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Research Article

Modeling of acrylamide formation and browning ratio in potato chips by artificial neural network

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The artificial neural network (ANN) modeling approach was used to predict acrylamide formation and browning ratio (%) in potato chips as influenced by time × temperature covariants. A series of feed-forward type network models with back-propagation training algorithm were developed. Among various network configurations, 4-5-3-2 configuration was found as the best performing network topology. Four neurons in the input layer were reflecting the asparagine concentration, glucose concentration, frying temperature, and frying time. The output layer had two neurons representing acrylamide concentration and browning ratio of potato chips. The ANN modeling approach was shown to successfully predict acrylamide concentration ($R = 0.992$) and browning ratio ($R = 0.997$) of potato chips during frying at different temperatures in time-dependent manner for potatoes having different concentrations of asparagine and glucose. It was concluded that ANN modeling is a useful predictive tool which considers only the input and output variables rather than the complex chemistry.

Keywords: Acrylamide / Artificial neural network / Modeling / Potato chips / Predictive tool

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1 Introduction

After the discovery of acrylamide in thermally processed foods [1], a number of theoretical mechanisms have been proposed for its formation. Most probably, acrylamide in food results largely from the Maillard reaction between amino acids (primarily asparagine) and a reactive carbonyl (*e.g.*, glucose and fructose), proceeding through intermediates that include a Schiff's base [2–5]. A recent study revealed that, besides acrylamide, 3-aminopropionamide, which may be a transient intermediate in acrylamide formation, was also formed during heating when asparagine was reacted in the presence of glucose [6].

Several intrinsic and extrinsic factors, such as the initial concentration of reactants and their ratio, temperature and time of processing, water content, pH, the concentrations, and the reactivity of the components present have been shown to influence the levels of acrylamide in thermally processed foods [7]. With respect to acrylamide, so far only limited data have been reported in the literature with detailed kinetic analysis [8–11]. In order to predict and to control the amount of acrylamide formed, formation mechanisms and kinetics of acrylamide in function of process and product variables need to be known. Considering the various possible formation mechanisms of acrylamide, it seems to be an almost impossible task to elucidate the kinetics of all the pathways involved. Artificial neural network (ANN) modeling, on the other hand, may be a viable alternative to the kinetic models. While the use of phenomenological models requires a simultaneous solution of a large number of nonlinear algebraic equations that need long and exhaustive iterative processes, the solution based on an ANN technique is simpler and quicker, and it consists of a solution of a system of linear algebraic equations [12].

An ANN is a nonlinear mathematical model that learns from the examples through iterations. ANNs are made of a large number of nodes or artificial neurons, which are disposed in a parallel structure. Each ANN has one input layer containing one node for each independent variable, one or more hidden layers, where the data are processed, and one output layer, containing one node for each dependent variable. The data from the input layer are propagated through the hidden layer and then to all network, which are associated with a scalar weight. Neurons in the hidden and output layers calculate their inputs by performing a weighted summation of all the outputs they receive from the layer before. Their outputs, on the other hand, are calculated by

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Abbreviations: ANN, artificial neural network; **RMSE,** root mean square error transforming their inputs using a nonlinear transfer function. Then, the network output is compared with the actual output provided by the user. The difference is used by the optimization technique to train the network. Thus, the training process requires a forward pass to calculate an output and a backward pass to update the weights in feed-forward back-propagation networks [12–14].

A great advantage of ANN models is that, they do not require prior knowledge of the relationship between the input and output variables, and instead of that, they figure out these relationships through training. Therefore, complex processes can be optimized to produce the desired outputs using successfully trained ANN models. In order to reduce acrylamide levels in food, a systematic evaluation of potential strategies is required for processing conditions. A successfully trained ANN model for the prediction of acrylamide concentration and browning ratio of potato chips is thought to give useful information for the optimization of frying process. The objective of this study was to model the formation of acrylamide and browning in potato chips during frying as a function of the independent variables of asparagine concentration, glucose concentration, temperature, and time by using the ANN modeling approach.

