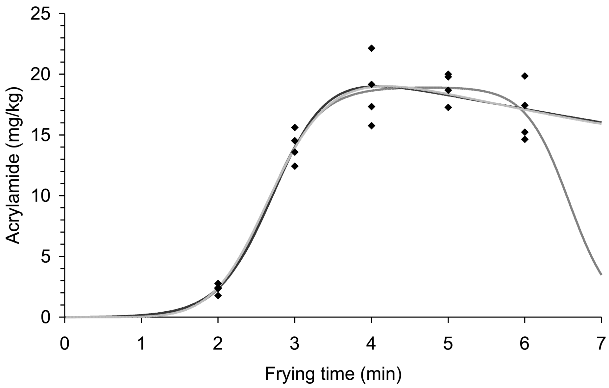

Figure 3. Acrylamide concentration (symbols) *versus* time in potato slices (1.5 mm) fried for 2–6 min, fitted with Logistic-Fermi (dark gray line), Logistic-Exponential (black line) and Empirical (light gray line) models.

decrease of water content from 7% to 2%, the formation of acrylamide rapidly increased. A similar pattern was found in an earlier study on acrylamide formation in crisps when slices of Saturna potatoes were deep fried for 2–4.5 min at 160°C [18].

3.3 Mathematical modeling

The precursors for acrylamide formation are not homogeneously distributed within potatoes and vary between potatoes [29]. Subsequently, these concentrations change during processing due to different reactions and physical processes that occur, such as degradation reactions, water evaporation, starch gelatinization and competing Maillard reactions. Therefore, the use of mechanistic models derived from aqueous model systems to describe the formation of acrylamide in real food systems is not possible without combining these models with heat and mass transfer models to account for these changes. Heat and mass transfer models have been developed for potato products [25], but most of these models need to be adapted or modified to account for the physical changes that occur during frying [26], and the inhomogeneous distribution and diffusion of precursors within potatoes. Using models that only give a mathematical description of the formation or degradation of acrylamide bypasses the problem of having to consider all the mechanisms that occur during processing of foods. The semi-empirical and the total empirical models proposed by Corradini and Peleg [17] describe the formation and degradation of acrylamide by mathematical functions rather than by underlying mechanisms.

The concentration *versus* time relationship of acrylamide in the potato crisps was "force-fitted" with these models, meaning that the empirical parameters are chosen in such a way that the residual sum of squares is minimized without any mechanistic restraints, such as knowledge of the underlying reaction networks. Figure 3 shows the fit of these three models with the data from the potato crisp models. The estimated parameters found for the three models are shown in Table 1. The SD, obtained by linear approximation in the nonlinear regression routine, of some parameters was found to be quite high. This is the case for k_2 of the Logistic-Fermi model, τ of the Logistic-Exponential and a and b of the Empirical model. These high SD could be due to the limited timescale. Especially the parameter estimates for the degradation part in the Logistic-Fermi and Logistic-Exponential model strongly depend on the availability of data points during the degradation of acrylamide. Monte Carlo simulations revealed that the parameter estimates were approximately normally distributed and correlation plots of the simulated parameter estimates showed no strong correlation between model parameters (results not shown). Therefore, the low precision of the parameter estimates is mainly due to the fact that the data do not contain enough information to extract precise model parameters. Of course, this is not strange because these datasets were not collected with the tested models in mind. However, if these models are going to be used for prediction, future experiments should be directed to an optimal experimental design with regard to precision of parameter estimates.

The fit of the three models, however, is practically indistinguishable. The Logistic-Fermi model behaves differently in that it shows a strong decrease after 6 minutes. Unfortunately, there are no data points to validate this. The three models seem to be indistinguishable up until 6 min. We applied model discrimination, using the AIC, to investigate whether a statistical analysis would show differences. The model with the lowest Δ_{AIC}, the difference between the AIC values with the lowest value as reference, performs the best from a statistical point of view [23]. The results are shown in Table 2. The model with the highest number of parameters (Logistic-Fermi) performs less, though not substantial, but based on this we prefer the Logistic-Exponential and Empirical model. These two perform equally well. Based on the simplicity and the lowest score on model discrimination parameters, one could say that the Empirical model is favored.

