Acrylamide in cereal products: A review

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Abstract

The review summarises the results of almost 5 years of academic and industrial research on acrylamide in cereal products. Significant progress in this field has been made during that time, as reflected by the numerous publications on this subject. In addition to studies of their formation, mechanisms and toxicological studies, ways to minimise acrylamide in heat-treated starch-rich foods have been the main focus. Therefore, this review will first give a brief overview of acrylamide formation and toxicology, including its mitigation in potato products, with further focus being on cereal products. In the latter commodities, acrylamide can be limited either by selecting suitable raw materials, e.g. flours produced from varieties low in asparagine and of a low extraction rate, respectively, or by optimisation of the production technology. The latter strategy not only comprises technological measures such as temperature control and selection of the oven type, but also product formulation and the use of low molecular additives.

Keywords: Acrylamide; Bakery products; Cereal; Technology; Formulation; Additives

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1. Introduction

In April 2002, the Swedish National Food Authority and the University of Stockholm jointly announced the determination findings of considerable levels of acrylamide in heat-treated carbohydrate-rich foods (Swedish National Food Administration, 2002). The announcement followed an earlier feeding study which had reported the formation of acrylamide in animal feed (Tareke et al., 2000). These findings attracted worldwide interest, because acrylamide has been classified as “probably carcinogenic to humans” by the International Agency on Research on Cancer (IARC, 1994), and exposure to high levels was found to cause damage to the nervous system. After rapid confirmation of these observations (Ahn et al., 2002), numerous research activities concerning the extent of exposure, origin of acrylamide in food, health risk to humans, and mitigation of acrylamide in food were initiated (Fig. 1).

The first breakthrough in acrylamide research was the simultaneous discovery by several groups that acrylamide is formed from reducing sugars and asparagine in the Maillard reaction in a complex mechanism (Mottram et al., 2002; Stadler et al., 2002; Weisshaar and Gutsche, 2002; Yaylayan et al., 2003; Zyzak et al., 2003). Later, additional formation mechanisms, e.g. from peptides, proteins, and biogenic amines, were identified (Buhlert et al., 2006; Claus et al., 2006a, b; Granvogl et al., 2004; Yaylayan et al., 2004). With this fundamental knowledge detailed studies to reduce acrylamide in food products were initiated. However, achievements made for potato products cannot necessarily be transferred to cereal products due to differing process technology and limiting precursors. Therefore, comprehensive investigations for each food commodity were required.

This review provides an extensive summary of the current state of knowledge concerning different parameters affecting acrylamide formation and reduction in cereals products, ranging from plant breeding to process parameters and changes of the formulation. Furthermore, the application of low molecular additives will be critically discussed. The progress and complexity of the research are also highlighted by the large number of different products, indicating the constraints faced by manufacturers in finding practicable solutions.

2. Toxicology of acrylamide

2.1. Dietary acrylamide intake

Estimation of dietary acrylamide intake has been made for several populations comprising different dietary records (Dybing et al., 2005; Fohgelberg et al., 2005; Hilbig et al., 2004; Hilbig and Kersting, 2006; Konings et al., 2003; Matthys et al., 2005; Sommerfeld and Dehne, 2006). The calculated average acrylamide intake ranges from 0.3 to 0.6 μg/kg body weight per day for adults, while children and adolescents tend to ingest more acrylamide on a per bodyweight basis (0.4–0.6 μg/kg). This can be ascribed to a combination of childrens’ higher caloric intake as well as their higher consumption of certain acrylamide-rich foods, such as French fries and potato crisps (Dybing et al., 2005; Wilson et al., 2006). The foods with the highest contribution to acrylamide intake vary from country to country according to national dietary patterns and methods of food preparation. In general, potato products, coffee, and bakery products are the most important sources. In Germany, for example, bread and bread rolls account for ~25% of the acrylamide intake due to the high consumption of almost 240 g/day.

As acrylamide is present in a wide range of foods, reduction in only one specific food product will fail to minimise the consumers’ burden. Another effect of the diversity of acrylamide-containing foods is that they contribute significantly to the total micro- and macronutrient composition of the diet (Wilson et al., 2006), which must also be taken into account when suggesting ways for acrylamide reduction. Peterson and Tran (2005) calculated that foods with high acrylamide levels contribute to 38% of the total daily energy intake, 47% of total daily iron intake, and 42% of total daily folate intake in the...
United States. Additionally, smoking elevates acrylamide intake significantly by 1–2 μg/cigarette.

2.2. Metabolism of acrylamide

Owing to its polarity and low molecular mass, acrylamide is readily incorporated and distributed in animals and humans, as shown in isotope experiments (Sumner et al., 1992). However, it is likely that interactions of acrylamide with the food matrix such as dietary proteins influence its uptake (Schabacker et al., 2004). After ingestion, acrylamide is rapidly distributed through in the whole body via the bloodstream. It can be found in the thymus, liver, heart, brain, kidneys (Abramsson-Zetterberg et al., 2005), and even in human breast milk (Sörgel et al., 2002).

The conjugation of acrylamide to glutathione, as well as its epoxidation to glycidamide in the liver via cytochrome P450, represent the major metabolic routes (Sumner et al., 1992). Interestingly, toxicokinetic studies revealed that the second pathway becomes increasingly important at lower acrylamide levels in the bloodstream (Doerge et al., 2005).

The formation of glycidamide is considered to be the critical step for the genotoxic effects of acrylamide and its metabolites. Acrylamide and glycidamide, the latter at a much higher rate, can react with macro-molecules such as haemoglobin and enzymes (Wilson et al., 2006). Furthermore, glycidamide may react with DNA, leading to point mutations and cancer.

2.3. Carcinogenicity of acrylamide

Earlier experiments showed two relevant effects of acrylamide on health: carcinogenicity and neurotoxicity (Friedman, 2003). Since neurotoxic effects only occur at high acrylamide levels (NOAEL 0.5 mg/kg body weight and day), which cannot be reached via food, they can be disregarded when discussing health concerns from bakery products. In contrast, clear evidence of the carcinogenic and genotoxic effects of acrylamide and its metabolite glycidamide was found in various in vivo and in vitro studies (Wilson et al., 2006). In cell culture studies, acrylamide induced chromosomal breaks and point mutations, while experiments with mice and human cell lines treated with acrylamide showed increased gene mutation rates, especially exchange of adenine by guanine and guanine by cytosine, respectively. In animal experiments with mice, tumours were observed in the thyroid gland, testes, mammary gland, lung, clitoral gland, and brain (Rice, 2005). Additionally, a lifetime oncogenicity study with Fischer rats receiving up to 2 mg acrylamide per kg bodyweight revealed significant increases of tumours in the thyroid gland, testes, central nervous system, uterus, and other tissues (Johnson et al., 1986). These findings were only partly confirmed by Friedman et al. (1995). However, in all animal studies, high doses of acrylamide were used so that these results cannot easily be extrapolated to acrylamide intake via foodstuff in humans. For this reason, several epidemiological studies were conducted (Wilson et al., 2006) to assess the cancer risk for humans. A study by Mucci et al. (2003), using data from an existing population-based case–control study in Sweden, revealed no impact of dietary acrylamide on cancer of the bladder, bowel, and kidneys. Furthermore, no positive correlation was found between acrylamide and renal cell cancer, cancer of the pharynx, larynx, breast, or ovaries. Prospective studies, which are generally regarded to have a higher level of evidence than case–control studies, could not establish a correlation between acrylamide ingestion and breast or colon cancer.

