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Investigation of the Influence of Different Moisture Levels on Acrylamide Formation/Elimination Reactions Using Multiresponse Analysis

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The influence of water activity on the formation and elimination reactions of acrylamide was examined by means of multiresponse modeling on two different levels of complexity: basic equimolar asparagine−glucose systems and equimolar potato-based asparagine−glucose systems. To this end, model systems were first equilibrated to initial water activities in the range of 0.88−0.99 (corresponding roughly to the moisture gradient observed in French fries) and then heated at temperatures between 120 and 200 °C during different reaction times. For each sample, the concentration of acrylamide, glucose, asparagine, and aspartic acid was measured, as well as the extent of browning. A mechanistic model was proposed to model the five measured responses simultaneously. For both types of model systems, the model prediction was quite adequate, with the exception of the extent of browning, especially in the case of the potato-based model system. Moreover, the corresponding estimated kinetic parameters for acrylamide formation and elimination did not change significantly (based on a 95% confidence level) within the range of water activities tested, nor between the systems in the absence or presence of the potato matrix. The only remarkable difference was observed for the activation energy of acrylamide elimination, which was lower in the presence of the potato matrix, although not always significant. In general, these results confirm the generic nature of the model proposed and show that the influence of different moisture levels on acrylamide formation and elimination is minimal and that the addition of a potato matrix has little or no influence on the kinetic model and corresponding kinetic parameters.

KEYWORDS: Acrylamide; kinetics; multiresponse modeling; water activity; thermal treatment; food

INTRODUCTION

Acrylamide, a potential human carcinogen, is formed in substantial amounts in frequently consumed heat-treated foods (*1, 2*). Potato- and wheat-based products belong to the group of foodstuffs in which relatively high amounts of acrylamide have been detected. French fries and potato chips, containing the highest amounts of acrylamide, are responsible for a large portion of the intake of acrylamide (between 30 and 51% in Belgium) (*2–5*). These products are prepared by means of deep frying, which is a common method of food preparation because of the pronounced palatable sensorial characteristics of the final products. Frying is a coupled heat and mass transfer process in which oil acts as a heat transfer medium. After immersion of the food product into the oil, the food surface heats, and water begins to vaporize. As frying progresses, the evaporation front moves toward the center, a surface crust is formed, and eventually, the temperature of the food surface rises to that of the oil. Simultaneously, oil is absorbed into the food (*6, 7*). Additionally, a complex series of various chemical interactions take place between frying oil and food components, resulting in the formation of volatile and nonvolatile compounds (*6*). Typical flavors of fried foods, desirable or undesirable, mainly originate from the decomposition of lipids at high temperatures (*6, 8*). The formation of colors is considered to result from the Maillard reaction between proteins and carbohydrates (*6*). Acrylamide is formed as a side-product of the Maillard reaction between asparagine and carbohydrates (*9, 10*). According to Franke et al. (*11*), the formation of acrylamide is concentrated at the surface layer. This seems evident because only in this region are temperatures higher than 100 °C reached, and the local moisture content diminishes because of evaporation; these conditions promote acrylamide formation in addition to other pathways of the Maillard reaction. The combined effect of water activity and temperature on acrylamide formation was investigated in a previous study in a range from 0.11 to 0.92,

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corresponding to moisture contents ranging from 1.6 to 14.5% (*12*). In this range, the increase in water activity had only a slight increasing effect on the rate constant of acrylamide formation and the corresponding activation energy, especially observable at water activities corresponding to water contents ≥5%. This confirms the observations by Schieberle et al. (*13*) and Mestdagh et al. (*14*) of an increasing acrylamide concentration with increasing water content ranging from 0 to 25 and 0 to 65%, respectively, when heating asparagine−sugar systems at a selected temperature−time combination. Also, Amrein et al. (*15*) observed in potato powder an increased acrylamide formation rate up to a moisture content of ∼12% after which the reaction rate decreased again; these authors demonstrated that the temperature dependence of the rate constant of acrylamide formation increased strongly with decreasing moisture content at levels below 20%. Contrarily, other research groups observed an increased acrylamide concentration when the moisture content was decreased, especially when lowered to 5% or less (*16–18*). Most researchers studying the effect of moisture content on acrylamide formation focus on drier systems because under these conditions, this reaction is thought to accelerate. In French fries (with a thickness of 1 cm), however, the moisture gradient ranges from 20 to 70% (*19*). Since this product contributes to a large extent to the intake of acrylamide, kinetic studies concerning the influence of moisture on the rate constants of acrylamide formation and elimination should focus on systems with moisture levels relevant to these types of foodstuffs. In this way, predictions of acrylamide content can be made for different food products based on the moisture gradient observed. Moreover, most studies concerning the effect of moisture content concentrate on reactions directly involved in the formation or elimination of acrylamide. In real food products, however, it is of primary importance that the final product is acceptable to the consumer, implying that the focus should not only be on the acrylamide content but also on other product-related aspects such as color formation, fat content, texture, flavor, etc. Most of these aspects are directly related to the Maillard reaction, and thus, the progress of the Maillard reaction should also be taken into account when modeling the formation of acrylamide. In this context, multiresponse modeling can be a very useful tool since more than one response is taken into account.

Since the formation of acrylamide is dependent on the local moisture content and temperature established within a certain food region, it is important to quantify the combined effect of moisture content and temperature on the formation and elimination of acrylamide to predict the acrylamide content formed. Therefore, the objective of this study was to investigate the effect of different levels of moisture, chosen so that the moisture gradient, found within French fries, can be represented. The combined effect of relevant moisture contents, temperature, and time was studied using asparagine−glucose model systems in both the absence and the presence of a potato matrix by means of a multiresponse approach. This approach allows more precise parameter estimation in comparison to single response modeling and is also helpful in obtaining insight into the actual reaction mechanism.

MATERIALS AND METHODS

Preparation and Characterization of the Potato Matrix. A batch of potatoes of the variety Bintje (year of harvest: 2005) was purchased from a local farmer. They were cut into slices (with a thickness of 5 mm) and blanched for 10 min at 70 °C to prevent enzymatic browning. The blanched potato slices were mixed and stored in a freezer at −40 °C until lyophilization (Alpha 2-4, Martin Christ GmbH, Osterode, Germany) was carried out. The resulting matrix was characterized in terms of amino acid, sugar, and starch content.

The analysis of amino acids was performed using the EZ:faast amino acid analysis kit (Phenomenex, Torrance, CA) as described further in this section. The lyophilized potato samples were, however, first extracted in 25% acetonitrile in water (v/v) for 1 h at 40 °C, as described by Farkas and Toulouee (*20*). The concentration of sugars (glucose, fructose, and sucrose) was determined using an enzymatic test kit from r-Biopharm GmbH (Darmstadt, Germany). Prior to analysis, the samples were deproteinized with Carrez reagents. The total starch content was determined using the enzymatic test kit of Megazyme (Wicklow, Ireland).

Preparation of Model Systems. The basic model systems consisted of an equimolar mixture of L-asparagine (≥99.5%, Sigma-Aldrich) and D-glucose (99.5%, Sigma-Aldrich). To obtain a homogeneous mixture, both reactants were thoroughly mixed in the presence of water, subsequently frozen with liquid nitrogen, and finally freeze-dried (0.01 mbar vacuum pressure, Alpha 2-4, Martin Christ GmbH) until a powder was obtained.

The potato-based model systems consist of a 10% equimolar asparagine−glucose mixture and 90% lyophilized potato matrix, in which the glucose concentration (initially 5.27 g/kg dw (dry weight)) was replenished to the same level as the asparagine concentration (16.12 g/kg dw). This mixture was blended with some water, frozen with liquid nitrogen, and freeze-dried as described for the basic model systems.