Comparison with other studies, where the precise circumstances of the experiment are not well known, should be done cautiously. Nevertheless, we have fitted these three models to data from other studies [14, 27, 30, 31] to compare the results for the parameters and to perform model discrimination. Figures 4–7 show the fit of these three models with the data taken from literature. The estimated parameters found for the models are also shown in Table 1 next to our own results. The three models fitted the data of Kim *et al*. [14] visibly the same (Fig. 4), but the two Logistic models have very large deviations in their parameter estimation, which is probably caused by the absence of the degradation of acrylamide and the relatively low number of data points. The parameter estimation also resulted in negative time characteristics for the inflection point in the for-

Table 1. Estimates of parameters with their approximate SD (by linear approximation) for the Logistic-Fermi, Logistic-Exponential and Empirical models

Source	Initial temp.	Logistic-Fermi a µg/kg	k_1 min^{-1}	t_{c1} min	k_2 min^{-1}	t_{c2} min	Logistic-Exponential a µg/kg	k_1 min^{-1}	t_{c1} min	τ min	Empirical a	n	b	m
Knol *et al.* (this study) 2–6 min, 1.5 mm slices	180°C	$1.9\cdot10^4\pm8\cdot10^2$	3.0 ± 0.5	2.7 ± 0.1	3.5 ± 8	6.6 ± 1	$2.6\cdot10^4\pm6\cdot10^3$	2.8 ± 0.5	2.8 ± 0.1	15 ± 10	$4.1\cdot10^4\pm2\cdot10^4$	6.2 ± 1	$1.1\cdot10^3\pm1\cdot10^3$	6.7 ± 1
Elmore *et al.* [30] 10–60 min, 3 mm cakes	180°C	$6.6\cdot10^3\pm5\cdot10^2$	0.38 ± 0.09	16 ± 0.6	0.093 ± 0.05	68 ± 5	$9.1\cdot10^3\pm1\cdot10^3$	0.31 ± 0.07	17 ± 0.9	94 ± 31	$1.1\cdot10^5\pm7\cdot10^4$	3.2 ± 0.5	$2.0\cdot10^5\pm2\cdot10^5$	4.0 ± 0.4
Gökmen *et al.* [27] 0-60 min, 2 mm slices	150°C	$5.2\cdot10^3\pm9\cdot10^2$	0.33 ± 0.05	9.3 ± 0.5	0.050 ± 0.01	39 ± 8	$7.2\cdot10^3\pm6\cdot10^2$	0.29 ± 0.02	11 ± 0.5	37 ± 3	$4.3\cdot10^5\pm3\cdot10^5$	1.8 ± 0.2	$1.1\cdot10^4\pm6\cdot10^3$	3.2 ± 0.2
Gökmen *et al.* [27] 0-60 min, 2 mm slices	170°C	$1.6\cdot10^4\pm2\cdot10^4$	1.8 ± 2	3.3 ± 0.7	0.033 ± 0.02	25 ± 82	$1.2\cdot10^4\pm9\cdot10^2$	1.5 ± 0.4	3.5 ± 0.3	50 ± 8	$3.2\cdot10^4\pm4\cdot10^3$	4.0 ± 0.5	$6.0\cdot10^2\pm3\cdot10^2$	4.5 ± 0.4
Kim *et al.* [14] 0.5-10 min, 1 mm slices	180°C	$8.7\cdot10^4\pm7\cdot10^4$	2.3 ± 1	-0.025 ± 0.7	0.080 ± 0.2	77 ± 150	$1.2\cdot10^6\pm2\cdot10^6$	1.5 ± 0.1	-2.2 ± 1	$5.5\cdot10^3\pm2\cdot10^4$	$4.6\cdot10^4\pm2\cdot10^3$	1.4 ± 0.1	0.37 ± 0.07	1.5 ± 0.1
Kita *et al.* [31] 3-7 min, 1.5 mm slices	160°C	$2.1\cdot10^3\pm1\cdot10^3$	1.0 ± 0.1	4.8 ± 0.4	0.26 ± 0.4	12 ± 7	$2.0\cdot10^3\pm7\cdot10^2$	1.1 ± 0.09	4.7 ± 0.3	30 ± 43	$2.4\cdot10^4\pm6\cdot10^4$	3.3 ± 0.5	$3.7\cdot10^3\pm7\cdot10^3$	4.5 ± 0.7
Kita *et al.* [31] 2-5 min, 1.5 mm slices	185°C	$5.4\cdot10^3\pm7\cdot10^3$	1.3 ± 1	2.2 ± 0.3	0.013 ± 0.1	13 ± 96	$2.8\cdot10^3\pm6\cdot10^2$	1.3 ± 0.9	2.2 ± 0.2	$4.3\cdot10^3\pm1\cdot10^5$	$9.4\cdot10^2\pm3\cdot10^1$	24 ± 5	$5.7\cdot10^6\pm2\cdot10^7$	23 ± 5