Nevertheless, acrylamide remains “potentially carcinogenic to humans” unless more detailed studies provide clear evidence of the opposite. Therefore, acrylamide levels in foodstuff should be as low as reasonably achievable (ALARA principle). For this purpose, the formation routes of acrylamide need to be elucidated so that suitable measures can be taken.

3. Formation of acrylamide

This review mainly focuses on strategies for reducing mitigation strategies for acrylamide in cereal products, predominantly bakery products. However, to understand these strategies, knowledge of the underlying formation routes is required and therefore provided in the next section. For more detailed information, we refer to previously published reviews.

3.1. Formation via Maillard reaction

The first detailed insight into the formation of acrylamide was provided by Zyzak et al. (2003) (Fig. 2) and Yaylayan et al. (2003), confirming the hypothesis of stadler et al. (2002) and Mottram et al. (2002) that acrylamide is formed in the Maillard reaction from asparagine and carbonyl sources, such as reducing sugars. Although asparagine may in principle be converted to acrylamide by thermally induced decarboxylation and deamination (Yaylayan et al., 2003), in practice carbohydrates are necessary to affect the conversion of asparagine into acrylamide. While in theory many carbonyl compounds can enhance this reaction, it has been demonstrated that α-hydroxy carbonyl compounds, such as fructose or glucose, are much more efficient than others, due to the lowering effect on the activation energy (Yaylayan and Stadler, 2005). Furthermore, sugar breakdown products occurring in the Maillard reaction, for example glyoxal, significantly contribute to the pathways (Amrein et al., 2006). The first step in this reaction is the formation of a Schiff base intermediate as a low-energy alternative to the decarboxylation of the intact Amadori product. The Schiff base intermediate can either hydrolyse to form 3-aminopropionamide, a potent precursor of acrylamide (Granvogel et al., 2004), or undergo 1,2-elimination to directly form acrylamide. However, the exact formation mechanism of
acrylamide in the Maillard reaction is still not fully elucidated. Nevertheless, the formation from asparagine and reducing sugars in the Maillard reaction represents the main formation route, whereas other mechanisms provide only additional pathways.

3.2. Alternative routes for acrylamide formation

Although acrylamide in foods is predominantly formed via the Maillard reaction, several other formation mechanisms have been reported. Acrolein and acrylic acid can be formed by dehydration of glycerol, especially when fats are heated at an improperly high temperature. Acrylamide can be formed together with ammonia from the degradation of amino acids (Becalski et al., 2003). However, experiments with ammonium salts, oils, and acrolein indicate that this mechanism might be irrelevant for acrylamide formation in foodstuffs (Amrein et al., 2004; Weisshaar and Gutsche, 2002).

While 3-aminopropionamide was first identified as a transient intermediate in acrylamide formation from asparagine (Zyzak et al., 2003), it can also be generated in food by enzymatic decarboxylation of asparagine (Granvogl et al., 2004, 2005) and is a very potent precursor for acrylamide formation under certain reaction conditions. The contribution of this pathway to the total acrylamide formed during food processing still needs to be elucidated.

Yaylayan et al. (2004) reported acrylamide generation from the dipeptide carnosine in heated meat. This peptide hydrolyses to β-alanine, which further reacts with ammonium resulting from the Strecker degradation of amino acids. The reason why no, or only very little, acrylamide can be found in meat products is that acrylamide readily forms methyl derivatives, with still unknown toxicological effects.

A similar formation mechanism was suggested by Buhlert et al. (2006) in a model study using peptides, and confirmed by Claus et al. (2006a, b) for wheat gluten and gluten-supplemented wheat bread rolls. The key amino acid is protein-bound alanine adjacent to an amino acid with a β-H atom. If such proteins are heated, an
electrocyclic domino reaction leads to the formation of acrylamide and other acid amides, e.g. cinnamic amide from phenylalanine. This mechanism requires slightly higher temperatures than the formation via Maillard reaction and its contribution to total acrylamide in bakery products still needs to be assessed.

4. Brief overview on strategies for acrylamide reduction in potato products

It is apparent that many effective and simple ways for acrylamide reduction in potato products have been established during recent years. In order to highlight the differences but also commonalities between these and cereal products, a short overview on acrylamide reduction in potato products is provided in this review. For more detailed data, we refer to reviews published earlier (CIAA, 2006; Stadler and Scholz, 2004; Taeymans et al., 2004).

It has been demonstrated that the limiting factors for acrylamide formation in potato products are reducing sugars (Amrein et al., 2003), whereas asparagine is far more abundant. Hence, the selection of potato varieties low in reducing sugars offers a promising strategy for acrylamide reduction (Olsson et al., 2004; De Wilde et al., 2006a), as does the application of suitable storage practices with temperatures above 6 °C (De Wilde et al., 2005; Grob et al., 2003; Noti et al., 2003). Furthermore, increased nitrogen fertilisation increased free asparagines, but lowered reducing sugars and therefore acrylamide (De Wilde et al., 2006b).

In addition to pre- and post-harvest strategies, there are many other possibilities for acrylamide reduction in potato products. The addition of di- and trivalent cations has been proposed in the patent literature to reduce acrylamide in manufactured potato products (Elder, 2005; Elder et al., 2004). Furthermore, precursors were removed by blanching or soaking of the potato slices, which, combined with the application of organic acids (Gama-Baumgartner et al., 2004; Grob et al., 2003; Jung et al., 2003; Wicklund et al., 2006), led to an almost 70% decrease in acrylamide. The reduction of the pH in the system inhibits the formation of the Schiff base by favoring protonation of the amine group of asparagine. Similar effects were observed when asparaginase (Taeymans et al., 2004; Zyzak et al., 2003) or lactofermentation (Baardseth et al., 2004a, b) were applied.

