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Model studies on acrylamide formation in potato, wheat flour and corn starch; ways to reduce acrylamide contents in bakery ware

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Introduction

Acrylamide is of concern as a probable carcinogen in some strongly heated foods (1, 2), first of all in roasted and fried potato products (3–5). Also bakery ware may contain more than 1000 µg/kg acrylamide, typically when strongly heated (crisp bread) or when prepared with honey or inverted sugar in combination with ammonium carbonate.

Numerous paths of acrylamide formation have been discussed, predominantly the thermal degradation of the free amino acid asparagine with the support of fructose and glucose via an Amadori product (6–11). It was shown for potatoes that the potential of acrylamide formation (12) is proportional to the concentrations of asparagine and reducing sugars (13), which supports that at least for potato products this is the principal, if not exclusive path of acrylamide formation.

Studies on acrylamide formation are complicated by the important role of elimination (11, 12): easily 90% of the acrylamide formed is eliminated again and therefore, the concentration found often only represents a small fraction of that formed. Elimination rates are low in purified starch, but high in, for example meat (11), probably due to reaction with nucleophiles, such as cysteine. It will be shown below that it also occurs through reaction with sugars or their thermal degradation products.

For the search of ways to decrease acrylamide concentrations in foods, the background of acrylamide formation and elimination is of interest in order to enable a more systematic identification of foods, food components, or preparation procedures resulting in high acrylamide contents. Model experiments based on dried potato, wheat flour, and corn starch as matrix materials were performed with various additions of candidate components, submitting these mixtures to a standardized heat treatment. Matrices and conditions were chosen to simulate food preparation and reactions really taking place in a dough under the conditions applied during baking (4, 7, 9, 11, 14).

A pragmatic approach was chosen, aiming at obtaining information of direct applicability to food preparation, rather than details of the chemistry, since this chemistry is assumed to be complex. If only formation from free asparagine is considered, it involves a sequence of reactions and transformations. The yield of the conversion of asparagine to acrylamide is usually below 1%, thus the reactions compete with more efficient ones, depending on the food composition and thermal conditions. For instance, during heat treatment the reducing sugars may be rapidly depleted, but acrylamide formation continues, presumably supported by degradation product of sugars, such as hydroxy-acetone (11). Also elimination occurs through reaction with a variety of partners. Formation as well as elimination depends on the presence of water, i.e. on the size and shape of the food as well as details of the preparation conditions. It seems to be an almost impossible task to elucidate the kinetics of all these pathways.

Experimental

The matrix materials for the model experiments consisted of potato of the cultivar Lady Claire, grated and dried in an oven at 40 °C, dark wheat flour (Ruchmehl, Migros, Zurich, Switzerland) and corn starch (Maizena, Knorr, Thayngen, Switzerland). The dried potato contained 11.5 g/kg free asparagine as well as 180 and 370 mg/kg fructose and glucose, respectively. The flour contained 270 mg/kg free asparagine, the corn starch less than 10 mg/kg. Ammonium bicarbonate (NH_4HCO_3) and ammonium carbonate ($(NH_4)_2CO_3$) were from Fluka (Buchs, Switzerland), puriss, product numbers 9830 and 9716, respectively.

Model experiments were normally performed with 5 g test mixture in a 150 ml glass beaker. Sugars, asparagine, salts, and deuterated acrylamide (D_3-acrylamide, Cambridge Isotope Laboratories, Andover, USA, used for the determination of elimination) were added as a solution in water (usually 5 ml) and thoroughly mixed with the matrix material. Samples were dried at 40 °C during 1–2 h before being heated to the temperatures indicated. Heat treatments occurred in GC ovens (ThermoFinnigan, Milan, Italy).

Acrylamide was determined as described in reference (15). Briefly, water was added and the matrix material swollen at 70 °C. Then the sample was extracted using 1-propanol, the propanol/water mixture evaporated, the acrylamide re-dissolved from the residue into acetonitrile and this extract defatted with hexane. Analysis involved GC-MS with chemical ionization.

Reducing sugars were determined enzymatically as described in reference (11), using the test kit from Scil Diagnostics (Martinsried, Germany). Samples were blended with distilled water. Carrez I and Carrez II solutions were added. The mixture was thoroughly shaken, the pH adjusted to 7.0–7.5 with a few drops of KOH solution and foam broken by addition of 1-octanol (Fluka, Buchs, Switzerland). After filtration, samples were subjected to enzymatic analysis as described by the producer.

Free asparagine was measured as described by *Arnold et al.* (16). The sample was homogenized with water and allowed to settle or filtrated. Amino acids were converted to carbamates by reaction with 9-fluorenylmethylchloroformiate (FMOC-Cl) and analyzed on a 250×4.6 mm i.d. reverse phase column with fluorescence detection at 265/340 nm.

