Effect of NaCl on the decrease of acrylamide content in a heat-treated model food matrix

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Summary

Various amounts of NaCl between 0–10 wt% were added to the model food matrix consisting of an equimolar mixture of asparagine/glucose. The samples were heat-treated at 171.1 °C for 10 min and then the content of acrylamide (AA) was determined. Presence of NaCl in the matrix brings about a decrease of the AA content up to 40%. The decrease is not linear with the addition of NaCl; the dependence is hyperbolic-like with the tendency to reach a limit value for high NaCl additions. The highest decrement in the AA content is observed in the range 0–1 wt% of NaCl added. Differential scanning calorimetry measurements have shown that the elimination of AA via polymerization is strongly accelerated by NaCl. This reaction step, among other possible, brings about the decrease of AA content in the model food matrix.

Keywords

acrylamide; elimination; NaCl; GC-MS; differential scanning calorimetry

Several years ago it has been reported that acrylamide (AA) can be formed during thermal food processing [1]. Since AA is generally classified as "probably carcinogenic to humans", these findings are considered alarming. The highest AA content was repeatedly found in French fries and potato chips, and thus the attention was focused on heat-processed potato products [2-4]. Investigations of the reactions associated with the formation of AA revealed that the process is initiated with the reaction between reducing mono-saccharides and asparagine which indicates that AA might be a product of the Maillard reaction [5]. As found later, the AA formation from arginine and reducing mono-saccharides can also take place in a solid mixture of the compounds during heating to 190 °C [6]. Potato products have been associated with AA formation due to relatively high levels of AA precursors as well as the temperature of processing. However, there are also assumptions about other mechanism pathways indicating that AA formation in a real food matrix is a complicated physico-chemical process involving a number of reactions and interactions [7, 8]. In the recent period, papers on the quantitative description of the kinetics of AA formation have been published [9, 10].

The AA formation can be limited considerably by some additives such as amino acids and proteins [11, 12]. For example, croquettes prepared from fresh potatoes and coated with egg/breadcrumbs contained considerably reduced AA content after thermal processing [13]. In this paper we report the first evidence on the inhibition effect of a common food additive, i. e. sodium chloride, on the AA production in asparagine/glucose model system. The AA elimination branch of the overall mechanism of AA production is explored in the model food matrix formed by an equimolar mixture of asparagine/glucose.

MATERIALS AND METHODS

Chemicals

AA of p. a. purity was purchased from Fisher Scientific (Loughborough, UK) and deuterated 2,3,3-D3 AA (98 %) was purchased from Cambridge Isotope Laboratories (Andover, MA, USA). Sodium chloride of p. a. grade was pur-

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chased from Lachema (Brno, Czech Republic). Acetone SupraSolv® was obtained from Merck (Darmstadt, Germany), and asparagine, glucose, Acetonitrile R CHROMASOLV® and Methanol CHROMASOLV® from Sigma-Aldrich (Steinheim, Germany).

Techniques used

Agilent Technologies 6890 (Agilent Technologies, Palo Alto, USA) gas chromatograph equipped with an Agilent Technologies 5973 inert mass selective spectrometer was used for the determination of the AA content in the samples.

Metal Block Thermostat was purchased from Liebisch, Bielefeld, Germany, and EcoScan Temp JKT Temperature Meter equipped with Probe 3T520C was obtained from Eutech Instruments Europe B.V., Nijkerk, Netherlands. A Nylon filter (0.45 μm) was purchased from Supelco (Bellefonte, PA, USA).

Differential scanning calorimeter Perkin-Elmer DSC-7 (Perkin-Elmer, Norwalk, CT, USA) was used to study the AA polymerization. The temperature scale of the calorimeter was calibrated to the melting points of In, Sn and Zn, the enthalpy calibration was performed to the heat of fusion of In. Samples of 2-4 mg were placed in sealed aluminum pans and heated in the temperature interval 60–180 °C with the heating rate of 10 $K.min^{-1}$ where nitrogen was used as a purge gas. The endothermic peaks are oriented upwards.

AA determination

After cooling, D3-AA as internal standard and 5 ml of acetonitrile/methanol 80 : 20 (v/v) mixture were added, the vessel content was sonicated for 5 min, filtered and analyzed by GC-MS. 1 μl of the extract was applied into a splitless injector (purge time 0.5 min at 250 °C). Separations were carried out using an Agilent 122-3232 30 m x 0.25 mm x 0.25 μm fused silica capillary column coated with a DB-FFAP phase. The column was held at 50 °C for 1 min, then heated to 250 °C at a rate of 10 °C/min. The carrier gas (helium) flow was maintained at 0.8 $ml.min^{-1}$ by an electronic control of pressure. Under these conditions AA and D3-AA eluted at 13.2 min. The content of AA was determined from the ratio of the peak area of AA to the peak area of the known concentration of spiked D3-AA. The detection was carried out by the mass detector working in a selected ion monitoring mode; the ions were obtained by negative chemical ionization procedure using methane as the reagent gas. The mass of the most intense fragments was 70.15 and 73.15 m/z, respectively.