The most crucial parameters for acrylamide reduction in potato products are heat regulation and moisture control. The key control point confirmed by several experiments, mainly model studies, is adherence to a maximum frying temperature of 175 °C (Grob et al., 2003). However, even if a suitable temperature maximum is applied, other factors such as the load of the fries in the fryer or the surface-to-volume ratio are also important (Taubert et al., 2004). A low surface-to-volume ratio provides significantly lower acrylamide levels as it is only generated in the crust (Surdyk et al., 2004). Furthermore, the application of vacuum frying might also offer an opportunity to reduce acrylamide, since lower temperatures can be applied without altering the sensory properties of the crisps (Granda et al., 2004). If potato slices were pre-dried prior to frying, the frying time could be reduced, resulting in lower acrylamide levels (Pedreschi et al., 2007).

In addition to optimising the process parameters, various additives have been applied to reduce acrylamide. It was demonstrated by Fernández et al. (2003) that acrylamide levels were significantly reduced by addition of a flavonoid-containing blend of spices. The reduction in acrylamide could not be ascribed to reduced pH. Instead, the authors proposed a reaction of acrylamide and/or its precursors with the polyphenols. Similar results have been reported by Becalski et al. (2004), who observed a 25% decrease in the acrylamide content of fried potato slices when rosemary (Rosmarinus officinalis L., an herb with high polyphenolic content) was added to the olive oil used for frying. Other antioxidants had no, or only marginal, effects (Ryderberg et al., 2003; Vattem and Shetty, 2003). In contrast, the addition of fish meat, nearly pure protein, significantly reduced acrylamide (Taeymans et al., 2004), which is probably due to the reaction of previously formed acrylamide with the SH and amino groups of the proteins (Schabacker et al., 2004).

However, these results cannot easily be extrapolated to cereal products such as bread, bread rolls, and gingerbread because the limiting precursor in this food group is asparagine instead of reducing sugars. Moreover, acrylamide formation is much more complex due to the influence of microbial process steps (e.g. fermentation) and additives (e.g. ammonium hydrogen carbonate). Because bakery products with a consumption of ~240 g/day contribute approximately 25% to the daily acrylamide intake, individual studies, as summarised in Table 1, were essential to reduce the consumers’ burden.

5. Strategies for acrylamide reduction in cereal products

5.1. Impact of raw material

While the impact of variety, harvest year, fertilisation, and storage conditions on the acrylamide content of potato products has been extensively studied (De Wilde et al., 2005, 2006a, b; Grob et al., 2003; Noti et al., 2003; Olsson et al., 2004), data on cereal products are so far rather limited. Springer et al. (2003) reported a significant influence of the variety on the free asparagine in rye, with contents ranging from 319 to 791 mg/kg. However, the impact on acrylamide formation was not investigated although a high correlation with asparagine contents can be expected due to the limiting effect of this amino acid on acrylamide formation in cereal products (Surdyk et al., 2004). Interestingly, asparagine in the varieties Born and Nikita were higher in cereals obtained from organic farming compared with those from conventional agriculture (Springer et al., 2003). In contrast, a recent study by Zörb...
### Table 1
Studies on the mitigation of acrylamide in cereal products (non-exhaustive list)

<table>
<thead>
<tr>
<th>Study</th>
<th>Topic</th>
<th>Key findings</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Impact of raw material</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Springer et al. (2003)</td>
<td>Rye bread: influence of variety, farming system, and extraction rate</td>
<td>Variety has significant influence on Asn, AA was not studied; organic farming causes higher Asn. Extraction rate has impact on Asn in flour</td>
</tr>
<tr>
<td>Taeymans et al. (2004)</td>
<td>Wheat: influence of variety</td>
<td>Impact of variety on Asn in wheat is remarkable, AA was not assessed</td>
</tr>
<tr>
<td>Claus et al. (2006b)</td>
<td>Wheat, rye, and spelt bread: impact of variety, harvest year, fertilization, sprouting, and extraction rate</td>
<td>Variety has significant influence on Asn and AA (varies by 540%), as well as harvest year (dry conditions favor AA formation). Sprouting enhances enzyme activities and thus Asn and AA. N-fertilizer amount correlates almost linearly with AA as well as extraction rate</td>
</tr>
<tr>
<td>Muttucumaru et al. (2006)</td>
<td>Wheat: influence of S deficiency</td>
<td>Wheat grown under S deficiency contains much more Asn and AA (80% red. when fertilization is sufficient)</td>
</tr>
<tr>
<td>Haase et al. (2003)</td>
<td>Wafers: influence of extraction rate</td>
<td>When increasing extraction rate from type 550–1050 AA is almost doubled</td>
</tr>
<tr>
<td><strong>Impact of formulation and product composition</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vass et al. (2004)</td>
<td>Wheat crackers: sugar type, NH$_4$HCO$_3$</td>
<td>Replacing invert sugar syrup by sucrose reduced AA by 60%. NH$_4$HCO$_3$ increases AA</td>
</tr>
<tr>
<td>Amrein et al. (2004)</td>
<td>Gingerbread: influence of NH$_4$HCO$_3$</td>
<td>AA is significantly reduced when NH$_4$HCO$_3$ is replaced by NaHCO$_3$</td>
</tr>
<tr>
<td>Graf et al. (2006)</td>
<td>Semi-finished biscuit: influence of acid, NH$_4$HCO$_3$, and sucrose</td>
<td>Replacing NH$_4$HCO$_3$ by NaHCO$_3$ lowers AA by 70%, replacing invert sugar syrup by sucrose provides further reduction. Tartaric acid also has AA lowering effect</td>
</tr>
<tr>
<td>Claus et al. (2007)</td>
<td>Wheat bread: impact of baking agents and NaCl</td>
<td>Enzyme-bearing bakery improvers have no influence on AA. NaCl lowers AA levels up to 2%, higher addition results in AA increase</td>
</tr>
<tr>
<td>Weisshaar (2004)</td>
<td>Baking ingredients: AA-forming potential</td>
<td>Baking ingredients like almonds, sesame, and poppy seed have a high AA-forming potential, thus elevating AA in bakery products</td>
</tr>
<tr>
<td><strong>Process technology</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surdyk et al. (2004)</td>
<td>Wheat bread: baking temperature, limiting precursor</td>
<td>AA is linearly increased with time and temperature, no decrease even at high temperature. 99% of AA is located in the crust, and Asn is limiting precursor in bakery products</td>
</tr>
<tr>
<td>Bråthen and Knutsen (2005)</td>
<td>Bread: time–temperature regime</td>
<td>Linear increase of AA with time and temperature without decrease at higher temperatures (in contrast to model systems)</td>
</tr>
<tr>
<td>Claus et al. (2007)</td>
<td>Wheat bread: impact of fermentation, time–temperature regime, and oven type</td>
<td>Dough fermentation reduces acrylamide in bread by 50%. Linear increase of AA with time and temperature; longer baking time at lower temperature is favorable. Convection ovens cause higher AA levels than desk ovens</td>
</tr>
<tr>
<td>Springer et al. (2003)</td>
<td>Crispbread: temperature profile</td>
<td>Changing the temperature profile decreases AA significantly</td>
</tr>
<tr>
<td>Vass et al. (2004)</td>
<td>Wheat crackers: temperature profile</td>
<td>Changing the profile from linear 220 °C to a gradient from 230 to 190 °C could lower AA by 60%</td>
</tr>
<tr>
<td>Rufián-Henares et al. (2006)</td>
<td>Breakfast cereals: impact of extruder technology</td>
<td>Direct expansion extrusion cooking process (DEEC) gives rise to AA when compared to pellet-to-flaking extrusion cooking (PFEC)</td>
</tr>
<tr>
<td>Baardseth et al. (2004)</td>
<td>Crispbread: lactic acid fermentation</td>
<td>Lactic acid fermentation reduces AA by 70% (same effect as pH reduction)</td>
</tr>
<tr>
<td><strong>Impact of additives</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jung et al. (2003)</td>
<td>Corn chips: addition of acids</td>
<td>Addition of acids and reduction of pH lowers AA formation</td>
</tr>
<tr>
<td>Levine and Smith (2005)</td>
<td>Cracker model: addition of acids, sulfur containing amino acids, antioxidants and polyphenols</td>
<td>Consumable acids lower AA via pH reduction sulfur containing amino acids might react with AA. Antioxidants and polyphenols also reduce AA</td>
</tr>
<tr>
<td>Vass et al. (2004)</td>
<td>Wheat crackers: application of asparaginase</td>
<td>Application of asparaginase during dough preparation could significantly reduce AA by 70% without sensory changes</td>
</tr>
<tr>
<td>Bråthen et al. (2005)</td>
<td>Wheat bread: addition of glycine</td>
<td>Glycine reduces AA by more than 80% (very high doses applied)</td>
</tr>
<tr>
<td>Fink et al. (2006)</td>
<td>Dough: spraying with glycine</td>
<td>Significant reduction of AA when sprayed 8 times</td>
</tr>
<tr>
<td>Claus et al. (2007)</td>
<td>Wheat bread: addition of cysteine</td>
<td>Cysteine reduces AA by forming adducts</td>
</tr>
<tr>
<td>Vattem and Shetty (2005)</td>
<td>Cereals: addition of legume proteins</td>
<td>Legume proteins reduces AA probably by reaction with the SH and NH$_2$ groups</td>
</tr>
<tr>
<td>Elder et al. (2004)</td>
<td>Bread: application of divalent cations</td>
<td>20% decrease of AA when divalent cations (Ca$^{2+}$, Mg$^{2+}$) is added to the dough</td>
</tr>
</tbody>
</table>