Results

Correlation of acrylamide formation with asparagine and sugar concentrations

For potatoes, excellent correlation was shown for the potentials of acrylamide formation with the product of the concentrations of the reducing sugars and asparagine (R^2=0.9055, (13)). This correlation was confirmed by addition of glucose or fructose to potato containing little reducing sugar. In figure 1, the yield of the conversion of asparagine to acrylamide is plotted against the content of reducing sugars calculated as moles per mole of asparagine. The results from the study of 61 potatoes of different cultivars analyzed by *Amrein et al.* (13) served as background (◆). On top, data is shown for Lady Claire potato containing 0.04 moles reducing sugars per mole of asparagine. To the dry potato, glucose (▲–▲) or fructose (■–■) was added to result in a molar ratio of reducing sugar/asparagine of up to 1.92. Glucose increased the acrylamide content to values near the lower, fructose to near the upper edge of the range observed in the samples richer in endogenous reducing sugar. This agrees with the expectations from the previous finding that fructose is about twice as effective in promoting acrylamide formation as glucose (11).

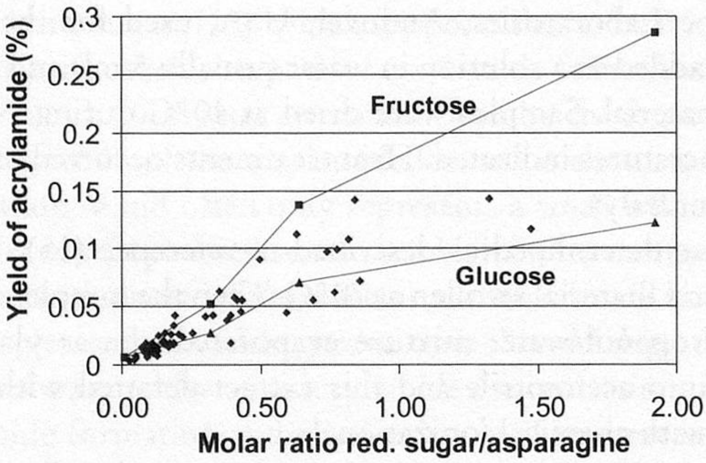

Figure 1 **Yield of the conversion of asparagine to acrylamide plotted against the molar ratio of reducing sugars/asparagine in 61 samples of potatoes and in a potato containing extremely little reducing sugar with either glucose or fructose being added**

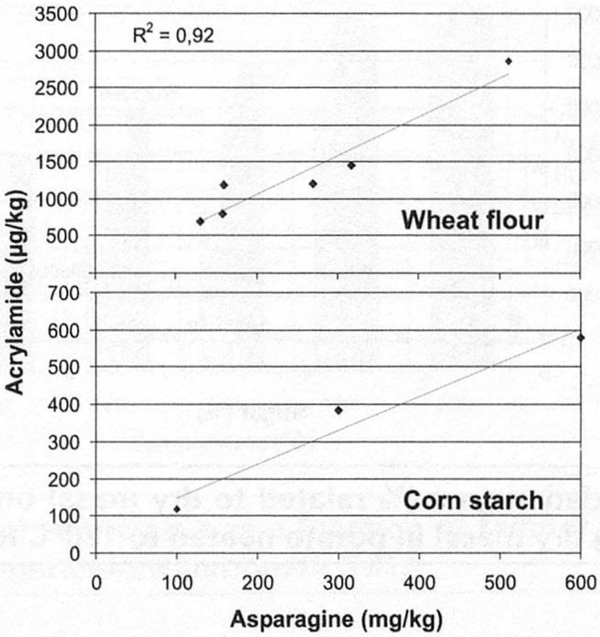

Figure 2 **Correlation of asparagine with the acrylamide formed at 180 °C in flour and corn starch, the latter with added asparagine**

Figure 2 shows the correlation between the contents of asparagine and acrylamide in six samples of wheat flour after heating to 180 °C for 30 min. The coefficient of the correlation reached 0.92. This might be higher than the coefficient of correlation between reducing sugars and acrylamide in potatoes, i.e. in wheat flour the asparagine is as determining as the reducing sugars are in potato.

Since corn starch contains little asparagine, 100, 300 or 600 mg/kg asparagine was added, fortifying it to the range of levels found in the samples of wheat flour. The acrylamide observed after heating to 180 °C correlated with this asparagine. Some five times less acrylamide was formed because of the low content of reducing sugars in corn starch.

The experiments with flour and with corn starch were performed at a high temperature in order to simulate processes in a dark crust, but also to promote formation of acrylamide from sources other than asparagine, if there were any, assuming that at high temperature a broader range of chemical reactions would take place. However, the results do not indicate significant contributions to acrylamide formation through paths other than asparagine and reducing sugars or degradation products of the latter.

Type of sugar

Figure 3 compares the efficiencies of fructose, glucose, and sucrose in supporting acrylamide formation. Various amounts of these sugars were added to dried grated potato. After drying, the mixtures were heated to 120 °C for 40 min.