Table 2. Model discrimination results for the Logistic-Fermi, Logistic-Exponential and Empirical models

Source	Initial temp.	Logistic-Fermi p	n	MS[a)]	SS[b)]	AIC$_c$[c)]	Δ_{AIC}	Logistic-Exponential p	n	MS	SS	AIC$_c$	Δ_{AIC}	Empirical p	n	MS	SS	AIC$_c$	Δ_{AIC}
Knol *et al.* (this study) 2-6 min, 1.5 mm slices	180°C	5	20	$3.3\cdot10^6$	$5.0\cdot10^7$	311.3	3.0	4	20	$3.3\cdot10^6$	$5.3\cdot10^7$	308.5	0.2	4	20	$3.3\cdot10^6$	$5.2\cdot10^7$	308.3	0.0
Elmore *et al.* [30] 10-60 min, 3 mm cakes	180°C	5	12	$1.6\cdot10^5$	$1.1\cdot10^6$	160.0	2.7	4	12	$1.9\cdot10^5$	$1.5\cdot10^6$	157.7	0.4	4	12	$1.9\cdot10^5$	$1.5\cdot10^6$	157.3	0.0
Gökmen *et al.* [27] 0-60 min, 2 mm slices	150°C	5	10	$2.2\cdot10^4$	$1.1\cdot10^5$	120.6	16.8	4	10	$8.0\cdot10^3$	$4.8\cdot10^4$	103.8	0.0	4	10	$1.9\cdot10^4$	$1.1\cdot10^5$	112.3	8.5
Gökmen *et al.* [27] 0-60 min, 2 mm slices	170°C	5	10	$1.3\cdot10^6$	$6.5\cdot10^6$	161.7	27.7	4	10	$6.5\cdot10^5$	$3.9\cdot10^6$	147.7	13.6	4	10	$1.7\cdot10^5$	$9.9\cdot10^5$	134.1	0.0
Kim *et al.* [14] 0.5-10 min, 1 mm slices	180°C	5	6	$7.0\cdot10^6$	$7.0\cdot10^6$	178.8	80.3	4	6	$7.1\cdot10^5$	$1.4\cdot10^6$	113.3	14.8	4	6	$6.1\cdot10^4$	$1.2\cdot10^5$	98.5	0.0
Kita *et al.* [31] 3-7 min, 1.5 mm slices	160°C	5	6	$1.8\cdot10^3$	$1.8\cdot10^3$	129.2	58.1	4	6	$9.2\cdot10^2$	$1.8\cdot10^3$	73.3	2.2	4	6	$6.3\cdot10^2$	$1.3\cdot10^3$	71.1	0.0
Kita *et al.* [31] 2-5 min, 1.5 mm slices	185°C	5	6	$9.5\cdot10^4$	$9.5\cdot10^4$	153.0	84.4	4	6	$4.7\cdot10^4$	$9.3\cdot10^4$	96.9	28.3	4	6	$4.2\cdot10^2$	$8.3\cdot10^2$	68.6	0.0

a) Residual mean squares.
b) Residual sum of squares.
c) Corrected Akaike information criterion.