AA: acrylamide; Asn: asparagines.
et al. (2006) did not confirm an influence of the farming system on asparagine. Only alanine and valine were significantly affected while the first was decreased in organic farming and the latter was increased. Amrein et al. (2003) also failed to observe an impact of farming systems on the asparagine and acrylamide in potato products. However, the results of Springer et al. (2003) might also be ascribed to differences in the nutrient supply, especially nitrogen. Claus et al. (2006b) investigated the influence of cereal varieties on precursors and acrylamide contents using nine wheat, two spelt, and two rye cultivars, confirming a crucial impact of the plant variety. Asparagine levels in flour from sprouted wheat grains with higher nitrogen dosage, which is comparable to the results reported by Taeymans et al. (2004). Consequently, acrylamide varied between 14 and 74 μg/kg, corresponding to a 5.4-fold rise. In general, varieties of higher protein quality will result in higher acrylamide contents. However, Tommi, a cultivar high in crude protein, did not enhance acrylamide formation, thus, demonstrating that selection of suitable varieties provides an easy measure for acrylamide reduction.

As earlier reported by Olsson et al. (2004), harvest year has a crucial impact on asparagine in potatoes. Similar results for wheat and rye were found by Claus et al. (2006b), who studied the influence on one rye and three wheat samples. The asparagine content was significantly lower in all samples from the 2004 harvest as compared to 2003. As a result, acrylamide was also reduced in breads prepared from 2004 flour with a reduction of up to 62% for the cultivar Enorm. These varying contents in asparagine, crude protein and acrylamide were ascribed to differing weather conditions. The growth period was extraordinarily dry in 2003, with the average temperature being 2 °C higher than in 2004 with approximately 300 more hours of sunshine. Previous reports showed that crude protein and amino acid contents depend on the growth temperature (Hansen et al., 2004; Vigue and Li, 1976) and humidity (Lerner et al., 2006).

Unfavorable weather conditions can also result in sprouting, a severe problem in cereal production. As a consequence, protease activities may be almost doubled (Claus et al., 2006b), resulting in significantly higher asparagine levels in flour from sprouted wheat grains. Because asparagine is the limiting precursor in cereal products, acrylamide levels of breads produced from such flours are also remarkably increased. Therefore, flours from sprouted wheat or rye should not be used for bakery products, even when blended with other flours.

As climatic conditions cannot be influenced by farmers, fertilisation is a key factor in crop production. It was previously demonstrated that N-fertilisation positively influenced acrylamide formation in potato products (De Wilde et al., 2006b). However, inverse effects have been reported for bakery products (Claus et al., 2006b). The authors reported significantly increased amounts of asparagine in wheat grains with higher nitrogen dosage, which was ascribed to an improved utilisation (Lerner et al., 2006). When a zero level of fertiliser (0 kg N/ha) was compared with the highest dosage (220 kg N/ha), the acrylamide in breads increased four-fold from 10.6 to 55.6 μg/kg. In contrast to potatoes, reducing sugars in wheat were not affected by fertilisation, which agrees with the results of Zahedi et al. (2004). Since N-fertilisation is a prerequisite to increase crop yields and flour quality, elevated acrylamide contents resulting from this measure appear to be inevitable. However, nitrogen fertilisation should be minimised.