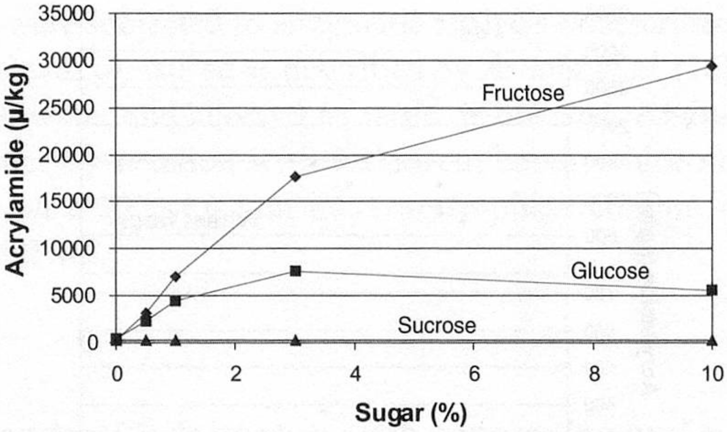

Figure 3 **Effect of added sugars (% related to dry mass) on the acrylamide contents (µg/kg dry mass) in potato heated to 120 °C for 40 min**

Addition of sucrose, not being a reducing sugar, showed no effect. Fructose increased the acrylamide contents almost linearly up to a concentration of about 2 %. This is in agreement with the finding that the 120 °C potential of acrylamide formation correlates linearly with the concentration of the endogenous reducing sugars (13). With higher additions, the increase of the acrylamide contents slowed down, presumably because of increased elimination (corresponding to 54 % of the deuterated acrylamide at 3 % fructose, but 75 % at 10 % fructose). The yield of converting asparagine into acrylamide reached 0.45 %.

Addition of the same amounts of glucose enhanced acrylamide contents less efficiently than fructose. The difference was modest up to concentrations of around 1 %. Then contents slowly increased up to 3 % glucose and fell again at 10 % glucose.

Elimination

Elimination was determined by addition of D_3-acrylamide. As shown previously (12), at 160 °C and in the presence of 19 % humidity (sample in a closed vial), some deuterium was exchanged against hydrogen. Since the experiments shown below determined elimination at up to 200 °C, though without humidity, the method was checked with ^{13}C-labeled acrylamide: D_3-acrylamide and ^{13}C-acrylamide were admixed to wheat flour at 1000 µg/kg. After heating to 200 °C for 30 min, the elimination corresponded to 54 and 54.5 % for deuterated and ^{13}C-labeled acrylamide, respectively, indicating that the deuterated acrylamide could be used when test samples are dry.

Figure 4 shows the dependence of elimination on the presence of sugars for temperatures between 120 and 200 °C. Sugars were added at 40 %, for fructose resembling the mixtures used to prepare gingerbread. Ammonium carbonate was admixed at 1 %, as commonly applied for bakery ware. Sucrose showed no effect up to 160 °C. The enhanced elimination at higher temperatures might be caused by decomposition

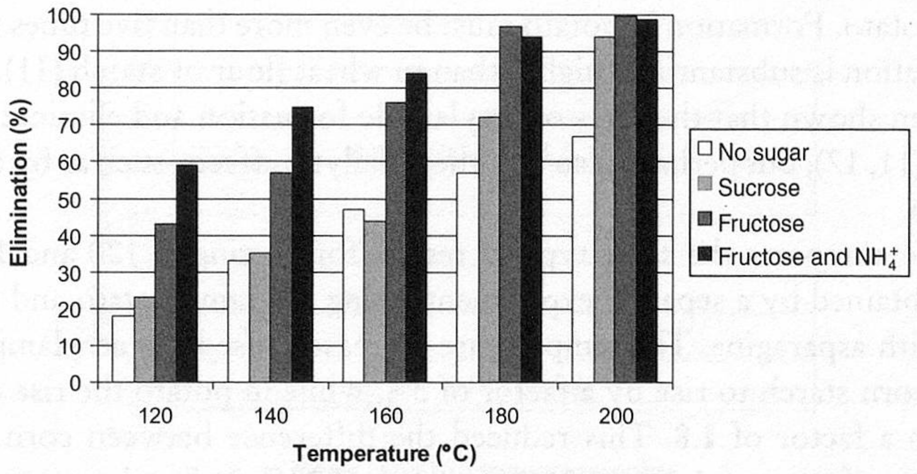

Figure 4 **Elimination of acrylamide as a function of temperature and addition of sugars and ammonium carbonate (NH_4^+)**

products of sucrose. Fructose strongly increases elimination even at 120 °C. Particularly at low temperature, ammonium supports elimination. Compared to the plain wheat flour, fructose combined with ammonium carbonate increased elimination at 120 °C by a factor of 3.2. At 180 °C, elimination may exceed 95 %, i.e. is likely to be more relevant in determining acrylamide concentrations than the rate of formation.

Effect of matrix

Figure 5 shows acrylamide contents (in terms of yield of converted asparagine) as a function of fructose added to potato, wheat flour and corn starch (40 min at 120 °C). Corn starch and wheat flour were fortified with asparagine to the concentration in potato (1.15 % referring to dry weight). Acrylamide contents did not