2 Materials and methods

2.1 Preparation of potato chips

Potato tubers were washed, peeled, and cut into slices of 1 mm thickness using a slicer. Diameters of potato slices were adjusted to 5 cm using circular cutter. By fixing the dimensions of potato slices, any variation in the rate of heat transfer, which would further affect the rate of acrylamide formation, was limited during frying. Slices were dipped into solutions (0, 5, and 10% of glucose) for 1 h to obtain slices with three levels of glucose. Slices with two levels of asparagine were also obtained using tubers of different varieties prior to dipping treatment. Sugars and asparagine levels of slices were determined by HPLC using the procedure described by us elsewhere [15].

Slices were then fried at 160, 170, or 180°C. Frying times were 2, 3, 4, and 5 min for 160 and 170°C and 1.5, 2, 2.5, and 3 min for 180°C to obtain a crispy texture. Fried chips were drained over a wire screen for 5 min to remove excess oil. The samples were photographed to determine the browning ratio and analyzed for acrylamide by GC-MS. Measurements of sugars, asparagine, acrylamide, and browning ratio were repeated three times and the mean values were used to train ANN.

2.2 Analysis of potato chips for acrylamide

An Agilent 6890 gas chromatograph (GC) coupled to an Agilent 5973 quadrupole mass spectrometer (MS) was used for the quantification of acrylamide in potato chips without derivatization using the method of Castle *et al.* [16] with some modifications. $^{13}C_3$-acrylamide (1000 ng/g) was added to 2 g of finely ground potato chips as the internal standard along with 20 mL of methanol. The sample was extracted for 3 min using a homogenizer. Following Carrez clarification, the extract was centrifuged at 10 000 rpm for 10 min using a 0.45 μm microspin PVDF centrifuge filter (Alltech, Deerfield, IL, USA). One microliter of clear supernatant was injected (splitless, injector temperature of 150°C) onto an HP INNOWAX column (30 m × 250 μm id, 0.25 μm film thickness; Agilent Technologies, Wilmington, DE, USA). The temperature program for GC was as follows: isothermal for 0 min, increased at a rate of 10°C/min from 80 to 250°C, and isothermal for 13 min. The flow of the carrier gas helium was 1.0 mL/min. The analysis was performed using electron ionization (70 eV) and SIM. The ions monitored for identification of acrylamide were 71, 55, and 27 using *m/z* 71 for quantification. The ions monitored for identification of the internal standard, $^{13}C_3$-acrylamide were 74 and 58. The LOD and the LOQ for acrylamide were 15 and 50 ng/g in potato chips, respectively. Signal response was linear over a concentration range between 50 and 1000 ng/g of acrylamide. The CV was 9% or lower for three repetitive measurements of acrylamide in potato chips.

2.3 Digital image analysis of potato chips for browning ratio

Digital images were taken from a digital image acquisition system consisting of an HP Photo Smart color digital camera (maximum resolution 5.1 mega pixel) placed vertically at a distance of 25 cm from the sample. The angle between the axes of the lens and the sources of illumination was approximately 45°. Illumination was achieved with two fluorescent daylight lamps (60 cm in length) with color temperature of 6500 K. Captured images were stored in a PC in jpeg format without compression.

In fried potato images, there were three regions which typically had bright yellow (Region 1), yellowish brown (Region 2), and dark brown (Region 3) colors. After the mean red, green, and blue values of the pixels of these three regions were determined, pixels of the fried potato images were segmented into three sets (Set-I, Set-II, and Set-III) based on their Euclidian distances to the representative mean values by using a Matlab code (VectorQuantize) described by us elsewhere [17]. The browning ratio (Eq. 1) which is defined as the normalized area of Set-III pixels was computed from the segmented image.

$$\text{Browning ratio} = \text{Set-III pixels}/\text{Total pixels} \qquad (1)$$

2.4 ANN modeling

A series of feed-forward type network models with back-propagation training algorithm were developed in this