Owing to flue gas desulphurisation, SO₂ emission in Germany has been reduced by almost 90%, and S-deposit to soil decreased from 80 to 5 kg S/ha (Federal Environment Agency, 2005). Consequently, sulphur fertilisation is required in some areas to prevent S-deficiency of some crops (Resemann et al., 2004). The influence of sulphate-deprived wheat on amino acids, especially asparagine, reducing sugars, and acrylamide was investigated by Muttucumaru et al. (2006) in greenhouse experiments. While the amount of sulphur had no significant impact on reducing sugars and only small effects on most other amino acids, asparagine and glutamine were remarkably lower when sulphur was applied. Asparagine decreased from 92.1 mmol/kg (mean of three varieties studied) to 4.62 mmol/kg when sulphur fertilisation was sufficient with similar observations being made in field experiments. Consequently, acrylamide in heated flours decreased by 80% to 816 μg/kg (average of three varieties). These findings contrast with the results of Claus et al. (2006b), who did not find an impact of additional sulphur fertilisation. This difference probably relates to differences in the sulphur status of the field sites used in the two studies. Therefore, soil sulphur should be determined prior to sowing and, if necessary, adjusted to the recommended level of 40 kg/ha (Finck, 1991).

Apart from crop fertilisation, the quality of cereal flours is also influenced by technological measures. Extraction rate, as indicated by the ash content, was assumed to be the most relevant factor directly affecting acrylamide levels in bakery products. Haase et al. (2003) reported almost doubled acrylamide levels in wafers when type 1050 flour (~1.05% ash) was used instead of type 550 (~0.55% ash). The authors ascribed these observations to increased reducing sugars in flours of higher ash content, which seems a very unlikely explanation since asparagine was shown to be the limiting factor in cereal products (Surdyk et al., 2004). Springer et al. (2003) suggested that higher asparagine contents in the outer layers of the grain resulted in higher acrylamide levels in model systems. These observations were confirmed by Claus et al. (2006b) for wheat and rye flours. With higher ash contents, increasing amounts of asparagine were extracted. Furthermore, protease activity was increased, resulting in an enhanced release of amino acids from proteins. Accordingly, the asparagine contents rose from 13.7 to 48.5 mg/100 g and acrylamide increased by 250% to 115 μg/kg. While flours containing higher amounts of dietary fiber and ash are
highly valued from a nutritional point of view, they cause elevated acrylamide levels in bread. Nevertheless, minimisation of acrylamide in breads by avoiding high extraction rate flours would be contradictory.

5.2. Impact of technology

5.2.1. Formulation and product composition

The formulation and composition of bakery products contribute substantially to their acrylamide levels. However, in contrast to potato products, trials with cereals and bakery goods showed few commonalities due to variation in the recipes and technology (Stadler and Scholz, 2004).

Although asparagine is the limiting factor in bakery products, sugars also play a crucial role. It was demonstrated by Vass et al. (2004) that replacing invert sugar syrup with sucrose in wheat crackers reduced acrylamide by 60%. Similar effects were also observed for gingerbread (Amrein et al., 2004). These results can be explained by a lack of reactive carbonyls, namely fructose and glucose, which led to a strong decrease of the Maillard reaction in general. Therefore, the products obtained were insufficiently browned and had to be coloured. In contrast, Taeymans et al. (2004) reported that sucrose resulted in acrylamide formation in gingerbread, biscuit, and cracker models when NaHCO₃ was used instead of citric acid, sodium hydrogen carbonate (NaHCO₃) was used instead of citric acid, which could not be ascribed to a higher pH. Therefore, when NaHCO₃ was used instead of citric acid, sucrose was almost devoid of acrylamide, which could at least partly be explained by a pH reduction (De Vleeschouwer et al., 2006). Amrein et al. (2006) demonstrated that addition of ammonium hydrogen carbonate (NH₄HCO₃) did not increase acrylamide when sucrose was used instead of invert sugar syrup. It has been reported that NH₄HCO₃ significantly enhances acrylamide generation in gingerbread, biscuit, and cracker models (Amrein et al., 2004; Graf et al., 2006; Taeymans et al., 2004; Vass et al., 2004; Weisshaar, 2004). In all products, acrylamide was reduced by approximately 70% when sodium hydrogen carbonate (NaHCO₃) was used instead of NH₄HCO₃. NaHCO₃ led to only small increases in acrylamide in a glucose–asparagine system (factor 2), which may be due to a slightly higher pH. Therefore, when NaHCO₃ was used in combination with citric acid, gingerbreads were almost devoid of acrylamide, which could at least partly be explained by a pH reduction (De Vleeschouwer et al., 2006). Amrein et al. (2006) recently studied the mechanism of the enhancing effect. They demonstrated that glyoxal, resulting from thermal sugar decomposition, formed 250 times more acrylamide in the presence of asparagine than did fructose. The reaction pathway from hexoses to glyoxal and finally to acrylamide is as follows: ammonium is released from NH₄HCO₃ and reacts readily with the carbonyl group of glucose and fructose due to its nucleophilic character. The imines formed allow generation of glucosones and, further on, hydroxyethanal, erythrose, and glyoxal by retro-aldol reaction, which are much more reactive with asparagine in acrylamide formation. Additionally, Levine and Smith (2005) reported a significant contribution of NaHCO₃ to acrylamide elimination, indicating two favourable effects of NaHCO₃. Therefore, NH₄HCO₃ should be avoided in sweet bakery products to minimise acrylamide levels. The slightly alkaline character of gingerbreads resulting from NaHCO₃ could be avoided by application of consumable acids (Amrein et al., 2004). Nevertheless, changes in the recipe on an industrial scale may lead to products, which are not accepted by consumers and should therefore critically be evaluated.

The impact of other baking agents on acrylamide formation was studied by Claus et al. (2007). Enzyme-containing bakery improvers, especially amylase, amylglucosidase, and, to a lesser extent, protease are widely used in bread and bread roll production and might have an impact on acrylamide. While all preparations used enhanced amylase activity and, thereby, reducing sugars, no impact on asparagine content was observed. Consequently, acrylamide remained unchanged by the use of enzyme-containing bakery improvers.

Kolek et al. (2006) reported a significant effect of NaCl on acrylamide formation in model systems. After addition of 1% NaCl to the model mixture and heating, acrylamide was reduced by 40%, whereas increased amounts of NaCl even slightly supported acrylamide reduction. This is in agreement with other studies and might be explained by inhibition of the formation of a Schiff base between reducing sugars and asparagine (Gökmen and Şenyuva, 2007). Claus et al. (2007) reported a decrease in acrylamide when up to 2% NaCl was used in wheat bread. At higher NaCl levels, however, acrylamide contents significantly increased, which was ascribed to an inhibition of the yeast growth by the salt (Voelker, 2005). Similar effects were observed by Levine and Smith (2005), who reported a stronger decrease in acrylamide when 3.5 g NaCl was applied compared with a 7.5 g addition. However, this approach is only of scientific interest since products with salt concentrations above 3% are not accepted by the consumer.