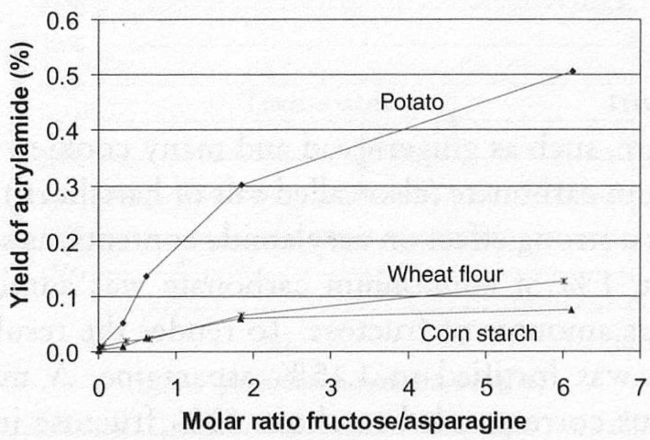

Figure 5 **Yield of acrylamide from asparagine in potato, wheat flour and corn starch in dependence of the fructose added**

differ significantly between wheat flour and corn starch, but were about five times higher in potato. Formation in potato must be even more than five times faster, since also elimination is substantially higher than in wheat flour or starch (11). It has previously been shown that the rates of acrylamide formation and elimination depend on acidity (11, 17), but perhaps also on other catalytic effects, such as by ammonium (see below).

Figure 6 compares the same type of results for heating at 120 and 150 °C. The data was obtained by a separate experiment, using the same potato and corn starch fortified with asparagine. The temperature increase caused the acrylamide concentration in corn starch to rise by a factor of 3.8, while in potato the rise only corresponded to a factor of 1.8. This reduced the difference between corn starch and potato from a factor of 5.1 at 120 °C to 2.2 at 150 °C. It fits the general rule that catalytic effects are more important at lower temperatures.

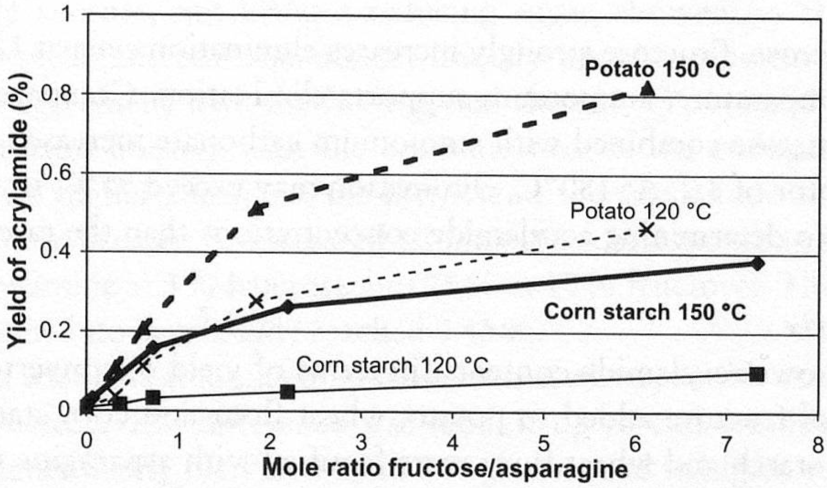

Figure 6 **Yield of conversion of asparagine into acrylamide in corn starch and potato at 120 and 150 °C**

Effect of ammonium

Some bakery ware, such as gingerbread and many cookies, is traditionally prepared with ammonium carbonate (also called salt of hartshorn) to grow the dough. This ammonium has a strong effect on acrylamide contents, as shown in figure 7. In a model experiment, 1 % of ammonium carbonate was admixed to wheat flour together with various amounts of fructose. To render the results comparable with figure 5, the wheat was fortified to 1.15 % asparagine. A molar ratio fructose/asparagine of six thus corresponded to about 10 % fructose in the flour. Samples were heated to 120 °C for 40 min. Between 54 and 75 times more acrylamide was formed with ammonium. The conversion of asparagine to acrylamide ("yield") rose from some 0.1 % to 3.5 %, which is far above the values shown in previous figures.

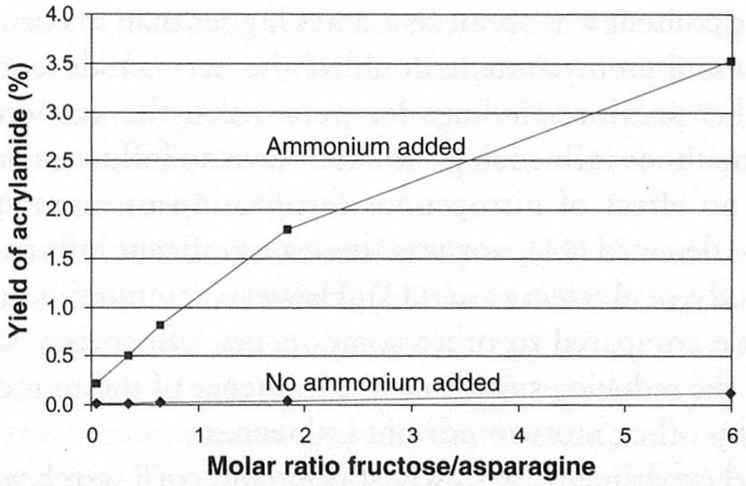

Figure 7 **Effect of 1% ammonium carbonate added to wheat flour together with various amounts of fructose; heated to 120°C for 40 min**

In an experiment with wheat flour not fortified with asparagine, the addition of 10% fructose resulted in a mole ratio fructose/asparagine of 274. Addition of 1% ammonium carbonate and the same heating (120°C at 40 min) converted 4.8% of the asparagine into acrylamide, which is slightly above the 3.5% shown in figure 7. A similar yield is in agreement with the model involving a bimolecular reaction of asparagine and fructose as rate-determining step, provided elimination is constant.