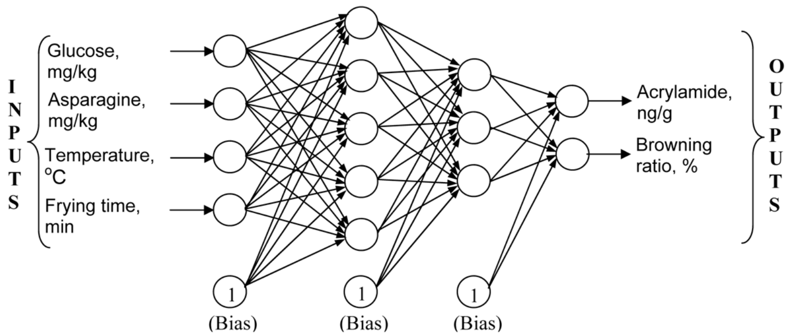

Figure 1. Structure of ANN.

study. These networks have one input, one or two hidden and one output layers to predict the acrylamide concentration and browning ratio (Fig. 1). The input layer consisted of four neurons corresponding to glucose and asparagine concentrations of potatoes, frying time, and temperature, while the output layer had two neurons representing the acrylamide concentration and browning ratio of potato chips. The number of hidden layers and the number of its nodes were chosen according to ANN performance. The commercial software package, MATLAB® 7.0 (MathWorks, Natick, MA, USA) was used for ANN modeling.

The experimental dataset totally consisted of 72 data points. Fifty-four data points were used for training the ANN while the remaining 18 data points were used for testing (validation) the performance of ANN. Inputs were normalized prior to training and validation of the ANN model. Logistic sigmoidal function (Eq. 2)

$$f(x) = [1 + \exp(-x)]^{-1} \tag{2}$$

and, purelin function (Eq. 3)

$$f(x) = x \tag{3}$$

were used as the transfer functions in hidden and output layers, respectively. An intermediate learning rate of 0.1 and momentum constant of 0.1 were used as the training parameters. The modified form of Levenberg–Marquardt algorithm by Bayesian regularization process (*trainbr*) was employed for training. Controlled training methodology was applied to overcome the network overtraining problems [18]. The network weights of the lowest testing error during the whole training process were used for performance testing of ANN models. The number of hidden layers and the neurons within each hidden layer were determined on the basis of a performance evaluation for various ANN configurations. A total of 45 networks were tested by varying the number of neurons in hidden layers from 2 to 10. The optimum ANN configuration which gave the lowest root mean square error (RMSE) and the highest coefficient of determination (R) for the testing dataset was selected:

$$\mathrm{RMSE}_A = \sqrt{\frac{\sum_{i=1}^{N} \left(A_i^{\mathrm{pred}} - A_i^{\exp t}\right)^2}{N}} \tag{4}$$

$$\mathrm{RMSE}_{\mathrm{BR}} = \sqrt{\frac{\sum_{i=1}^{N} \left(\mathrm{BR}_i^{\mathrm{pred}} - BR_i^{\exp t}\right)^2}{N}} \tag{5}$$

The parameters $A_{\mathrm{i}}^{\mathrm{pred}}$ and $\mathrm{BR}_{\mathrm{i}}^{\mathrm{pred}}$ represent the predicted acrylamide and browning ratio outputs from the ANN model for the given inputs while $A_{\mathrm{i}}^{\mathrm{expt}}$ and $\mathrm{BR}_{\mathrm{i}}^{\mathrm{expt}}$ are the desired outputs (*i.e.*, experimentally measured) from the same input values. N represents the number of data points.