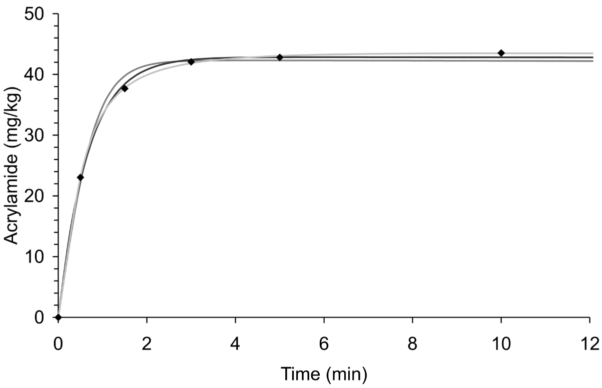

Figure 4. Average acrylamide concentration (symbols) *versus* time in potato model samples (1 mm) fried for 0.5–10 min with an initial temperature of 180°C, fitted with Logistic-Fermi (dark gray line), Logistic-Exponential (black line) and Empirical (light gray line) models. Original data are from Kim *et al*. [14].

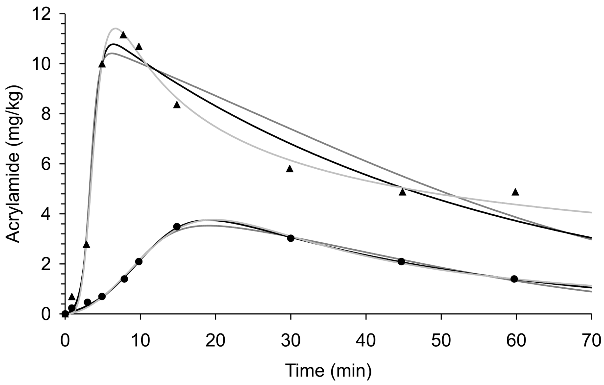

Figure 6. Average acrylamide concentration (symbols) *versus* time in potato slices (2 mm) fried for 0–60 min with an initial temperature of 150°C (•) and 170°C (▲), fitted with Logistic-Fermi (dark gray line), Logistic-Exponential (black line) and Empirical (light gray line) models. Original data are from Gökmen *et al*. [27].

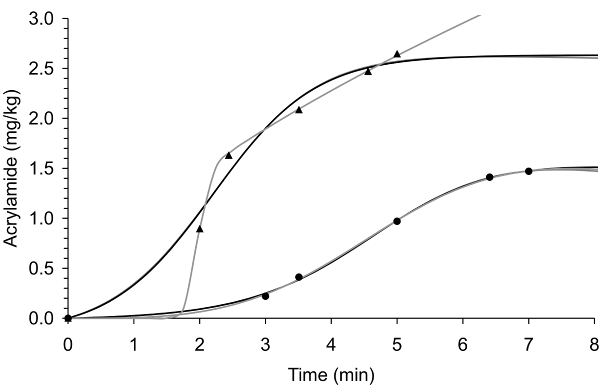

Figure 5. Average acrylamide concentration (symbols) *versus* time in potato slices (1.5 mm) fried for 2–7 min with an initial temperature of 160°C (•) and 185°C (▲), fitted with Logistic-Fermi (dark gray line), Logistic-Exponential (black line) and Empirical (light gray line) models. Original data are from Kita *et al*. [31].

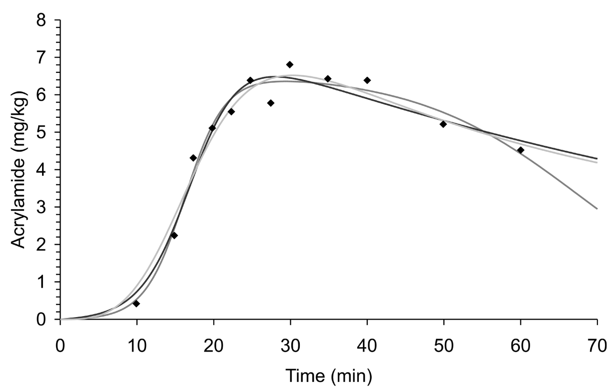

Figure 7. Average acrylamide concentration (symbols) *versus* time in potato cakes (3.0 mm) fried for 10–60 min with an initial temperature of 180°C, fitted with Logistic-Fermi (dark gray line), Logistic-Exponential (black line) and Empirical (light gray line) models. Original data are from Elmore *et al*. [30].