Equilibration of Model Systems at Different Water Activities. For the kinetic experiments, the model systems, prepared as described previously, were divided into portions of 1.15 g in small open containers. After being dried above P_2O_5, samples were kept at 4 °C in closed jars for 4 weeks with the relative humidity controlled using saturated salt solutions. Saturated salt solutions of KCl ($a_w = 0.88$), $Sr(NO_4)_2$ ($a_w = 0.92$), KNO_3 ($a_w = 0.96$), and K_2SO_4 ($a_w = 0.99$) were selected based on the tables reported by Greenspan (*21*).

Determination of Water Content. The moisture content of the model systems equilibrated at a certain water activity was determined by means of an automated Karl Fischer titration (KF Titrino 701, Metrohm, Herisau, Switserland). The two-component technique was applied with Hydranal-Titrant 5 (Riedel-de Haën, Seelze, Germany) as the titrating solution and Hydranal-Solvent (Riedel-de Haën, Seelze, Germany) as the working medium. The working medium was titrated to dryness before adding the sample (∼50 mg). To ensure complete dissolution of the sample, the content of the container was mixed for 2 min at a fixed stirring speed before starting the titration. The titration end point was detected using bivoltametric indication.

Heat Treatment. Samples were heated in hermetically closed reactor tubes (Inox, 8 mm × 100 mm, custom-made), which were filled with the samples equilibrated at a certain a_w in a closed environment (Captair Pyramid, Erlab, France) filled with dry nitrogen gas, to avoid water resorption during handling of the samples. Heat treatment of the reactor tubes was performed in a thermostated oil bath (UH2D, Grant Instruments Ltd., Cambridge, U.K.) at 120, 140, 160, 180, and 200 °C. For kinetic experiments, samples were taken at different heating times, which were chosen depending on the treatment temperature applied. After thermal treatment, samples were immediately cooled in ice water to stop any further reaction. Next, the samples were diluted 10 times and stored at −40 °C until further analysis.

During the heating and subsequent cooling phase of the samples, the temperature was registered within the closed reactor tubes at regular time intervals (4 s) using thermocouples (type T, Thermo Electric Benelux, Balen, Belgium) connected to a datalogger (TM 9616, Ellab, Roedovre, Denmark). The registered temperature−time profiles are included in the corresponding data analysis (see Kinetic Data Analysis).

Analysis of Acrylamide. Acrylamide was analyzed by gas chromatography coupled to mass spectrometry with chemical ionization without prior derivatization, based on the method described by Biedermann et al. (*22*). More details concerning the analysis were described previously (*23*).

Analysis of Amino Acids. The analysis of amino acids was performed using the EZ:faast amino acid analysis kit (Phenomenex).

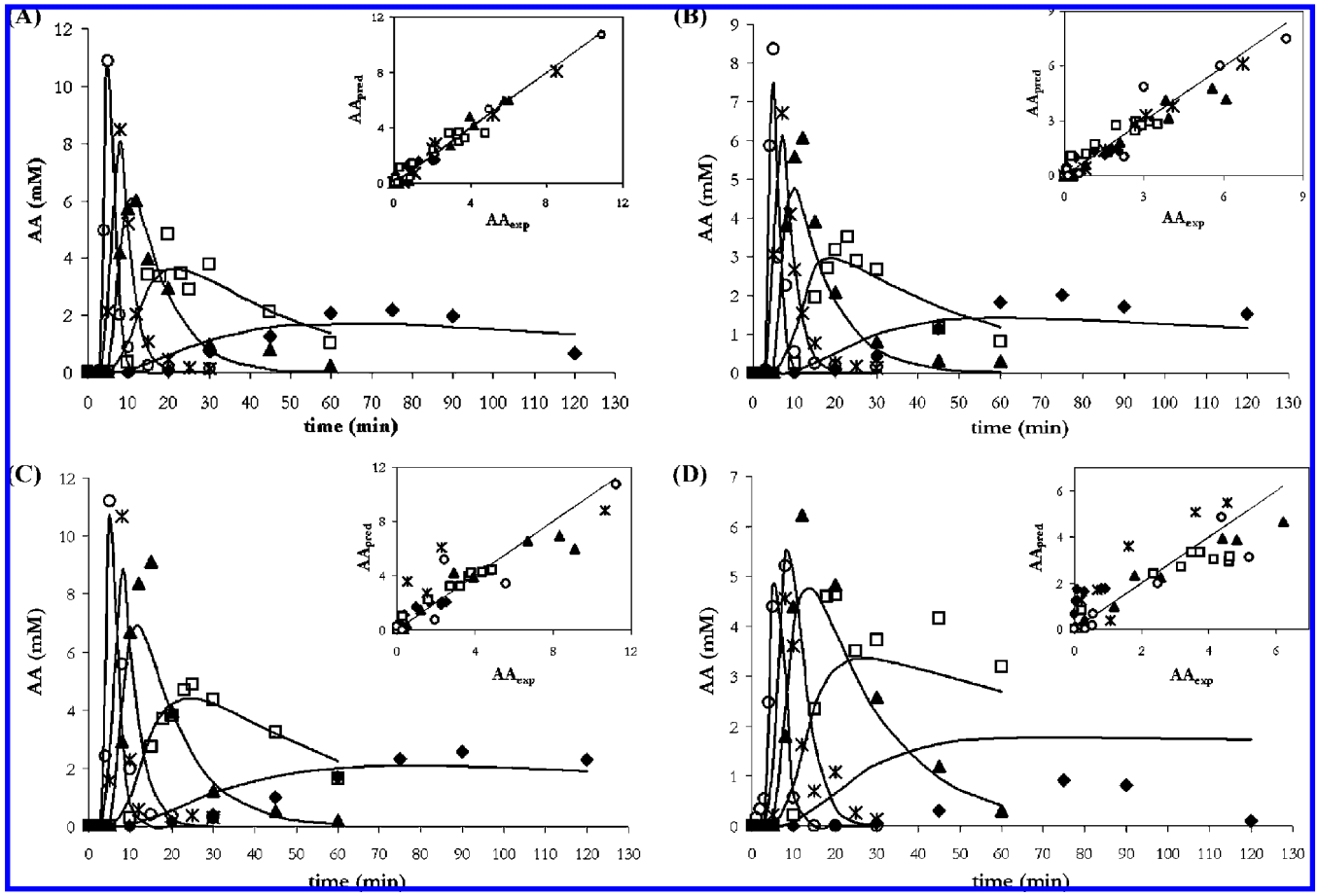


Figure 1. Time course of acrylamide concentration in equimolar asparagine−glucose model systems equilibrated at different initial water activities at 4 °C: $a_W = 0.88$ (**A**); $a_W = 0.92$ (**B**); $a_W = 0.96$ (**C**); and $a_W = 0.99$ (**D**), heated at 120 °C (◆), 140 °C (□), 160 °C (▲), 180 °C (×), and 200 °C (○). The solid lines represent the fit of the **Scheme 2** model, while experimental data are represented by symbols. Insets show the corresponding parity plot where the full lines have a slope of 1 (perfect fit).

Thermally treated samples were diluted so that the total amino acid concentration was maximally 0.01 M. The procedure for sample preparation consists of a solid phase extraction step, followed by a derivatization step and liquid/liquid extraction. Derivatized samples were analyzed by gas chromatography coupled to mass spectrometry. Samples were injected (2.0 μL) at 250 °C in split mode (1:15) onto a Zebron ZB-AAA column (10 m × 0.25 mm i.d., Phenomenex). The oven temperature was initially set at 110 °C (1min) and further increased to 320 °C at a rate of 30 °C/min. Helium was used as the carrier gas at a constant flow rate of 1.1 mL/min. Detection was carried out in electron ionization mode in a scan range from *m/z* 45 to 450. Quantification for asparagine was performed based on the ratio of the peak area of the *m/z* 155 ion to the peak area of the *m/z* 158 ion for the internal standard, norvaline. Aspartic acid was quantified based on the ratio of the peak area of the *m/z* 216 ion to the peak area of the internal standard.