Ingredients other than salt, flour, and baking agents may also affect the acrylamide content of bakery products. Weisshaar (2004) studied the impact of roasting on acrylamide formation in almonds, hazelnuts, sesame, and poppy seeds. With the exception of hazelnuts, all other typical baking ingredients significantly increased the acrylamide levels depending on the surface-to-volume ratio. These results were confirmed by Amrein et al. (2005), who found a correlation between the asparagine and acrylamide contents in these products. Consequently, the application of these ingredients in sweet bakery products as well as in bread rolls might significantly enhance acrylamide content, especially since they are often applied directly to the surface.

Similar observations were reported by Springer et al. (2003) for caster flour used in crispbread production. When optimised flour was used in combination with a changed temperature profile, acrylamide could be reduced by almost 50%. Presumably, this can be ascribed to a lower asparagine content of the blend but details were not given.
5.2.2. Process technology

Heat regulation and final moisture content are crucial factors for the formation of acrylamide (Stadler, 2006). Several studies were conducted to assess the effects of time and temperature during baking (Biedermann and Grob., 2003; Bråthen and Knutsen, 2005; Claus et al., 2007; Elmore et al., 2005; Surdyk et al., 2004). Surdyk et al. (2004) and Claus et al. (2005) demonstrated that acrylamide is predominantly generated in the outer crust layer where more than 99% can be found, while only trace amounts are detectable in the crumb (Sadd and Hamlet, 2005). This can be ascribed to the lower temperatures of only 100 °C in the inner parts of bakery products. Therefore, Surdyk et al. (2004) assumed that acrylamide found in the crumb originates from carry-over effects from the crust. Taeymans et al. (2004) investigated the impact of the time–temperature regime on acrylamide formation in biscuits using an oven temperature of 220 °C. Interestingly, remarkably lower surface temperatures (120 °C) were observed, which was ascribed to the cooling effect of evaporating water while the centre temperature did not exceed 80 °C, which is in full agreement with Surdyk et al. (2004). However, they found 270 μg/kg acrylamide in the crust and 128 μg/kg in the crumb. An explanation for the observation was not given, but it is likely that the acrylamide found in the crumb also resulted from carry-over effects. It could clearly be demonstrated that acrylamide formation is directly linked to the time–temperature regime during baking. While acrylamide contents in dry cereal systems reached a maximum between 180 and 200 °C, a decline at higher temperatures due to a faster rate of degradation was observed (Biedermann and Grob, 2003; Bråthen and Knutsen, 2005) (Fig. 3). In contrast, acrylamide in wheat bread increased linearly with time and temperature (Bråthen and Knutsen, 2005; Claus et al., 2007; Surdyk et al., 2004), which can be ascribed to the higher water content and the above-mentioned cooling effect. These results are in good agreement with previous model studies (Becalski et al., 2003; Stadler et al., 2002; Tareke et al., 2002). Furthermore, the dry and hard bread crust might limit the mobility of acrylamide and, therefore, further reactions (Claus et al., 2007). Additionally, in this study, the impact of time and temperature on the sensory properties of the resulting breads was tested. The breads baked at 200 °C/70 min and 240 °C/50 min were nearly identical regarding flavour, colour, and odour, however, acrylamide formation was remarkably higher under the latter conditions (124.1 μg/kg vs. 92.4 μg/kg). These results show that prolonged heating at lower temperatures is a suitable measure to acrylamide minimisation during baking. This is in agreement with the results of Surdyk et al. (2004), Taeymans et al. (2004), and Haase et al. (2003) who reported a decrease in acrylamide of up to 30% when rye bread was baked at lower temperature for a longer time. The reasons for the conflicting results obtained by Amrein et al. (2004) remain to be elucidated. However, since colour and flavour formation are also inextricably linked to the Maillard reaction, changes in the time–temperature profile might also lead to insufficiently browned products requiring additional ingredients for flavour enhancement. Therefore, changes have to be critically evaluated and acrylamide mitigation by merely optimising the heat regime will fail.

In addition to temperature, the heat transfer to the product surface is also crucial, as already suggested by Haase et al. (2003). Claus et al. (2007) studied the differences between deck and convection ovens using wheat bread baked at 220 and 260 °C for 60 min. In this study, a significant impact of the oven type on the acrylamide content of bread was observed. At 220 °C, acrylamide levels increased by 60% from 109.6 μg/kg in breads baked in a multi-deck oven to 173.9 μg/kg in convection oven, whereas the increase at 260 °C was only

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*Fig. 3. Effect of cooking time at 180 °C on acrylamide levels in potato (x), rye (●), and wheat (■) cakes (Elmore et al., 2005).*
35%. This is probably due to higher formation rates at elevated temperatures. Similar effects were found for French fries by Matthaß et al. (2003). The higher acrylamide levels in breads baked in a convection oven most probably resulted from the forced air circulation, leading to faster and more intense drying of the bread crust. Since low moisture contents enhance acrylamide formation during the Maillard reaction, deck ovens are advantageous to reduce acrylamide levels in bakery products. These effects may, at least partially, be avoided by applying a higher relative humidity during baking (CIAA, 2006). Springer et al. (2003) decreased acrylamide formation in crispbread production by optimisation of the temperature profile of the oven. To keep a maximum product moisture of 8%, the oven inlet temperature was slightly increased while the outlet temperature was decreased. A similar approach was suggested by Vass et al. (2004) for the production of crackers. When the temperature course was changed from constantly 220 to 230 °C at the beginning to 190 °C at the end, acrylamide was decreased by about 60%. This can be ascribed to the lower temperature at the end of the baking time, when intense Maillard reactions occur. However, this implies longer baking times and, consequently, reduced line efficiencies (Stadler, 2006). Nevertheless, such carefully optimised baking processes are an appropriate tool for acrylamide reduction.

Analogous to oven type, extruder technology used in breakfast cereal production is crucial for acrylamide generation. Rufián-Henares et al. (2006) studied the impact of two different extrusion technologies, pellet-to-flaking extrusion cooking (PFEC) and direct expansion extrusion cooking (DEEC). Because of the higher moisture content of puffed breakfast cereals, an intensive drying and tempering step has to be applied in order to equilibrate humidity to approximately 10%, which improves shelf life. Higher thermal input during the DEEC process gives rise to acrylamide levels higher than those observed in breakfast cereals manufactured by the PFEC process. In contrast, other authors (CIAA, 2006; Stadler, 2006) reported that acrylamide levels of breakfast cereals made by extrusion puffing were at the lower end of the scale, with levels usually below 100 μg/kg. The extrusion cooker gelatinises starch but hardly develops Maillard products since the water in the cereal is evaporated at the end of the extruder with little or no toasting. In most other processes, there is a distinct toasting step for the development of flavour and colour and, therefore, a tendency for acrylamide to exceed 100 μg/kg.