3 Results and discussion

ANN structure optimization process lies in selecting the adequate number of neurons in layers. The number of nodes in the input layer and the neurons in the output layer was already defined. So, the objective of the ANN topology optimization was limited to select the adequate number of neurons in the hidden layer or layers. The criterion used consisted of selecting the number of neurons that gave a minimum final error during the training and testing of the ANN configurations. Figure 2 shows the prediction errors and corresponding correlation coefficients for acrylamide predictions of several hidden layer configurations of ANNs. According to the error results for two types of network (one or two hidden layer configurations), two hidden layer configurations had comparatively better performances. Prediction errors of acrylamide were higher for all network combinations as compared with browning ratios. Lower prediction errors for the acrylamide concentration were obtained from hidden layer(s) with five neuron combinations (5-4; 5-3; 5-2; 5-1; 5-0). The lowest prediction error

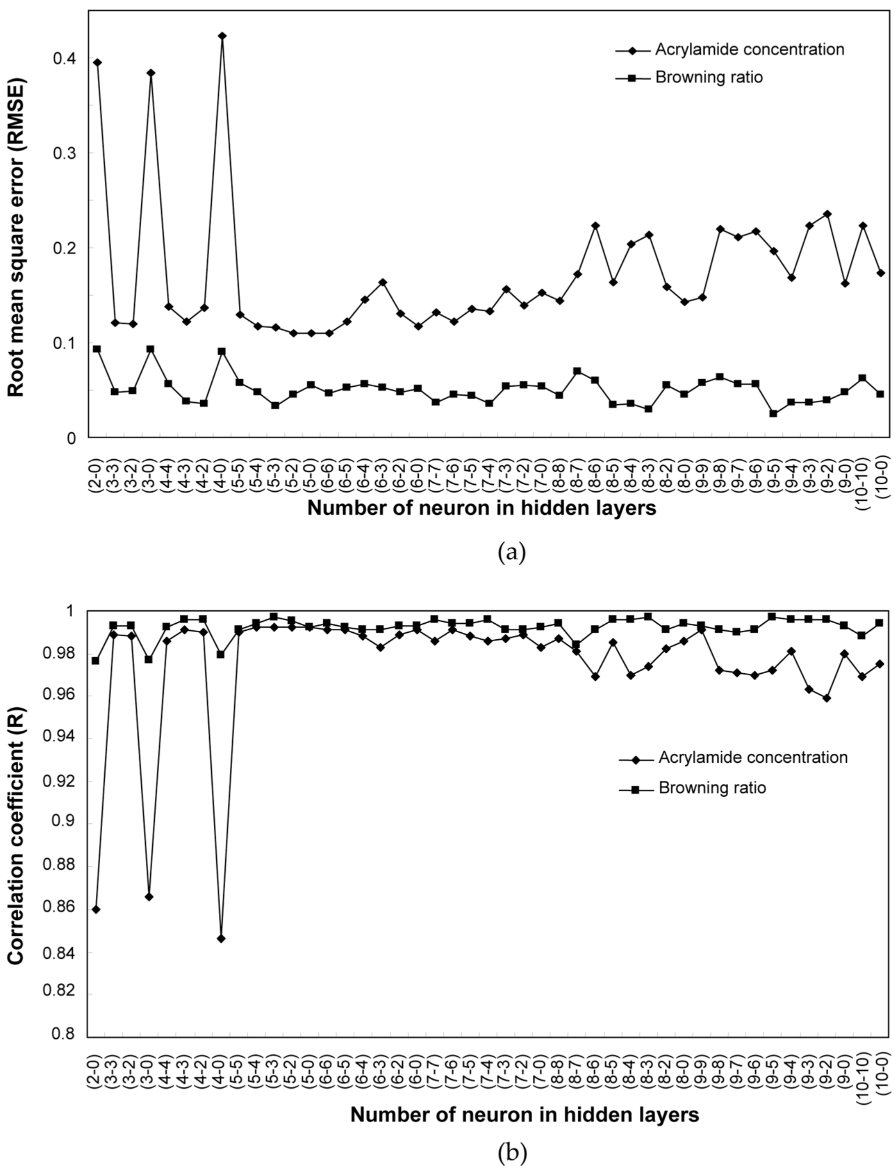

Figure 2. (a) Associated prediction errors for acrylamide and browning ratio with different ANN configurations. (b) Correlation coefficients between predicted and measured acrylamide and browning ratio with different ANN configurations.

for the browning ratio was obtained with a hidden layer combination of 5-3. As a result, the optimum configuration was 4-5-3-2 for both output parameters (Fig. 1). Attempting to improve the results by changing some of the network parameters such as learning rate and momentum constant did not improve the predictive performance of the ANN model.