Analysis of Sugars. Samples were diluted (1:100 to 1:1000, depending on the sugar concentration) and analyzed by high-performance anion-exchange chromatography (HPAEC; Dionex Bio-LC system, Sunnyvale, CA) using a CarboPac PA1 column (4 mm × 250 mm) with a corresponding guard column at 30 °C. An isocratic gradient of 150 mM sodium hydroxide was used as the eluent for sample analysis at a flow rate of 1 mL/min. After 10 min, the eluent concentration was increased to 200 mM NaOH to regenerate the column. Sugars (i.e., glucose, fructose, and sucrose) were detected using an ED_{50} electrochemical detector in the pulsed amperometric detection mode (PAD; Dionex) and quantified by use of an internal standard, lactose.

Analysis of Browning. Browning was determined spectrophotometrically by measuring the absorbance at 470 nm. When necessary, samples were diluted with reagent-grade water. The corresponding melanoidin concentration, formed from asparagine and glucose, could be calculated from absorbance measured by using the Lambert−Beer equation with an extinction coefficient of 282 L/mol cm, as described by Knol et al. (*24*). In the case of the potato-based systems, removal of solid particles prior to spectrophotometrical measurement of browning was required. Therefore, 1.5 mL of the thermally treated diluted samples was centrifuged (Eppendorf centrifuge 5417R, Hamburg, Germany) for 5 min at 1000*g*, after which the absorbance of the resulting supernatant was measured at 470 nm.

Repeatability of Heat Treatment and Subsequent Analyses. To asses the standard error of heat treatment and the subsequent analyses for the different responses, five identical samples were heated at 120 and 200 °C. For both temperatures, the resulting standard error on the concentration of the different responses, measured in the five identical samples, was calculated and was found to be maximally 10%.

Kinetic Data Analysis. On the basis of the proposed reaction network, a kinetic model was built by deriving a differential equation for each reaction step. These equations contain rate constants k as parameters. The temperature dependence of the rate constants k can be quantified by means of the activation energy E_a (J/mol) according to the Arrhenius equation

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

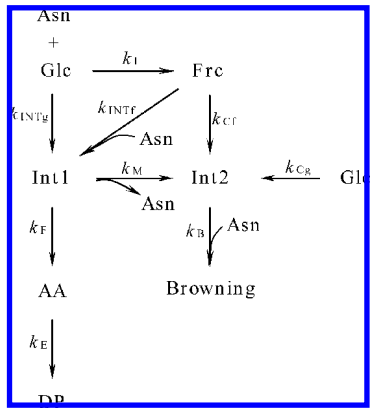
where R is the universal gas constant (8.3145 J/mol K), T is the temperature, and k_{ref} is the reaction rate constant at a reference temperature (T_{ref}) of 160 °C. Substitution of eq 1into the differential equations set up for each reaction step renders the mathematical model to be solved using numerical integration of the registered temperature−time profile of each sample. The corresponding kinetic parameters, reaction rate constants, and activation energies, of the various reactions, were estimated by nonlinear regression using the determinant criterion

Table 1. Overview of Saturated Salt Solutions Used To Obtain Predefined Water Activities at 4 °C and Corresponding Water Content for Equimolar Asparagine−Glucose Mixtures in the Presence or Absence of a Potato Matrix

		water content (%)	
salt	ERH (%) at 4 °C	basic system	potato-based system
KCl	88	10.4 ± 0.285[a]	18.5 ± 0.039[b]
$Sr(NO_3)_2$	92	14.5 ± 0.080[a]	19.2 ± 1.694[c]
KNO_3	96	29.6 ± 0.045[a]	21.2 ± 0.247[b]
K_2SO_4	99	34.2 ± 0.783[b]	25.0 ± 0.330[b]

[a] Standard error based on two independent measurements. [b] Standard error based on three independent measurements. [c] Standard error based on four independent measurements.

Scheme 1. Proposed Reaction Network for Formation and Elimination of Acrylamide from Asparagine and Glucose through the Maillard Reaction under Dry Conditions

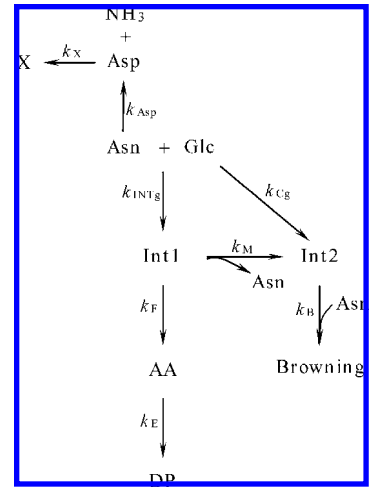


by means of the software package Athena Visual Studio v11.0 (www.athenavisual.com). The criterion applied replaces the commonly used least-squares minimization to comply with statistical demands for multiresponse modeling (*25*). The goodness-of-fit of the model was evaluated by scrutiny of residuals.

RESULTS AND DISCUSSION

Modeling of Acrylamide Formation and Elimination in Basic Asparagine−Glucose Mixtures. To study the effect of water activity on the formation and elimination reactions of acrylamide, four different water activities were selected at which equimolar asparagine−glucose mixtures were equilibrated and for which the corresponding water content of the model system (**Table 1**) spans the moisture gradient found in French fries (*19*). To this end, asparagine−glucose mixtures were equilibrated above saturated salt solutions at 4 °C to result in water activities ranging from 0.88 to 0.99. The resulting mixtures were heated during different reaction times at temperatures between 120 and 200 °C. One should be aware that the water activities reported in this study are the initial ones, obtained after equilibration at 4 °C, and are not constant during heating since water activity changes due to temperature changes and since water also is consumed and/or produced because of reactions occurring. Acrylamide concentrations, representing the net result of simultaneous formation and elimination reactions, were measured and are shown in **Figure 1A−D** by the data points as a function of time for the water activities tested. The combined effect of temperature and time on acrylamide concentration already was demonstrated in previous studies (*12, 23, 24*). Acrylamide is formed starting from temperatures around 120 °C. The higher the reaction temperature, the faster the concentration of acrylamide increases to a maximum after which the concentration decreases again due to elimination reactions predominating and/or precursors being exhausted. The maximum net concentration of acrylamide attained generally increases with increasing temperature; this trend is, however, less clear in the case of an initial water activity of 0.99 (**Figure 1D**). The phase in which the acrylamide concentration diminishes is much more pronounced in low moisture asparagine−sugar mixtures as compared to more diluted mixtures (*23, 26*), and the concentration even falls to zero within a narrow time range for temperatures equal to 160 °C or higher. This increased elimination is likely to be related to a higher concentration of reactive products formed under these more concentrated conditions.

Scheme 2. Modified Reaction Network for Formation and Elimination of Acrylamide from Asparagine and Glucose through the Maillard Reaction under Dry Conditions



Establishment of a model, apt to describe the changes in acrylamide concentration under varying conditions of initial water content, was one of the main purposes of this study. The simultaneous formation and elimination of acrylamide can be modeled by means of a simplified model taking into account acrylamide formation (second-order reaction) and elimination (first-order reaction) reactions and an additional Maillard reaction (second-order) between asparagine and glucose. The model describes the data accurately (model fit not shown), as demonstrated in a previous study for another range of water activities (*12*). The model proposed has nevertheless some limitations. First, the model consists of six kinetic parameters that need to be estimated based on only one response measured (single response modeling). This results in parameter estimates with a high degree of uncertainty. Consequently, significant differences between model systems with different initial conditions are difficult to discriminate. Moreover, since the proposed model is an empirical model, disregarding details of the complex chemistry, the estimated values are only apparent. Second, it seems that under the dry initial conditions applied to the asparagine−glucose mixtures, alternative reactions such as other side reactions of the Maillard reaction and/or caramelization reactions become of more importance as compared to diluted systems. Consequently, considering only the reactions directly affecting acrylamide content becomes less acceptable. That is why a more detailed mechanistic model was built, wherein important common intermediates of the Maillard reaction and caramelization reactions were considered next to acrylamide formation and elimination reactions. This model (**Scheme 1**) is