RESULTS AND DISCUSSIONS

For the measurements, NaCl in the amount of 0, 1, 5 and 10 wt% was added to the equimolar mixture of asparagine/glucose. For each addition of NaCl, 27 samples were heated in the metal block thermostat at 171.1 °C for 10 min and subsequently analyzed for the AA content. The results are presented in Table 1.

In order to illustrate the effect of NaCl on the reduction of AA content, Fig. 1 shows the relative amount of AA content in the NaCl-containing mixtures after heat treatment related to the equimolar mixture of asparagine/glucose without addition of NaCl. As can be seen from Fig. 1, the decrease is not linear with the addition of NaCl; the dependence is hyperbolic-like with the tendency to reach a limit value for high NaCl additions. The highest decrement in the AA content is observed in the range 0–1 wt% of the added NaCl.

Some authors assume that the overall mechanism of acrylamide production consists of two reaction branches, i. e., AA formation in the matrix and AA elimination [10]. We tried to determine whether the elimination branch is affected by the presence of NaCl. The effect of NaCl has been studied by the differential scanning calorimetry (DSC); the DSC records are shown in Fig. 2. Pure NaCl, pure AA and the mixture AA/NaCl 1 : 1 (w/w) were heated at the heating rate of 10 $K.min^{-1}$. As seen from Fig. 2, the record of NaCl is a horizontal line which indicates that no process occurs in NaCl when heated up to 180 °C. The DSC record of pure

Tab. 1. Content of acrylamide in the equimolar mixture of asparagine and glucose after heat treatment at 171.1 °C for 10 min.

Acrylamide content	Addition of NaCl			
	0	1 wt%	5 wt%	10 wt%
average [$\mu g.g^{-1}$]	267	181	171	160
standard deviation [$\mu g.g^{-1}$]	30	9	10	22
relative standard deviation [%]	11	5	6	14

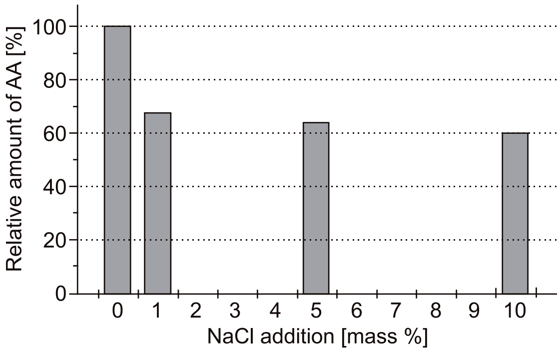

Fig. 1. Relative amount of acrylamide in the equimolar mixture of asparagine and glucose after heat treatment at 171.1 °C for 10 min, as a function of NaCl addition.

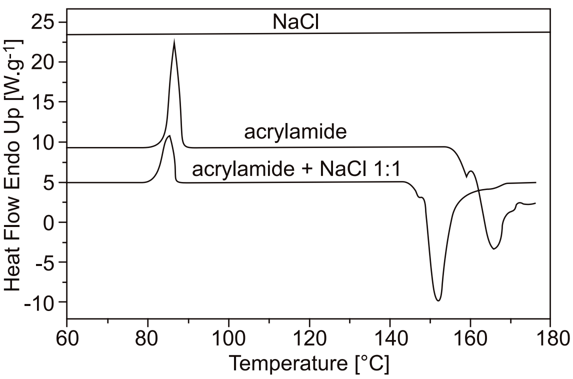

Fig. 2. DSC records of NaCl, pure acrylamide and the mixture of acrylamide/NaCl 1:1, heating rate 10 $K.min^{-1}$.

AA shows an endothermic peak with the onset temperature 82 °C corresponding to melting of AA. At 156 °C, an exothermic peak starts connected obviously with the polymerization of AA. In the DSC record of the mixture of AA/NaCl it can be seen that the melting occurs at the same temperature as for pure AA. However, the polymerization peak is shifted by 12 °C to lower temperatures so indicating a strong acceleration of the AA polymerization by NaCl. The elimination of AA may occur not only by AA polymerization to biologically inactive polyacrylamide, but in a real food matrix also by the reaction of AA with other species. The DSC measurements have shown that the AA elimination by polymerization is strongly accelerated by the presence of NaCl which is apparently a reason of the lower AA content in the model food matrix with the addition of NaCl.

CONCLUSIONS

Presence of NaCl in the model food matrix of asparagine/glucose brings about a decrease of the AA content after a heat treatment. The decrease is not linear with the addition of NaCl; the dependence is hyperbolic-like with the tendency to reach a limit value for high NaCl additions. The highest decrement in the AA content, by 32%, is observed in the range 0–1 wt% of the added NaCl. This finding is important for practical application in technological thermal food processing since the addition of NaCl around 1 wt% is common in many food products. By DSC measurements it has been shown that the elimination of AA via polymerization is strongly accelerated by NaCl. This reaction step, among other possible, brings about the decrease of AA content.

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