Apart from temperature and machinery used in the production of cereal products, process handling also plays a role in acrylamide formation. As demonstrated in previous studies (Claus et al., 2007; Fredriksson et al., 2004; Lindsay and Jang, 2005), fermentation time has a strong impact on acrylamide levels. In these studies, fermenting yeast consumed high amounts of free asparagine. A decrease of 60% (Claus et al., 2007) and 90% (Fredriksson et al., 2004), respectively, in the limiting precursor in cereal products was reported. Consequently, acrylamide decreased by the same rate during the first hour of fermentation and subsequently remained constant. Therefore, prolongation of the fermentation time to at least 1 h was found to be sufficient for acrylamide reduction in industrial bread production, whereas fermentation exceeding 3 h, as suggested by Fredriksson et al. (2004), was unsuitable due to the degradation of the gluten network and subsequent flattening of breads and bread rolls. Additionally, as the yeast’s capacity for asparagine metabolism is limited (Fink et al., 2006), further fermentation does not result in further acrylamide reduction.

Lactofermentation, as used in sourdough preparation, has also been assessed for its acrylamide decreasing potential. As reported by Baardseth et al. (2004a, b), acrylamide in crispbread was reduced by 75% when a fermentation step using lactic acid bacteria (NCIMB 40450) was applied. This effect is due to the reduced pH (3.7 compared to 6.0 in the control) rather than to consumption of asparagine by the bacteria. These results were confirmed by Fredriksson et al. (2004), who reported a decrease in asparagine after 72 h fermentation with spontaneous sour dough. However, after an extended fermentation time of 96 h, asparagine contents exceeded the initial level, which was ascribed to the endogenous proteolytic activity of the micro-organisms. Furthermore, lactic acid bacteria seemed to have a strongly negative effect on yeast fermentation, which might lead to elevated acrylamide levels in breads produced with sourdough as compared with samples exclusively fermented with yeast.

5.2.3. Impact of additives

Because modification in formulation, process technology and management always bear the risk of sensory changes in products, thus affecting consumer acceptance, low molecular additives such as consumable acids, amino acids, and cations have recently been gaining attention.

The addition of consumable acids is a very simple but efficient method to minimise acrylamide in bakery products. When increasing amounts of citric acid were added to baked corn chips, acrylamide decreased almost linearly (Jung et al., 2003), which was ascribed to a lower pH. At both concentrations used (0.1% and 0.2%), no negative effects on sensory properties were observed. Similar effects were reported when lactic, tartaric, citric, and hydrochloric acids were added to semi-finished biscuits and cracker models (Graf et al., 2006; Levine and Smith, 2005; Taeymans et al., 2004). In all studies, acrylamide decreased with increasing amounts of acid, thereby reducing the pH by 30% (ΔpH ~1.5) or more (Fig. 4). With little effect on acrylamide elimination, its generation is significantly reduced due to hydrolysis of the carboxamide group leading to aspartic acid at lower pH. Furthermore, reduced pH values resulted in only moderate Maillard reactions, accompanied by lower acrylamide formation.
Unfortunately, milder Maillard reactions result in decreased browning and flavour formation; as a result, the addition of acids needs to be individually determined for each product (Stadler, 2006). Furthermore, an acidic flavour of bakery products is only accepted in the case of sourdough, which further limits the applicability of such methods.

The application of asparaginase represents another strategy for acrylamide reduction. As in the presence of acids, asparagine is hydrolysed to aspartic acid, thus inhibiting acrylamide generation in the Maillard reaction. When the enzyme preparation was added to wheat cracker production, acrylamide levels decreased by at least 70% without any changes in the colour or flavour of the products (Vass et al., 2004). In corn-based foods, Teras et al. (2004) reported an asparagine reduction of up to 90%, however, details concerning the acrylamide levels were not provided. Although asparaginase addition seems to be very promising for acrylamide mitigation, it is rather expensive compared with other strategies. Therefore, it is unlikely that asparaginase will be used to produce low-price foodstuffs such as bread or bread rolls. However, after approval as a food additive, its use for both patisserie articles and coffee appears to be more promising.

Recently, the impact of several amino acids on acrylamide formation and its elimination was assessed in various studies. Bråthen et al. (2005) applied glycine to dough prior to fermentation and produced breads and flat breads according to common manufacturing practice. While acrylamide reduction of up to 80% was achieved for flat breads, it decreased from 202 to <25 μg/kg in breads, corresponding to an approximate 90% reduction. However, the amounts of glycine applied were very high. With 1.5% and 3.0% (based on flour weight), the observed effect may mainly be ascribed to competition with asparagine in the Maillard reaction. In another study, the dough surface was sprayed with a 10% glycine solution prior to baking and acrylamide levels were assessed (Fink et al., 2006). After a single application, no effect on acrylamide could be observed, while repeating the spraying eight times resulted in a reduction of 16%. In contrast, Sahagian and Van Eijck (2005) observed an almost 60% decrease when dipping potato cakes in a glycine solution, which was explained by a competition with asparagine for reducing sugars. Alternatively, acrylamide may also react with the nucleophilic amino group of glycine through Michael addition (Stadler, 2006). Therefore, the application of glycine to the surface could be a means to reduce the acrylamide content of commercial bread, especially, since it is more effective than other approaches such as optimisation of the process technology.

Apart from glycine, different sulphur-containing amino acids and peptides such as methionine, cysteine, and glutathione were successfully used for acrylamide reduction in bakery products. Acrylamide formation was decreased by almost 50% when cysteine and methionine were added to cracker (Levine and Smith, 2005) or potato dough (Elder, 2005), which was ascribed to competition with asparagine. However, as methionine was suggested to be a minor precursor of acrylamide formation (Stadler et al., 2002), these results might be misleading. Furthermore, cysteine as well as glutathione exhibit reactive SH-groups which might react with acrylamide to form cysteine-S-β-propionamide (S-(3-amino-3-oxopropyl)-cysteine). This was already assumed by Flückiger and Salih (2006) when studying the impact of cysteine on acrylamide in crispbread. Interestingly, in this study, no effect was observed when cysteine was added directly to the dough. Conversely, Claus et al. (2007) observed an almost 50% decrease in asparagine when cysteine was added to bread dough prior to fermentation while its application as a solution to the bread surface showed no effect, probably due to the limited mobility of cysteine in the dry crust. The limiting effects of this amino acid could be ascribed either to competition with asparagine or to reaction with the acrylamide already generated (Friedman et al., 1965). In the latter case,
cysteine-S-\(\beta\)-propionamide was formed (Claus et al., 2007), as already assumed by Clayes et al. (2005). This was confirmed by mass spectrometric investigations. However, cysteine also has properties, which limit its applicability in foodstuffs. In particular, it is gluten weakening and its application results in flatter breads. Furthermore, an off-flavour can be observed at higher levels (Claus et al., 2007).