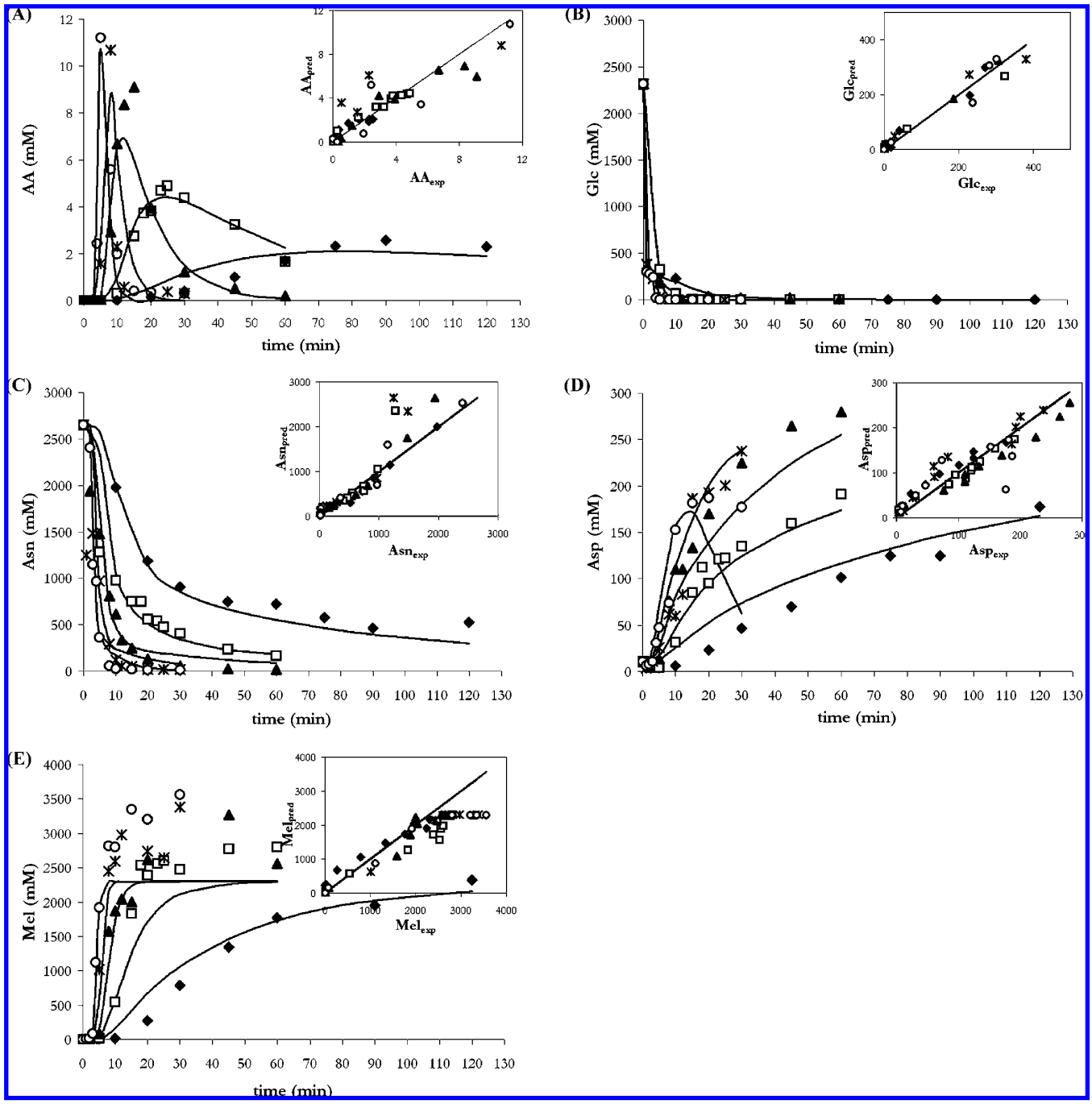


Figure 2. Time course of acrylamide (**A**), glucose (**B**), asparagine (**C**), aspartic acid (**D**), and melanoidins (**E**) in an equimolar asparagine−glucose model system equilibrated at an initial water activity of 0.96 at 4 °C, heated at 120 °C (◆), 140 °C (□), 160 °C (▲), 180 °C (×), and 200 °C (○). The full lines represent the fit of the **Scheme 2** model, while the experimental data are represented by symbols. Insets show the corresponding parity plot where the full lines have a slope of 1 (perfect fit).

based on the reaction schemes proposed by Knol et al. (*24*) and Wedzicha et al. (*27*), extended with additional caramelization reactions.

Quantification of Reactants and Main Products. Next to acrylamide, the most obvious responses to be measured, based on the proposed reaction network, are the precursors asparagine and sugars and the extent of browning. These responses are shown in **Figure 2A−E** for an initial water activity of 0.96, for which the trends observed as a function of temperature and time are comparable to the other water activities tested (data not shown).

During heating of asparagine and glucose, the concentration of reactants decreased as a function of time (**Figure 2B**,**C**). The loss of glucose, however, occurred much faster than the loss of asparagine, independently of the initial water activity of the model systems and of the reaction temperature applied. The same observation was reported by other research groups studying acrylamide formation or the Maillard reaction in general (*16, 24, 28*). The slower loss of asparagine can be explained by the fact that the amino acid is, next to being consumed in the initial and final stage of the Maillard reaction, partly regenerated in the intermediate stage, whereas glucose is only consumed in different reactions. The main reactions in which glucose is consumed are the initial stage of the Maillard reaction, caramelization reactions, and an isomerization reaction. However, since no measurable fructose was detected, it is supposed that

the isomerization from glucose to fructose is negligible under the given circumstances or that the reactions consuming fructose occur faster than fructose is formed. Therefore, the initially proposed reaction network (**Scheme 1**) was simplified by neglecting the isomerization reaction from glucose to fructose and consequently also the formation of Int1 and caramelization products from fructose. During amino acid analysis, considerable amounts of aspartic acid were detected that increased as a function of time and with increasing heating temperature (**Figure 2D**). The only logical explanation for the occurrence of this compound is that it is formed from asparagine through chemical conversion due to the heating temperatures applied (*29, 30*). The formation of aspartic acid also was observed in diluted buffered asparagine−sugar mixtures heated in the same temperature range (*31*), where the supposed deamidation was confirmed by changes in pH. At higher temperatures, the concentration of aspartic acid levels off, and at 200 °C, the concentration even decreases slightly after longer heating times. This indicates that aspartic acid is not only formed but is also participating in reactions in which it is consumed, possibly with (unidentified) reaction products (likely of glucose). In the proposed reaction network, the nature of these reactions remains unspecified; the group of reactions consuming aspartic acid is indicated by X.

The extent of browning originating from Maillard browning products (melanoidins) can be related to the number of sugar molecules incorporated into the melanoidins by means of the molar extinction coefficient of these specific melanoidins (*28*). Melanoidins are brown polymers that are formed by linkage of sugar degradation products, called osuloses (Int2), by amino compounds. In more concentrated amino acid−sugar systems, such as in this study, caramelization reactions are assumed to be of more importance than in diluted systems. Sugar degradation products are formed, which are to a large extent similar to those formed through the initial stage of the Maillard reaction and thus contribute to the products represented by the group of osuloses (Int2) (*28, 32*). These products can, however, also polymerize without the intervention of amino compounds, resulting in the formation of brown caramels. The quantification of these polymers is complicated, and the extent to which they contribute to browning is not determinable. Thus, the quantification of browning measured in terms of melanoidins is not totally correct. The effect of temperature and time on browning is shown in **Figure 2E** for an initial water activity of 0.96. A similar trend was observed for the other water activities tested. The formation of brown products is highly dependent on temperature as the formation increases with increasing temperature and results in a plateau after longer heating times. The level of the plateau attained also increases with increasing temperature. For all temperatures tested, a lag-phase was observed for browning, which was shortened with increasing temperature. Other research groups, making the same observation (*24, 28*), attributed this lag-phase to the fact that browning products are end products that require a certain reaction time to be formed. However, the duration of this phase is comparable to the lag-phase observed in more diluted asparagine−glucose mixtures (*31*), suggesting that the duration is independent of the initial moisture content of the systems and that the lag-phase is mostly related to the dynamic heating conditions, as shown in De Vleeschouwer et al. (*31*). On the basis of the information obtained from the responses measured, the proposed reaction network was adapted and is presented in **Scheme 2**.