Ammonium carbonate is effective also at low concentrations. Figure 8 shows a model experiment with corn starch, simulating the concentrations (referring to dry weight) of the key compounds in potato: 1% asparagine and 1% fructose were added together with the amounts of ammonium carbonate shown (in logarithmic scale) on the x-axis. At the concentration typical for potato, corresponding to about

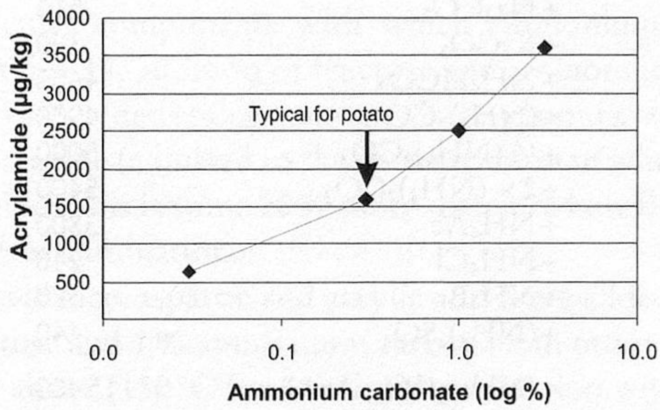

Figure 8 **Acrylamide contents in corn starch fortified with 1% asparagine, 1% fructose and the ammonium carbonate shown on the (logarithmic) x-axis; heated to 120°C for 40 min**

0.3% ammonium carbonate (11), the acrylamide content was approximately tripled. In real potato, the content was about five times higher than in corn starch (figure 5).

The tripled ammonium content doubled the acrylamide concentration. This seems to contradict previous findings for potato that the ammonium fertilization and the farming methods influencing the latter have no influence on acrylamide formation. In fact, no effect of nitrogenous fertilization or ammonium contents of potatoes could be detected (11), nor was there a significant influence of the farming method in the study of *Amrein et al.* (13). However, ammonium concentrations in potato varied little compared to other components influencing acrylamide formation, particularly the reducing sugars, i.e. the influence of the ammonium concentration is obscured by other, more important influences.

Further model experiments with wheat flour and corn starch were performed to better understand the role of ammonium: does it form acrylamide by reaction with a carbon source or does it merely accelerate the formation by the known route? Gingerbread was imitated by mixing wheat flour (60%) and fructose (39%) with 1% of the salts listed and D_3-acrylamide to monitor elimination. Mixtures were heated to 150 °C for 30 min.

As shown in the first line of table 1, in the absence of added salt (just water; reference sample), 580 µg/kg of acrylamide was found. The addition of sodium or potassium carbonate slightly reduced the acrylamide content, probably the increase in formation through the increased pH being overcompensated by an even stronger increase of elimination (from 73 to 89 and 86%, respectively, as listed in the right column).

Table 1
Model experiments with wheat flour or corn starch, fructose (39% in the flour) and various components of interest (1%); heated to 150 °C for 30 min; Asn = asparagine

	Model mixture		*Acrylamide (µg/kg)*	*Elimination (%)*
1	Wheat flour + fructose		580	46
2		+ Na_2CO_3	510	78
3		+ K_2CO_3	390	72
4		+ NH_4HCO_3	4600	72
5		+ $(NH_4)_2CO_3$	4900	68
6		+ ½ $(NH_4)_2CO_3$	5000	52
7		+ 2 × $(NH_4)_2CO_3$	5400	60
8		+ NH_4Ac	3800	72
9		+ NH_4Cl	240	78
10		+ NH_4Br	380	44
11		+ $(NH_4)_2SO_4$	440	54
12		+ $(NH_4)_2CO_3$, Asn 3 ×	15400	66
13		NH_3 added to sugar	4900	56
	Corn starch + fructose			
14		+ $(NH_4)_2CO_3$	< 10	
15		+ 270 mg/kg Asn	5900	30

Addition of ammonium carbonate or bicarbonate increased the acrylamide content some eight times, which is far less than observed at 120 °C (figure 7). There was no significant difference between carbonate or bicarbonate (lines 4 and 5). Halving or doubling the addition of ammonium carbonate (lines 6 and 7) had little effect on the acrylamide concentration, i.e. at 1 %, ammonium was not a limiting partner of a rate-determining reaction step.

The effect of ammonium acetate was slightly weaker than that of the carbonate. The chloride, bromide and sulfate salts of ammonium, however, resulted in a reduction of the acrylamide content rather than an increase.

The experiment of line 12 was designed to check whether a precursor other than asparagine, such as a compound reacting with ammonium, substantially contributed to acrylamide formation. The asparagine content was tripled, keeping the additions of fructose and ammonium carbonate constant. The resulting acrylamide concentration was also tripled. This rules out another precursor contributing by more than some 20 % to the acrylamide formation (otherwise the acrylamide concentration had been increased by a factor of less than three). In particular, it confirms that ammonium does not directly form acrylamide, but either accelerates the reaction from asparagine to acrylamide or hinders a competing reaction.