Figure 3 shows the correlation between measured and predicted levels of acrylamide and browning ratio of potato chips. As confirmed for both training and testing datasets, there was a strong prediction capability of the optimum ANN configuration (4-5-3-2 network topology) used in this study.

An important use of predictive model is to conduct "what if" experiments, whereby the response to an imposed change in reaction conditions (*e.g.*, concentration, temperature, and time) can be determined without actually doing the experiment. For complicated reactions like the Maillard reaction, the main shortcoming of kinetic models is the use of simplified reaction networks on the basis of several assumptions to derive the governing equations. Nevertheless, a pragmatic approach of ANN modeling that considers only the input and output variables rather than the complex chemistry can already be sufficient for obtaining information of direct applicability to food processing.

The experimental observations in previous studies have confirmed that acrylamide concentration rapidly increases to an apparent maximum followed by a slow decrease afterward [8–11, 19, 20]. This kind of behavior for the changes of acrylamide concentration suggests that acrylamide is not an end product in the Maillard reaction. In addition to the complexity of chemical reaction network, the yield of acryl-

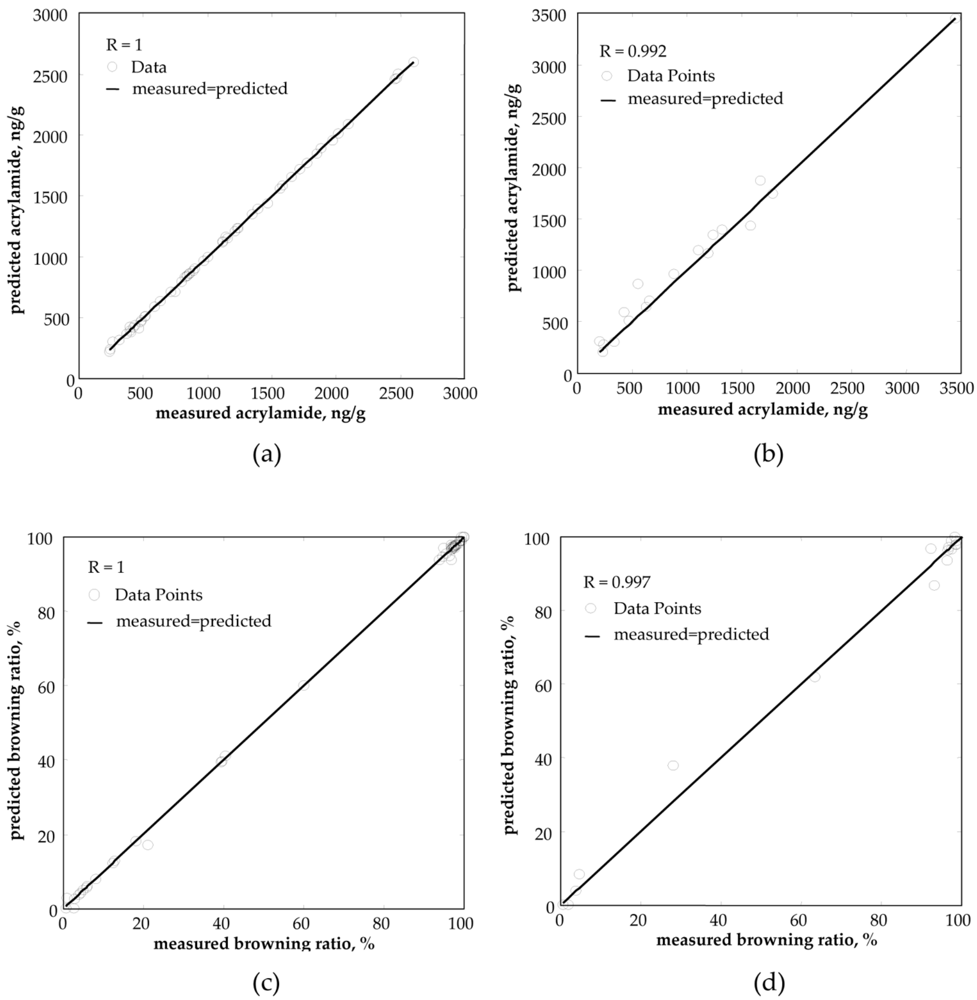

Figure 3. Correlations between predicted and measured acrylamide concentrations, (a) training and (b) testing datasets; and between predicted and measured browning ratios, (c) training and (d) testing datasets.

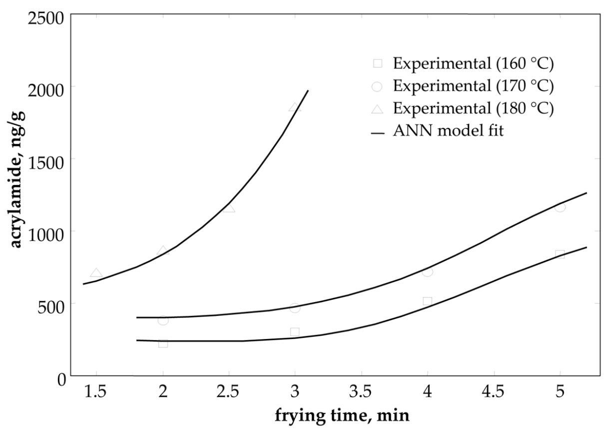