Multiresponse Modeling of Reactions in Basic Asparagine−Glucose Systems. The reaction network, as presented in **Scheme 2**, was translated into a mathematical model by setting up differential equations for each reaction step

$$\frac{d[Asn]}{dt} = -k_{INT_g}[Asn][Glc] + k_M[Int1] - k_B[Int2][Asn] - k_{Asp}[Asn][NH_3] \quad (2)$$

$$\frac{d[Glc]}{dt} = -k_{INT_g}[Asn][Glc] + k_{C_g}[Glc] \quad (3)$$

$$\frac{d[Int1]}{dt} = -k_{INT_g}[Asn][Glc] - (k_F + k_M)[Int1] \quad (4)$$

$$\frac{d[Int2]}{dt} = -k_M[Int1] + k_{C_g}[Glc] + k_B[Int2][Asn] \quad (5)$$

$$\frac{d[browning]}{dt} = k_B[Int2][Asn] \quad (6)$$

$$\frac{d[AA]}{dt} = k_F[Int1]k_E[AA] \quad (7)$$

$$\frac{d[DP]}{dt} = k_E[AA] \quad (8)$$

$$\frac{d[Asp]}{dt} = k_{Asp}[Asn][NH_3] - k_X[Asp] \quad (9)$$

$$\frac{d[X]}{dt} = k_X[Asp] \quad (10)$$

where [compound] represents the concentration of the different compounds, k is the reaction rate constant, and t is the reaction time. Initially, at time $t = 0$, the concentration of acrylamide, Int1, Int2, melanoidins, acrylamide degradation/elimination products, and the reaction products of aspartic acid (X) are considered to be zero, whereas for the reactants and aspartic acid, the initial concentrations measured were considered.

To describe the effect of temperature on each of the different reaction rate constants, the Arrhenius equation (eq 1) was inserted into the individual differential eqs 2–10, as described in Kinetic Data Analysis. The resulting model was fitted on the five responses simultaneously, shown in **Figure 2A−E** by the solid lines. The fit for acrylamide, glucose, asparagine, and aspartic acid was quite accurate at all heating temperatures tested, with the exception of the fit for acrylamide at 120 °C. The adequate description of the experimental data by the model also can be seen in the parity plots, given as an inset in the corresponding figure for each response, in which the data points are close to the line with a slope of 1 (perfect fit), and no clear trend is observed within the data points. The model did, however, not predict the lag-phase observed for the aspartic acid concentration as a function of time, presumably since no intermediates for the formation of aspartic acid from asparagine were incorporated in the model. The reason for this is that there is simply no experimental information available about these intermediates, so it is unjustifiable to include this in the kinetic model. In reality, the deamidation of asparagine occurs presumably via a succinimide intermediate (*33*). The melanoidin concentration is only predicted well by the model during the shorter heating times, with the exception of 120 °C. For longer heating times, the experimental melanoidin concentration, which is proportional to the absorbance measured at 470 nm, continues to increase, where in the model, the concentration levels off to a value of 2.3 M, corresponding to the initial sugar concentration. This anomaly can be explained by the presumably formed caramel color contributing to increased absorbance measured at 470 nm. The latter could, however, not be converted to the corresponding concentration of caramel colors. The model fit, as presented for an initial water activity of 0.96 (at 4 °C) in

Table 2. Estimated Kinetic Parameters Based on **Scheme 2** Model and Multiresponse Data Describing Acrylamide Formation and Elimination in Asparagine−Glucose Model Systems, Equilibrated at Different Initial Water Activities between 0.88 and 0.99 (at 4 °C), Heated at Temperatures between 120 and 200 °C

	a_W			
T_{ref} = 160 °C	0.88	0.92	0.96	0.99
$k_{F_{ref}}$ (10^{-3} min^{-1})	2.29 ± 0.43[a]	3.57 ± 1.38	3.45 ± 1.19	1.45 ± 0.42
$k_{E_{ref}}$ (min^{-1})	0.11 ± 0.02	0.10 ± 0.04	0.09 ± 0.04	0.05 ± 0.03
$k_{INT_{ref}}$ (M^{-1} min^{-1})	1.11 ± 0.61	1.70 ± 1.05	1.42 ± 0.59	1.43 ± 0.45
$k_{M_{ref}}$ (min^{-1})	0.58 ± 0.15	1.23 ± 0.49	0.56 ± 0.29	0.38 ± 0.17
$k_{B_{ref}}$ (M^{-1} min^{-1})	4.11 ± 10.77	3.90 ± 3.68	3.12 ± 3.87	0.90 ± 0.49
$k_{C_{ref}}$ (min^{-1})	indeterminate	indeterminate	0.05 ± 0.05	indeterminate
$k_{Asp_{ref}}$ (10^{-3} min^{-1})	15.77 ± 3.36	26.43 ± 5.76	20.33 ± 4.35	22.11 ± 6.51
$k_{X_{ref}}$ (10^{-3} min^{-1})	5.64 ± 4.06	indeterminate	0.70 ± 1.97	indeterminate
E_{a_F} (kJ/mol)	145.5 ± 15.9	159.2 ± 29.5	135.8 ± 27.3	84.6 ± 17.9
E_{a_E} (kJ/mol)	102.5 ± 15.4	113.2 ± 32.3	101.8 ± 34.5	143.4 ± 34.3
$E_{a_{INT}}$ (kJ/mol)	95.7 ± 21.6	117.5 ± 25.2	114.7 ± 28.8	120.8 ± 13.2
E_{a_M} (kJ/mol)	92.2 ± 22.2	105.7 ± 29.1	102.0 ± 36.9	40.0 ± 21.1
E_{a_B} (kJ/mol)	44.5 ± 17.5	180.3 ± 38.5	133.0 ± 50.6	124.5 ± 24.7
E_{a_C} (kJ/mol)	−4.0 ± 0.2	−6.7 ± 0.2	7.4 ± 6.6	−5.6 ± 0.1
$E_{a_{Asp}}$ (kJ/mol)	71.8 ± 6.7	105.4 ± 10.6	83.5 ± 10.6	98.4 ± 14.4
E_{a_X} (kJ/mol)	159.4 ± 29.8	668.9 ± 35.2	207.4 ± 120.1	indeterminate

[a] ±95% HPD interval.

Figure 2A−E, was comparable to the fit obtained for the other water activities tested (data not shown).