mation of acrylamide; this is probably caused by the relatively rapid formation of acrylamide. The fit of the three models to the data of Kita *et al*. [31] showed similar results (Fig. 5), both Logistic models showed large deviations in the parameters estimation because there was no degradation of acrylamide. The Empirical model for the data of 185°C has a deviant appearance, which is the results of the total empirical character of the model and the few number of data points. The larger timescale of the experiments by Elmore *et al.* [30] and Gökmen *et al.* [27] and the noticeable degradation of acrylamide (Figs. 6 and 7) resulted in a better parameter estimation for these studies. The Logistic-Fermi model, however, did show some irregularities with fitting the degradation of acrylamide.

Overall, one could say that our results are in the same order of magnitude with the other studies, but there are differences and these are probably due to the different experimental conditions, such as different temperature profiles, crisps thickness and timescale. Nevertheless, the models perform in a similar way. As with the results of our experiment, the approximate SD in some cases are high. The short timescale of some experiments and the low number of data points could be the reason for this high SD. The results for model discrimination are shown in Table 2. The Empirical and Logistic-Exponential model performed in all cases the best and of these two the Empirical one in all but one case, which is in line with our results and support our conclusions that the Logistic-Exponential and Empirical model are preferred for modeling the formation and degradation of acrylamide in potato crisps.

As discussed earlier, the parameters only apply for the specific experimental conditions; time-temperature profile of frying, potato variety, slice thickness and initial concentration of precursors. These factors are the key parameters affecting acrylamide formation from a viewpoint of heat and mass transfer facts. By keeping the experimental conditions the same, one could establish relationships between the mathematical parameters and the physical or chemical parameters that can influence acrylamide formation. Secondly, the same experimental conditions make it possible to really compare the results from modeling. This could perhaps even give a mechanistic meaning to the parameters in the Logistic models. Although this still has to be validated, one could suspect that parameter *a* or the "scale factor" could be related to the initial sugar content. Earlier studies showed the correlation between sugar content and acrylamide formation [32]. Furthermore, by establishing the temperature dependence of the mathematical parameters, one could predict the influence of different temperature profiles during frying. Serpen and Gökmen [33] have suggested the use of artificial neural networks to accomplish the same objective, namely the relationship between initial precursor content, time, temperature and acrylamide. Their study is based on the assumption of an isothermal process at the initial temperature, the actual temperature profile during frying is however based on the oil/potato ratio, the type of equipment and therefore in almost any case a non-isothermal process, with big differences in the actual temperature of the product and the oil surrounding it. The heating rate could also play a significant role in the formation of acrylamide and therefore should be included in the development of predictive models [17].

4 Concluding remarks

The present study shows that the formation of acrylamide in potato crisps can be modeled by applying Logistic-Fermi, Logistic-Exponential or Empirical models in accordance with an earlier study [17]. The Empirical model is preferred as it performed the best in the statistical evaluation. However, it also appeared that the precision of the estimates obtained is quite bad, and this puts a serious constraint on the use of these models if they are going to be used for prediction: the precision of predictions made with such imprecise parameters will go quickly out of hand. While we found two models to perform reasonably well in fitting, the next step should be to put much more emphasis on the precision of parameters. This calls for much more attention for experimental design to obtain precise estimates. Further research is on the way to establish the relationship between the model parameters and precursors content and to determine the influence of the temperature dependence on the model parameters. Once these relationships are established and with more precision in parameter estimation, the development of simple to use mathematical models to predict the formation of acrylamide in potato crisps could be realized. These tools could be useful for industry and manufactures to develop new mitigation strategies.

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