Figure 4. Simulated and experimental acrylamide concentrations of potato chips (for potato slices with "higher asparagine and lower sugar") at frying temperatures of 160, 170, and 180°C.

amide is too low during the Maillard reaction. Previously reported yields based on free asparagine ranged between 0.01 and 4.8% under various wet and dry experimental conditions [2, 20–24]. This fact further complicates the development of a kinetic model.

The time-dependent formation of acrylamide could be successfully simulated at all temperatures, asparagine, and glucose concentrations studied. Figure 4 illustrates the changes in acrylamide concentration of potato chips. Here, the solid lines represent the simulated values of acrylamide over a time range of 1.5–5 min at three temperatures ranging between 160 and 180°C, while the symbols "+", "Δ", and "o" indicate the experimental data points. The asparagine concentrations of potato slices were 3513 ± 224 and 5114 ± 378 mg/kg for two tuber varieties coded as "lower asparagine" and "higher asparagine", respectively. The sugar concentrations of potato slices dipped into solutions at three glucose concentrations were 5130 ± 246, 7978 ± 401, and 12 054 ± 881 mg/kg coded as "lower sugar", "medium sugar", and "higher sugar", respectively.

Like acrylamide concentrations, browning ratios of potato chips could be simulated well over a time range of 1.5–5 min for all dependent variables (Fig. 5). Simulated results for acrylamide concentration and browning ratio

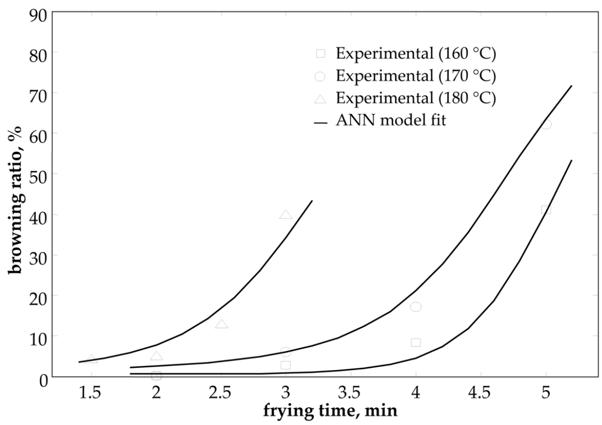

Figure 5. Simulated and experimental browning ratios of potato chips (for potato slices with "higher asparagine and lower sugar") at frying temperatures of 160, 170, and 180°C.