The 16 kinetic parameters, corresponding to the reaction network as presented in **Scheme 2**, were estimated simultaneously based on the experimentally determined responses of acrylamide, glucose, asparagine, aspartic acid, and melanoidins. The parameter estimation was performed as described in the Materials and Methods. The estimated parameters together with their 95% HPD (highest posterior density) interval are summarized in **Table 2**. The rate constant for acrylamide formation does not change significantly ($\alpha = 0.05$) in model systems with an initial water activity (at 4 °C) from 0.88 to 0.96. When the water activity increases to 0.99, a significant decrease is observed for $k_{F_{ref}}$ as compared to the lower range of water activities of 0.88−0.96. The same trend was observed for the corresponding activation energy E_{a_F}. When comparing the elimination rate constant $k_{E_{ref}}$, estimated at 160 °C, between different water activities tested, a gradual decrease was observed with increasing water activity from 0.88 to 0.99. This decrease was, however, only significant ($\alpha = 0.05$) when comparing the model systems with an initial water activity of 0.88 and 0.99. The estimated rate constant for acrylamide elimination was, however, 25−50 times higher than the corresponding estimated rate constant for acrylamide formation, which is in accordance with previously published data obtained in more diluted equimolar asparagine−glucose systems (*31*). The temperature dependence of $k_{E_{ref}}$ varied slightly between the different water activities tested but remained in all cases within the 95% HPD interval. The absolute value of E_{a_E} is slightly lower than the corresponding value for acrylamide formation, meaning that the elimination reaction(s) is less sensitive to changes in temperature. The same trend as observed for $k_{E_{ref}}$ and E_{a_E} as a function of initial water activity could be seen for $k_{INT_{ref}}$ and $E_{a_{INT}}$, representing the rate constant and corresponding activation energy for the initial step of the Maillard reaction. The rate constants for both acrylamide formation and elimination and for the initial stage of the Maillard reaction are not significantly different from the corresponding values reported by Knol et al. (*24*), using a comparable kinetic model without caramelization, for an equimolar diluted asparagine−glucose system. The activation energies are in the same order of magnitude as the ones reported by Knol et al. (*24*) but are slightly higher. These higher values can be explained by the lower water content of the model systems used in this study as compared to the study of Knol et al. (*24*) since the activation energy of nonenzymatic browning reactions (such as the Maillard reaction) generally decreases with increasing water content (*34*). The agreement in estimated kinetic parameters between this study and others confirms the usefulness of the proposed model to predict the changes in acrylamide concentrations in model systems. For the remaining reactions included in **Scheme 2**, indicated by Asp, M, B, C, or X, the reaction rate constants and corresponding activation energies also were estimated. These parameters remain mainly within the 95% confidence level for the range of water activities tested; they have, however, no physical meaning.

Modeling of Acrylamide Formation and Elimination in Potato-Based Asparagine−Glucose Mixtures. To validate the proposed kinetic model in more realistic systems and to determine the effect of a potato matrix on the kinetic parameters of acrylamide formation and elimination reactions, potato-based model systems were prepared and subsequently equilibrated above saturated salt solutions at 4 °C to obtain model systems with a water activity of 0.88, 0.92, 0.96, and 0.99, as described in the Materials and Methods. The water contents corresponding to different water activities, at which these equimolar potato-based model systems were equilibrated, are listed in **Table 1**. The net acrylamide concentrations measured (represented by the symbols), after thermal treatments between 120 and 200 °C during different treatment times, are shown in **Figure 3A−D** for the different water activities tested. The combined effect of temperature and time on acrylamide concentrations is comparable to the effect observed for the basic asparagine−glucose systems without an added potato matrix and equilibrated at the same initial water activity. In general, the difference between the maximal net acrylamide concentrations attained at the different reaction temperatures, is, however, less pronounced as compared to the systems without a potato matrix. This temperature effect on the concentration is nevertheless higher for an initial water activity of 0.88 as compared to the other water activities tested. For the rest, no pronounced differences were observed between model systems with different initial water activities. When comparing the trend within the net acrylamide concentration with the one observed for the corresponding systems without a potato matrix, the only clear difference is observed in the further progressed elimination in case of the basic model systems after the same heat treatment.

The net acrylamide concentrations measured after thermal treatment of the potato-based model systems could, such as for the basic model systems, be modeled by means of a simplified kinetic model (data not shown), comprising acrylamide formation and elimination reactions. As explained before, this model has some limitations and was therefore expanded to result in a more realistic mechanistic model, which has proven to approximate the different responses measured for the basic asparagine−glucose systems in a satisfying way. In the next section, the validity of this mechanistic model (**Scheme 2**) is tested for potato-based model systems.

Quantification of Reactants and Main Products. As for the basic asparagine−glucose model systems, after thermal treatment, different responses were measured next to acrylamide: the concentration of glucose, asparagine, and aspartic acid and the extent of browning in terms of melanoidins. These responses are represented in **Figure 4A−E** for an initial water activity of 0.96; the observed trends resulting from the applica-

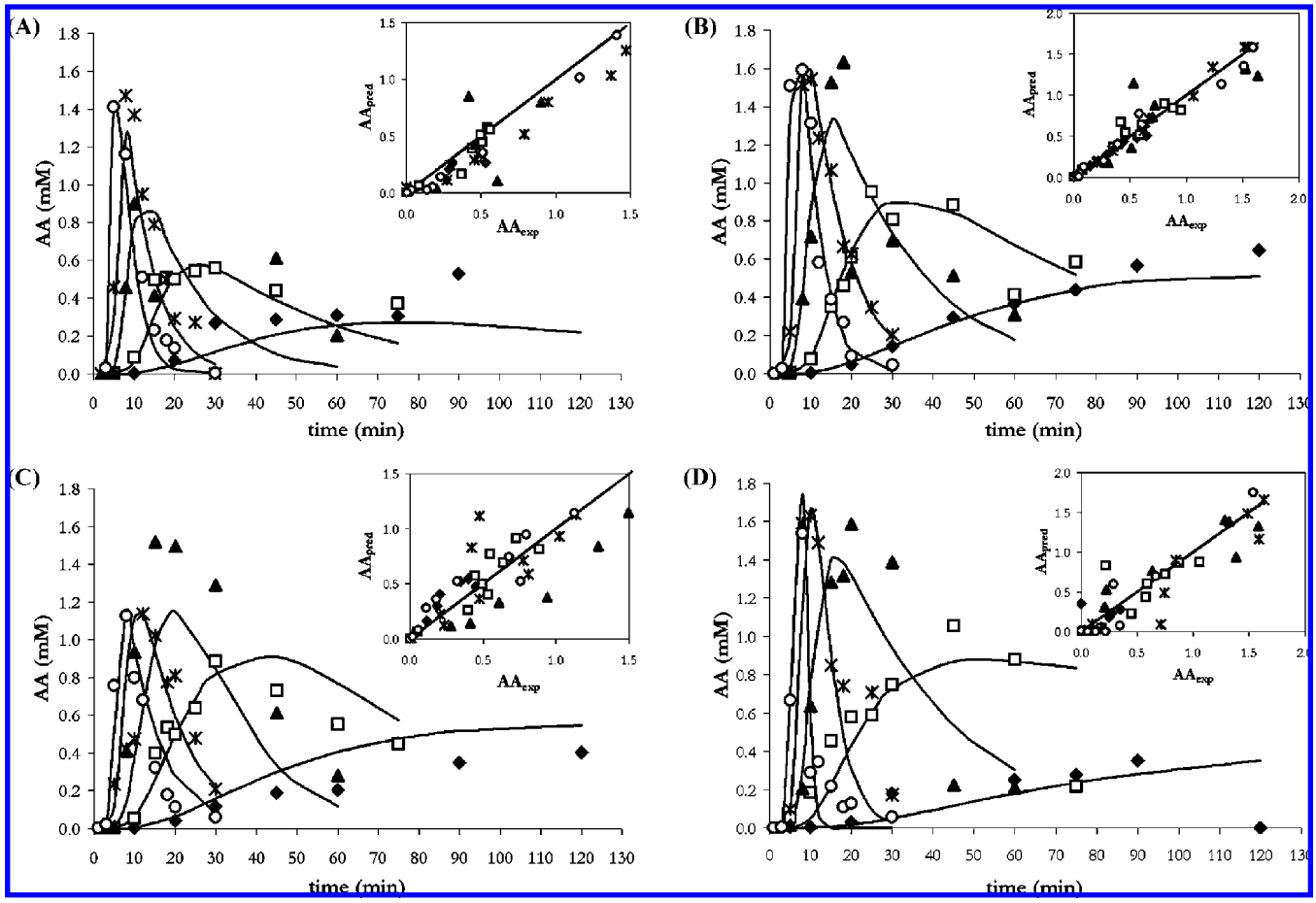


Figure 3. Time course of acrylamide concentration in equimolar potato-based asparagine−glucose model systems equilibrated at different initial water activities at 4 °C: $a_w = 0.88$ (**A**), $a_w = 0.92$ (**B**), $a_w = 0.96$ (**C**), and $a_w = 0.99$ (**D**), heated at 120 °C (◆), 140 °C (□), 160 °C (▲), 180 °C (×), and 200 °C (○). The solid lines represent the fit of the **Scheme 2** model, while the experimental data are represented by symbols. Insets show the corresponding parity plot where the solid lines have a slope of 1 (perfect fit).

tion of temperature are comparable to the other water activities tested (data not shown).