At increased pH, acrylamide formation is faster (also its elimination). However, the effect of ammonium carbonate is hardly linked with the pH, since the sodium or potassium carbonate would have to be even more effective then. In a next experiment, the hypothesis was checked that ammonium activates fructose. Ammonia solution was added to fructose in a quantity stoichiometrically corresponding to the ammonium added to the test sample in the form of carbonate. Then the water was removed at ambient temperature over weekend, which also removed the free ammonia. This treated fructose was added to flour. After heating, the acrylamide concentration was as high as when ammonium was added to the whole mixture (line 13).

The effect of ammonium carbonate was also tested on corn starch in order to check for other components in wheat flour which could interfere with acrylamide formation, in particular components with which ammonium could form acrylamide. As shown in line 14, addition of fructose and ammonium carbonate to corn starch did not provide a detectable amount of acrylamide, while a fortification with 270 mg/kg asparagine (adjusted to the concentration in wheat flour) resulted in 5900 µg/kg acrylamide. This is some 20 % more than in wheat flour, which might be explained by the lower elimination.

To add further evidence, aspartic and acrylic acid were added to corn starch fortified with 5 % fructose and 1 % ammonium carbonate in order to check whether at the conditions used above (150 °C for 30 min) their reaction with ammonium could result in a relevant quantity of acrylamide. As shown in table 2, 1 % aspartic acid resulted in 200 µg/kg acrylamide. At an about 40 times lower concentration, asparagine produced some 30 times more acrylamide, i.e. the contribution by acrylic acid and ammonium is irrelevant. The same applies to acrylic acid.

Table 2

Model experiments with corn starch, fructose (5%), ammonium carbonate (1%) and two candidates for acrylamide formation to be tested; heated to 150°C for 30 min

	Model mixture		*Acrylamide (µg/kg)*
1	Corn starch+fructose+$(NH_4)_2CO_3$		<10
2		+1% aspartic acid	200
3		+0.2% acrylic acid	150

Dependence of acrylamide contents on temperature

Figure 9 shows the acrylamide concentrations determined in model mixtures based on wheat flour heated to temperatures between 40 and 200°C for 30 min (every data point from a different sample). To facilitate comparison, acrylamide contents were calculated referring to the wheat flour.

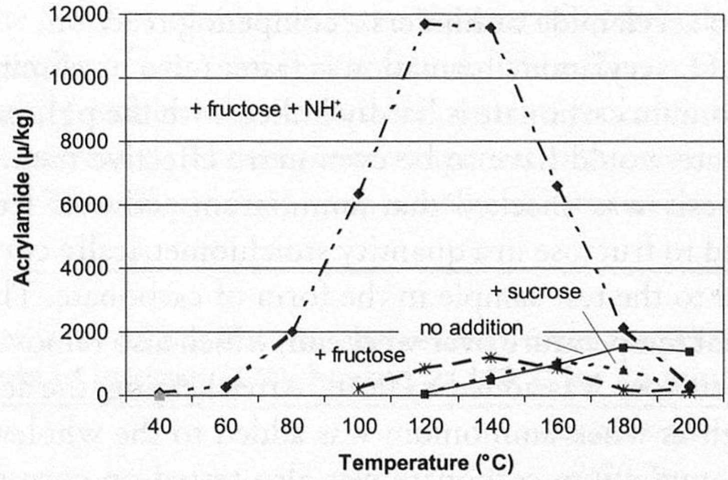

Figure 9 **Acrylamide contents at different temperatures, in model experiments based on wheat flour with and without addition of sucrose, fructose, and ammonium carbonate; heated for 30 min**

1. In **wheat flour** without additions (except of water, evaporated again before heating), the first acrylamide was detected after heating at 120°C (60 µg/kg). Concentrations were at a maximum in the sample brought to 180°C (1470 µg/kg) and slightly decreased with heating to 200°C (1390 µg/kg), i.e. elimination predominated formation.
2. With **40% sucrose,** acrylamide concentrations were almost identical with those in plain flour up to 160°C. As shown in figure 3, sucrose does not support acrylamide formation. At higher temperatures, acrylamide concentrations dropped again. The sample brought to 200°C contained seven times less acrylamide

than that without added sugar, which suggests increased elimination supported by sucrose degradation products (see also figure 4).

3. With **40 % fructose,** heating to 100 °C was sufficient to generate 200 µg/kg acrylamide. At 120 °C, the acrylamide concentration was 14 times higher than in the sample containing the same amount of sucrose or no sugar. A maximum of 1200 µg/kg was reached with heating at 140 °C. After heating to 180 °C, the acrylamide concentration was some seven times below the maximum, about nine times lower than in the sample without additions and some five times lower than in sample containing sucrose, showing the potential of fructose to eliminate acrylamide.
4. With addition of **39 % fructose and 1 % ammonium carbonate,** heating at 60 °C was sufficient to obtain 270 µg/kg acrylamide; at 80 °C it was already 2000 µg/kg. The maximum was reached at 120 °C (11 700 µg/kg, corresponding to a conversion of 8 % asparagine) and was 195 times higher than in the sample without additions. The sample heated to 200 °C merely contained 315 µg/kg acrylamide, i.e. about four times less than that without addition of fructose.