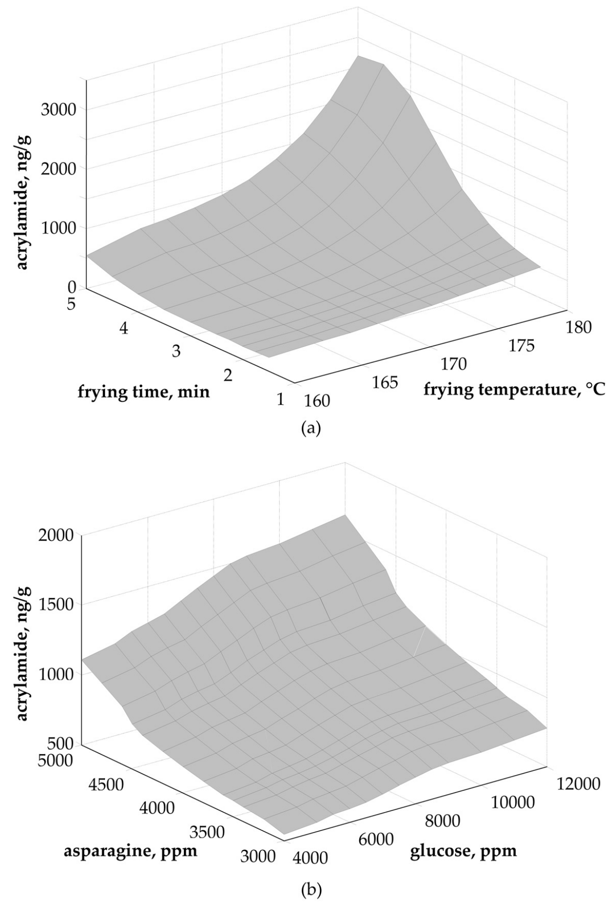

Figure 6. Surface plots of acrylamide formation as a function of (a) frying temperature and time (for potato slices with "lower asparagine" and "lower sugar"), and (b) asparagine and glucose concentrations (for frying at 180°C for 2 min).

emphasized the capability of ANN model as a predictive tool in determining the effects of both compositional and processing parameters on acrylamide formation and browning in potato chips during frying.

Using a successfully trained ANN model, it was possible to observe the combined effects of variables including time (1.5–5 min), temperature (160–180°C), sugar concentration (5000–12 000 mg/kg), and asparagine concentration (3500–5000 mg/kg) on acrylamide formation and surface browning ratio in potato chips. Surface plots illustrating the effects of time × temperature and asparagine × glucose covariants are shown in Fig. 6.

4 Concluding remarks

The present study successfully showed how an ANN modeling approach can be applied to predict the formation of acrylamide and browning in potato chips at different temperature and time combinations by the effects of glucose and asparagine. Contrary to kinetic models, ANN modeling is more realistic since it depends only on the experimental observations without assumption. It seems to be a feasible approach for the prediction of acrylamide concentrations in potato chips based on the parameters related to both potato composition and frying conditions. The prediction capability of ANN models offers an advantage for the optimization of processing conditions to minimize undesirable changes in foods.

An ANN model can be designed by taking all the parameters that can influence the formation of acrylamide during thermal processing. In its present form, the model can predict two output variables (acrylamide concentration and browning ratio) from only four input variables (sugar, asparagine, temperature, and time) which are known to influence the selected outputs. Recent studies have highlighted that some pretreatments of potato slices such as additions of citric acid [25], glycine [26], or cations [27] may be used to mitigate acrylamide formation during frying. However, these pretreatments are not commonly applied by the potato chip industry yet. If the processing conditions of potato chips are subjected to change involving these pretreatments, then the ANN model can easily be modified by introducing new input variables such as pH, the concentration of glycine, and cations after their effects on the formation of acrylamide and browning are determined experimentally.

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