Reaction mechanisms similar to the inhibiting properties of cysteine might be responsible for the observed acrylamine-lowering effects of different proteins and peptides. As described earlier, the addition of minced fish consisting of almost pure protein and legume proteins to potato products prior to frying significantly reduced acrylamide contents (Rydberg et al., 2003; Vattem and Shetty, 2005). Corresponding trials in cracker models (Levine and Smith, 2005) showed an almost 50% reduction when casein was used, and a slight decrease in the case of wheat gluten. Proteins bear reactive nucleophilic SH- and NH\(2\)-groups of amino acid side chains, which can form stable adducts with acrylamide similar to those formed by cysteine (Lingnert et al., 2002). However, proteins and peptides with low contents of lysine and cysteine might form acrylamide via the pyrolytic pathway, as reported by Claus et al. (2006a), thus increasing the levels in heat-treated foodstuffs. Furthermore, the application of animal proteins will affect the acceptability of such products by vegetarians, and proteins may also cause allergic reactions. Therefore, the addition of proteins for reduction of acrylamide must be carefully assessed.

Adding divalent cations such as Ca\(^{2+}\) or Mg\(^{2+}\) to the dough prior to baking showed a remarkable effect on the acrylamide contents of the products. Elder et al. (2004) reported an almost 20% decrease in acrylamide when these ions were applied, and a decrease of up to 50% at slightly acidic conditions (pH 5.5), which are common in many foodstuffs. Similar effects were reported for bread, where Ca\(^{2+}\) caused a 30% reduction in acrylamide content (CIIA, 2006), and crackers (Elder, 2005). Gökmen and Şenyuva (2007) studied the impact of bivalent ions on acrylamide formation in potato products and reported an almost linear negative correlation between acrylamide formation and added Ca\(^{2+}\) concentration. The acrylamide-decreasing effect of bivalent cations was ascribed to an inhibition of the formation of the Schiff base and thus acrylamide generation, as the reaction of carbohydrates and the \(\alpha\)-amino group of asparagine is the initial step. Interestingly, the resulting low acrylamide products were adequately brown, colour formation during Maillard reaction did not appear to be affected.

Dietary recommendations usually favour foodstuffs rich in dietary fibre due to their positive effects on the gut mucosa, which can at least partly be ascribed to its water- and contaminant-binding properties. Their water-binding effect might also lead to products with less acrylamide. Rydberg et al. (2003) described lower acrylamide contents in heated model systems when water-holding components such as dietary fibre were added, which was ascribed to less pronounced pyrolysis of the sample. However, in a more recent study, Mustafa et al. (2005) assessed the impact of different amounts of oat bran concentrate devoid of amino acids on acrylamide in yeast-leavened crispbread. In contrast to the results of Rydberg et al. (2003), no acrylamide-lowering effects were observed. Therefore, dietary fibre may be considered inefficient in foodstuffs.

Another polymeric carbohydrate, the non-colorific sweetener cyclodextrin, was recently tested for its acrylamide reducing properties in oat cereals (Plank and Kolvig, 2006). They demonstrated that acrylamide was significantly decreased, showing an almost linear correlation with the concentration of added cyclodextrin. This was explained by sequestration of asparagine in the hydrophobic core of the polymer. However, the application of cyclodextrin (E 459) in Germany is legally restricted and requires an approval for each product (ZZulV, 1998). At present, its addition for acrylamide reduction is not permitted.

In contrast to novel additives like cyclodextrin, natural antioxidants have been successfully used to reduce acrylamide levels. Mayer (2004) claimed positive effects when antioxidants were applied in breakfast cereal production, but no detailed data are given. Levine and Smith (2005) added ascorbic acid to cracker models and found effects on both acrylamide formation and elimination, thus leading to significantly lowered contents. The same effects were reported by Rydberg et al. (2003) when adding relatively high ascorbate doses. These observations can mainly be ascribed to the above mentioned effects and lower pH. The addition of rosemary to olive oil during frying also reduced the acrylamide levels in potato products by approximately 25% irrespective of the pH (Becalski et al., 2003). However, no mechanism of action was suggested. Instead, Levine and Smith (2005) ascribed the acrylamide lowering effect (up to 50%) of ferulic acid (4-hydroxy-3-methoxycinnamic acid) to its reaction with acrylamide precursors or intermediates in the formation of acrylamide. Similar observations were reported by Kurppa (2003) and Fernández et al. (2003), when a spice mix containing flavonoids was applied to potato crisps, and by Zhang et al. (2007) for the addition of bamboo leaf extracts. According to our observations (unpublished results) polyphenolics had a strong lowering effect on acrylamide formation in wheat bread, which may be explained by their reaction with asparagine (Kroll et al., 2003). Hence, polyphenols appear to be a very potent and valuable additive for acrylamide reduction in different bakery products and more detailed studies concerning this topic are required.

### 6. Conclusion

Since the first detection of acrylamide in foodstuffs in 2002, significant progress in understanding how acrylamide is generated has been made. Furthermore, many options and tools for reducing acrylamide in cereal products have been reported. In addition to changes in
the temperature–time regime of baking and fermentation, replacement of crucial baking additives such as NH₂HCO₃ or invert sugar syrup also proved very effective. In addition, the use of additives such as cysteine, bivalent cations, or polyphenols seems to be very promising for acrylamide reduction in cereal products. However, strategies useful for potato products are not necessarily transferable to bakery products due to different limiting precursors and completely different product technologies. As a result, manufacturers will have to identify the most promising solutions for their respective products. This is evident when gingerbread is compared with crispbread or bread rolls. Above all, manufacturers need to keep in mind consumer expectations regarding flavour, colour, and other sensory properties in order to ensure their products remain marketable.

The relative impacts of different formation mechanisms to total acrylamide levels also need to be assessed. This should help us to find suitable methods for its mitigation. In case of cereal products, more data from long-term agronomic studies are required to better understand and control the impact of the raw materials on acrylamide formation. It should be determined whether the type of fertiliser (calcium ammonium nitrate, ammonium sulphate, etc.) applied has an impact on amino acids and thus on acrylamide. Furthermore, the time of fertiliser application could play a crucial role.

The most promising field for acrylamide reduction is the addition of low molecular additives such as polyphenols, which have not so far been applied in cereal products. Nevertheless, trials with potato products indicate a high acrylamide-decreasing potential. Such additives ideally combine acrylamide reduction with little or no changes in product technology or, most importantly, sensory quality. Furthermore, possible health benefits from e.g. polyphenols could even enhance the consumer acceptance of such products.

References