Formation at low temperature

As shown above, ammonium accelerates acrylamide formation from asparagine and fructose particularly at low temperatures (figure 7, table 1, figure 9). In fact, it even enables slow formation of acrylamide at ambient temperature. Model experiments were performed with wheat flour and corn starch, again simulating the composition of gingerbread (40 % fructose; 1 % ammonium carbonate). After drying at RT over weekend, samples were kept at ambient temperature for 6 weeks before being analyzed. Some samples were initially warmed to 40 °C for 1 or 3 days.

As shown in line 1 of table 3, flour and fructose produced little acrylamide (20 µg/kg). Addition of 1 % ammonium carbonate increased the acrylamide content to some 1000 µg/kg, not significantly depending on whether or not the sample was initially warmed to 40 °C for 1 or 3 days.

Table 3
Model experiments on acrylamide formation at low temperature

	Model mixture	*Storage*	*Acrylamide (µg/kg)*
1	Flour + fructose	6 weeks RT	20
2	Flour + fructose + NH_4^+	6 weeks RT	990
3	Flour + fructose + NH_4^+	1 d 40 °C and 6 weeks RT	860
4	Flour + fructose + NH_4^+	3 d 40 °C and 6 weeks RT	1100
5	Corn starch + fructose	6 weeks RT	< 10
6	Corn starch + fructose	3 d 40 °C and 6 weeks RT	< 10
7	Corn starch + fructose + Asn + NH_4^+	6 weeks RT	340
8	Corn starch + fructose + Asn + NH_4^+	1 d 40 °C and 6 weeks RT	780
9	Corn starch + fructose + Asn + NH_4^+	3 d 40 °C and 6 weeks RT	890

Corn starch and fructose (lines 5 and 6) did not yield acrylamide above the detection limit. With asparagine being added at the concentration present in the wheat flour (270 mg/kg), fructose and ammonium carbonate (amounts as with flour), 6 weeks at ambient temperature resulted in 340 µg/kg of acrylamide (line 7), i.e. some three times less than in flour (line 2). With initial warming to 40 °C for 3 days, however, the concentrations resumed that in flour. It was concluded that ammonium carbonate catalyzes acrylamide formation to such an extent that 1000 µg/kg acrylamide may be reached at ambient temperature. The results obtained with corn starch support that asparagine, a reducing sugar, and ammonium are the only starting materials needed, even though in this matrix slightly more activation is needed than in wheat flour (3 days at 40 °C).

The confirmative experiments referred to in table 4 involved heating to 40 °C during 5 days and corn starch as matrix material. To all samples, 1 % ammonium carbonate was added. Only the combination of asparagine, fructose, and ammonium produced the acrylamide. Varying the asparagine concentration by the factor two resulted in half or twice as much acrylamide, again supporting that ammonium just acted as a catalyst.

Table 4
Model experiments on acrylamide formation in corn starch at 40 °C for 5 days

	Model mixture	*Acrylamide (µg/kg)*
1	Corn starch $+NH_4^+$	<15
2	$+Asn+NH_4^+$	<15
3	$+fructose+NH_4^+$	<15
4	$+Asn+fructose+NH_4^+$	650
5	$+½\,Asn+fructose+NH_4^+$	360
6	$+2\times Asn+fructose+NH_4^+$	1500

If acrylamide is formed at ambient temperature, it might also be formed in finished products, such as cookies. A sample of gingerbread was analyzed in November 2002 and May 2003. The acrylamide content decreased from 850 to 500 µg/kg, i.e. elimination predominated formation. This may be explained by an almost complete loss of ammonium during the baking process.

Conclusions

Source of acrylamide

Thermal decomposition of asparagine with the help of reducing sugars (or similar carbonyls) is the only relevant source of acrylamide. Acrylamide concentrations are correlated with the product of the concentrations of asparagine and the reducing sugars not only in potato, as shown previously (13), but also in wheat flour and corn starch. Reaction of asparagine with a reducing sugar seems to be the rate-determining step.

Sugars

Reducing sugars play an important role both in acrylamide formation as well as its elimination. Fructose is more effective in increasing acrylamide contents than glucose, particularly at concentrations exceeding 3 %. Above about 3 %, increased glucose even decreased the acrylamide content. The exchange of fructose by glucose could be a way to reduce acrylamide contents in bakery ware. Sucrose does not support acrylamide formation, but supports elimination at temperatures above some 160 °C.

Temperature

For the preparation of fried or roasted potato products, lower temperatures always help reducing acrylamide contents (18). For bakery ware, dependence on temperature is more complex. At temperatures above some 140 °C (30 min) and with the high concentrations used for preparing cookies, fructose easily supports elimination more efficiently than formation, i.e. higher temperatures may decrease acrylamide contents; at 180–200 °C the concentrations were even lower than in the wheat flour without added sugars.