All responses follow a similar trend as a function of temperature and time as described for the basic model system. The only remarkable difference is that the concentration of glucose decreases at a much slower rate in the potato matrix as compared to the systems without a potato matrix. Surprisingly, this slower decrease is only observed in the case of glucose and not for the asparagine concentration. This could imply that reactions in which only sugars are involved (as caramelization reactions) are mostly affected by the presence of the matrix. The decrease in the glucose concentration is, however, still faster than in the asparagine concentration, such as for the basic model systems. The course of the concentration of aspartic acid and of the melanoidins as a function of temperature and time is also comparable to the course in the basic model systems. In the case of aspartic acid, the decrease observed after longer heating times at higher temperatures is, however, already clear at 180 °C for the potato-based model system, whereas this was only observable at 200 °C for the basic model system. Also, the level of plateau attained for the melanoidins remains, in the case of the potato-based model systems, unchanged independently of the treatment temperature applied, while an increasing level was observed with increasing treatment temperature for the basic model systems. Moreover, the observed lag-phase for the melanoidins is very short as compared to that for the basic model systems.

Multiresponse Modeling of Reactions in Potato-Based Asparagine−Glucose Systems. The experimental data obtained for the five responses for the potato-based asparagine−glucose model systems after thermal treatment were described by the same kinetic model as was set up for the basic asparagine−glucose systems, based on the reaction network as given in **Scheme 2**. The resulting model fit is represented in **Figure 4A−E** by the solid lines for the model system with an initial water activity of 0.96. The concentration of acrylamide, precursors, and aspartic acid as a function of temperature and time was predicted accurately by the model, which is confirmed by the parity plots (given as insets in the corresponding panel for each response). In the case of acrylamide, the model fit for the lower temperatures is, however, less precise. A similar trend was observed for the other water activities tested (data not shown). An important anomaly was observed for the predicted values of the melanoidin concentration (given on the *Y*-axis on the right side of **Figure 4E**), which are ∼20 times higher than the concentrations measured experimentally (presented on the *Y*-axis on the left side). The overall trend predicted by the model, evolvement toward a plateau, is, however, the same as the one observed for experimental values. These differences in absolute values could have different causes, for example, that the method used to determine the extent of browning was not appropriate for use in these potato-based model systems. Another possibility is that the melanoidin formation proceeds very quickly since almost no lag-phase was observed for the experimental melanoidin concentrations, so that the compounds rapidly polymer-

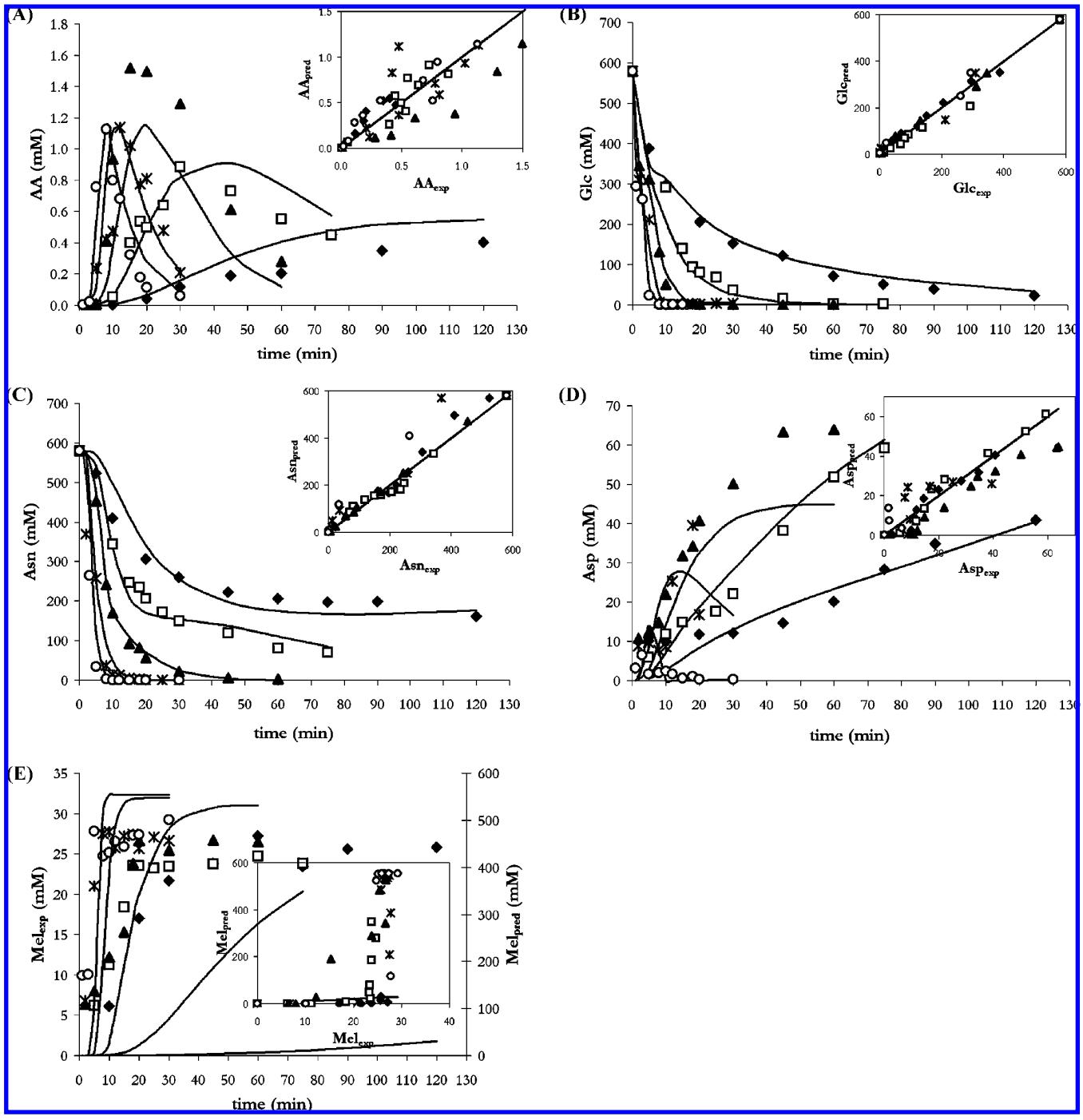


Figure 4. Time course of acrylamide (**A**), glucose (**B**), asparagine (**C**), aspartic acid (**D**), and melanoidins (**E**) in an equimolar potato-based asparagine−glucose model system equilibrated at an initial water activity of 0.96 at 4 °C, heated at 120 °C (◆), 140 °C (□), 160 °C (▲), 180 °C (×), and 200 °C (○). The solid lines represent the fit of the **Scheme 2** model, while the experimental data are represented by symbols. Insets show the corresponding parity plot where the solid lines have a slope of 1 (perfect fit).

ize to insoluble precipitates. Browning resulting from these precipitated compounds is not quantified by the method applied since this method presumably only measures browning from melanoidins in solution.

The kinetic parameters estimated and their corresponding 95% HPD interval, based on the experimental data for the five responses and the kinetic model as given in **Scheme 2**, are summarized in **Table 3**. The reaction rate constant for acrylamide formation shows no significant difference between the water activities tested, which confirms the trend observed in the basic model systems. The same observation can be made for the elimination rate constants. Moreover, both the acrylamide formation and the elimination rate constants estimated for the potato-based model systems are mostly within the 95% HPD interval of the corresponding values estimated for the basic model systems. The activation energies for the acrylamide formation reaction do not change significantly with a changing initial water activity, with the exception of the value for a water activity of 0.96. The E_{a_F} values do not differ significantly from the corresponding values of the model systems in the absence of a potato matrix in the case of an initial water activity of 0.88 and 0.92; for the systems with a higher initial water activity, the E_{a_F} value is, however, not enclosed within the 95% HPD interval. These estimates for E_{a_F} are in line with the values

Table 3. Estimated Kinetic Parameters Based on **Scheme 2** Model and Multiresponse Data Describing Acrylamide Formation and Elimination in Potato-Based Asparagine−Glucose Model Systems, Equilibrated at Different Initial Water Activities between 0.88 and 0.99 (at 4 °C), Heated at Temperatures between 120 and 200 °C

	a_W			
T_{ref} = 160 °C	0.88	0.92	0.96	0.99
$k_{F_{ref}}$ (10^{-3} min^{-1})	2.51 ± 1.70[a]	1.96 ± 0.50	0.83 ± 1.16	2.40 ± 0.94
$k_{E_{ref}}$ (min^{-1})	0.07 ± 0.04	0.05 ± 0.01	0.08 ± 0.04	0.04 ± 0.02
$k_{INT_{ref}}$ (M^{-1} min^{-1})	3.94 ± 3.46	3.09 ± 0.52	2.82 ± 0.69	3.50 ± 0.90
$k_{M_{ref}}$ (min^{-1})	0.96 ± 0.70	0.59 ± 0.17	0.17 ± 0.03	0.58 ± 0.24
$k_{B_{ref}}$ (M^{-1} min^{-1})	0.61 ± 0.33	3.00 ± 1.46	4.37 ± 2.54	1.76 ± 0.80
$k_{C_{ref}}$ (min^{-1})	indeterminate	indeterminate	indeterminate	indeterminate
$k_{Asp_{ref}}$ (10^{-3} min^{-1})	28.27 ± 8.00	15.71 ± 4.11	19.45 ± 4.63	36.45 ± 8.21
$k_{X_{ref}}$ (10^{-3} min^{-1})	1.53 ± 3.35	0.08 ± 0.36	indeterminate	0.51 ± 0.88
E_{a_F} (kJ/mol)	157.1 ± 44.6	147.5 ± 16.4	89.9 ± 11.9	171.5 ± 27.3
E_{a_E} (kJ/mol)	64.5 ± 35.4	70.6 ± 17.4	22.4 ± 31.7	180.5 ± 40.6
$E_{a_{INT}}$ (kJ/mol)	109.2 ± 36.4	105.3 ± 7.5	112.3 ± 10.7	125.7 ± 11.3
E_{a_M} (kJ/mol)	117.0 ± 43.3	121.0 ± 19.4	121.1 ± 8.0	118.2 ± 26.0
E_{a_B} (kJ/mol)	77.2 ± 33.2	114.2 ± 29.5	197.0 ± 44.0	129.5 ± 30.7
E_{a_C} (kJ/mol)	−23.8 ± 1.2	−21.7 ± 0.33	−22.2 ± 0.6	−12.0 ± 0.51
$E_{a_{Asp}}$ (kJ/mol)	93.2 ± 15.5	99.0 ± 14.3	87.0 ± 11.6	104.0 ± 11.6
E_{a_X} (kJ/mol)	357.9 ± 160.7	426.0 ± 242.5	indeterminate	475.8 ± 149.3

[a] ±95% HPD interval.

reported by Amrein et al. (*15*), using pure potato powder as a model system. An increasing trend was observed for the activation energy for the acrylamide elimination reaction with increasing water activity, with the exception of the system with an initial water activity of 0.96, as observed in the basic model systems. The absolute values for E_{a_E} are, however, mostly lower than the corresponding values estimated for the basic model systems, but even so, are mostly not significantly different from these values due to the relatively large HPD intervals. When examining the effect of initial water activity on the rate constant for the initial step of the Maillard reaction $k_{INT_{ref}}$, again the effect is negligible since no significant differences can be observed between the estimated rate constants for an initial water activity within a range of 0.88−0.99. The absolute values are, however, somewhat higher in the potato-based model systems than the corresponding values estimated for the basic model systems, although not always significantly. The temperature dependence of $k_{INT_{ref}}$ increases with increasing water activity, which is again analogous to the observation for basic model systems from which the absolutes values are not significantly different. The estimated kinetic parameters for the remaining reactions included in **Scheme 2** are not or hardly affected by a changing initial water activity and are also within the same order of magnitude as the corresponding values estimated for the basic model systems and even mostly within the 95% HPD interval; they have, however, no physical meaning.

In this paper, the effect of water activity was studied in equimolar asparagine−glucose model systems in a range from 0.88 to 0.99, corresponding to water contents representing the moisture gradient observed in French fries. In this quantitative study, multiresponse modeling was applied, including five different responses. A kinetic model was proposed including not only acrylamide formation and elimination reactions but also other pathways of the Maillard reaction leading to brown pigment formation, caramelization reactions, and other reactions occurring in the dry asparagine−glucose mixtures. First, the proposed model was applied to experimental data obtained in basic asparagine−glucose model systems. In this case, the model was apt to predict all five responses simultaneously in an adequate way. The estimated kinetic parameters showed that within the range of 0.88−0.99, the initial water activity had no significant effect on the rate constants and the corresponding activation energies of acrylamide formation and elimination, as well as on the initial reaction of the Maillard reaction. Second, the proposed model and corresponding kinetic parameters were validated in potato-based model systems and compared to the parameters estimated for the basic model systems to determine the effect of the added matrix. The same kinetic model could be used to predict the responses measured in a satisfying way, with the exception of the extent of browning. Despite the poor model fit for browning, the estimated kinetic parameters for both formation and elimination of acrylamide and the initial reaction step of the Maillard reaction are not significantly different from the values obtained in the absence of a potato matrix.

The adequate model fit and good agreement in parameters between systems with and without a potato matrix confirms the generic nature of the kinetic model proposed and proves that the potato matrix has almost no effect on the rate constants and the corresponding temperature dependence of the reactions considered. To increase the precision of the estimation process, it would be advisable to quantify also intermediate products of the Maillard reaction. This also makes it possible to clarify the effect of water activity on the different reaction steps of the Maillard reaction and caramelization reactions.

The research results obtained in this study imply that the concentration of acrylamide, with relation to French fries, is mainly determined by the process temperature and time applied and only little by the initial water activity. The temperature established in French fries is, however, dependent on the reaction time and on the distance from the center of the French fries and is related to the local water content. In terms of a process design for French fries, the focus should therefore be on the optimization of a temperature−time process resulting in minimal acrylamide concentrations.

ABBREVIATIONS USED

AA, acrylamide; Asn, asparagine; Asp, aspartic acid: DP, unidentified acrylamide degradation products; Frc, fructose; Glc, glucose: HPD, high posterior density; Int1, intermediate 1; Int2, intermediate 2: Mel, elanoidins; X, unidentified reaction products from aspartic acid. Subscripts: Asp, aspartic acid formation; B, browning; C, caramelization; E, elimination; exp, experimental; F, formation; g/f, from glucose/fructose; I, isomerization; INT, formation of intermediate from glucose or fructose and asparagine; M, Maillard; pred, predicted; ref, reference; X, unidentified reaction(s) consuming aspartic acid.

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