This complicates the prediction of optimized baking conditions. Under the experimental conditions, the small test samples were dry from the beginning and reached the temperatures of the oven in a short time. Baking often occurs at temperatures above 200 °C, but this does not mean that the product reaches this temperature. Strong baking to reduce acrylamide contents runs the risk that internal parts of the product only reach the conditions resulting in maximized acrylamide concentrations.

Ammonium

Ammonium carbonate and ammonium hydrogen carbonate are frequently used to raise dough. They strongly increase acrylamide contents – easily by more than a factor of ten. The yield of converting asparagine to acrylamide may increase from around 0.1 % to 5 %. In fact, bakery ware containing ammonium salts typically contains 200–1000 µg/kg acrylamide. The exchange by the sodium or potassium carbonate should drastically lower the acrylamide contents, but often presupposes the re-formulation of the product composition.

Ammonium seems to accelerate acrylamide formation through the activation of fructose. It does not react with a carbon source to form acrylamide. It enhances formation to such an extent that even long term storage at ambient temperature may result in acrylamide concentrations reaching or exceeding 1000 µg/kg. Hence mixtures containing ammonium salts should not be stored.

Summary

Model experiments based on potato, wheat flour and corn starch as matrix material and components tested for a contribution to acrylamide formation were performed to find ways to reduce acrylamide contents, with particular focus on bakery

ware. Also in wheat flour and corn starch, acrylamide concentrations are correlated with the product of the concentrations of asparagine and the reducing sugars. Several experiments indicate that at the conditions used during preparation of bakery ware there is no relevant contribution to acrylamide formation other than from asparagine. Sucrose does not support acrylamide formation, but accelerates elimination above about 160 °C and, thus, reduces acrylamide concentrations compared to samples free of sucrose. Fructose and glucose support formation as well as elimination, whereby elimination may prevail just as well as formation; at temperatures above 160 °C, elimination generally exceeds formation. Fructose introduces higher acrylamide concentrations than glucose. Ammonium carbonate or bicarbonate, applied to rise dough, strongly increases acrylamide concentrations by enhancing the yield of acrylamide from asparagine and reducing sugar. It enables formation even at ambient temperature.

Zusammenfassung

Experimente mit Modellmischungen auf der Basis von Kartoffel, Weizenmehl und Maisstärke sowie Komponenten, die an der Acrylamidbildung beteiligt sein könnten, dienten zur besseren Voraussage, wie Acrylamidgehalte in Backwaren vermindert werden können. Auch in Mehl- und Stärkemischungen sind die Acrylamidkonzentrationen mit dem Produkt aus den Konzentrationen von Asparagin und reduzierenden Zuckern korreliert. Verschiedene Experimente zeigen, dass unter den für die Zubereitung von Backwaren üblichen Bedingungen keine andere Ausgangssubstanz als Asparagin relevant zur Acrylamidbildung beiträgt. Saccharose unterstützt die Acrylamidbildung nicht, beschleunigt aber über ca. 160 °C die Elimination, d.h. senkt die Acrylamidkonzentration im Vergleich zu zuckerfreien Produkten. Fructose und Glucose beschleunigen sowohl die Bildung als auch die Elimination von Acrylamid, wobei die Elimination die Bildung übertreffen kann; über ca. 160 °C dominiert im Allgemeinen die Elimination. Fructose ergibt höhere Acrylamidgehalte als Glucose. Der Einsatz von Ammoniumcarbonat oder -bicarbonat als Triebmittel führt zu einer starken Erhöhung der Acrylamidkonzentrationen. Er erhöht die Ausbeute des Umsatzes von Asparagin und reduzierenden Zuckern zu Acrylamid. Ammonium ermöglicht die Bildung von Acrylamid sogar bei Raumtemperatur.

Résumé

Dans le but de mieux identifier les possibilités permettant de réduire la teneur en acrylamide dans des articles de boulangerie, des expériences ont été réalisées sur des mélanges modèles à base de pomme de terre, farine de blé et amidon de maïs additionnés de composants pouvant participer à la formation d'acrylamide. Comme dans les pommes de terre, les concentrations d'acrylamide dans la farine de blé et l'amidon de maïs corrèlent avec la concentration d'asparagine multipliée avec celle du sucre réducteur. Plusieurs expériences indiquent qu'aux conditions typiques uti-

lisées dans la préparation des articles de boulangerie, il n'y a pas de contribution essentielle à la formation d'acrylamide autre que celle de l'asparagine. Le sucrose ne soutient pas la formation d'acrylamide, mais accélère son élimination au-dessus de 160 °C environ. En comparaison avec les échantillons sans sucrose, il réduit les concentrations d'acrylamide. Le fructose et le glucose accélèrent la formation aussi bien que l'élimination; aux températures supérieures à 160 °C, l'élimination domine généralement la formation. Le fructose induit des teneurs d'acrylamide plus élevées que le glucose. Le carbonate ou bicarbonate d'ammonium, appliqué pour lever la pâte, conduit à une forte augmentation des concentrations d'acrylamide en élevant le rendement de la formation d'acrylamide à partir de l'asparagine et des sucres réducteurs. Il permet la formation d'acrylamide même à température ambiante.

Key words

Formation of acrylamide, bakery ware, ammonium salts, reducing sugars

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