

## Ways to Reduce the Acrylamide Formation in Cracker Products

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**Abstract:** The sources of reducing sugars and free asparagine of two different cracker products were identified, and acrylamide formation during baking was measured. The application of an asparaginase decreased the acrylamide content by at least 70% in both products. Replacing ammonium hydrogencarbonate by sodium hydrogencarbonate as baking agent and replacing reducing sugars by sucrose resulted in almost 80% less acrylamide in the wheat cracker. Decreasing free asparagine and reducing sugars in the ingredients and a lower end-temperature during baking lowered the acrylamide content of the potato cracker by about 50%.

**Keywords:** acrylamide; free asparagine; reducing sugars; asparaginase; cracker

### INTRODUCTION

The detection of acrylamide in a broad range of staple foods [1] led to world-wide activities to minimize the exposure because of the neurotoxic and carcinogenic properties of acrylamide [2]. Acrylamide is formed at elevated temperatures concurrently to nonenzymatic browning by the reaction of reducing sugars with the free amino acid asparagine, which delivers the backbone of the acrylamide molecule [3, 4]. The baking agent ammonium hydrogencarbonate strongly promotes the formation of acrylamide in bakery products [5, 6], but reducing sugars influence the acrylamide formation in these products as well [6, 7]. The aim of the present study was to identify the critical factors for acrylamide formation in a wheat cracker and a potato cracker, and to find ways to decrease their acrylamide content while maintaining the sensory properties.

### EXPERIMENTAL

Wheat crackers were prepared with wheat flour (type 400), water, sun flower oil, condensed milk, sucrose, inverted sugar syrup, NaCl, and baking agent (mixture of  $\text{NaHCO}_3$ ,  $\text{Na}_4\text{P}_2\text{O}_7$ , and  $\text{NH}_4\text{HCO}_3$ ). They were baked in an industry-scale oven at 220–230°C for 6 min. Potato crackers contained potato flakes, water, wheat flour (type 550), sun

flower oil, a starch preparation, NaCl, and were baked in an industry-scale oven with an increasing temperature profile of 190–230°C for 6 minutes. All ingredients and prescriptions were obtained from Midor AG (Meilen, CH). Asparaginase from *E. coli* (Fluka, Buchs, CH) was diluted in water and added to the dough during kneading (about 300 units per kg). Acrylamide analysis was performed with the GC-MS method of BIEDERMANN *et al.* [8], using  $^{13}\text{C}_3$ -acrylamide (CIL, Andover, Massachusetts, USA) and methacrylamide (Fluka) as internal standards. Free amino acids were extracted with 0.1 M HCl (Fluka) and determined by cation-exchange chromatography followed by post-column derivatization with ninhydrin as described in literature [6, 9]. Glucose and fructose were determined enzymatically using the kit from Scil diagnostics (Martinsried, Germany).

### RESULTS AND DISCUSSION

All ingredients of the two cracker products were analyzed for glucose, fructose, and free asparagine (Table 1). Flour was the only source for free asparagine in the wheat cracker, whereas glucose and fructose mainly originated from the inverted sugar syrup. The raw dough of the wheat cracker contained 190 times more reducing sugars than free asparagine, which therefore was a limiting

Table 1. Sources of reducing sugars and free asparagine in the two cracker products

| Ingredient             | Glucose + fructose (mg/kg) | Free asparagine (mg/kg) | Contribution to total reducing sugars (%) | Contribution to total free asparagine (%) |
|------------------------|----------------------------|-------------------------|---|---|
| <b>Wheat cracker:</b>  |                            |                         |   |   |
| Flour (type 400)       | 822                        | 63                      | 6.9                                       | 100                                       |
| Sucrose                | 155                        | 0                       | < 0.1                                     | 0   |
| Inverted sugar syrup   | 597 275                    | 0                       | 92.8                                      | 0   |
| Condensed milk         | 564                        | 0                       | 0.2                                       | 0   |
| Raw dough              | 7 228                      | 38                      | 100                                       | 100                                       |
| <b>Potato cracker:</b> |                            |                         |   |   |
| Potato flakes          | 2 088                      | 6 000                   | 77  | 99.1                                      |
| Flour (type 550)       | 1 069                      | 96                      | 23  | 0.9                                       |
| Starch preparation     | 0                          | 0                       | 0   | 0   |
| Raw dough              | 836                        | 1 869                   | 100                                       | 100                                       |

factor for acrylamide formation and a starting point to decrease the acrylamide content in this product. The situation for the potato cracker was different: The potato flakes were the main source for free asparagine and for reducing sugars. The flour type 550 was a relevant source for reducing sugars only although it contained more of free asparagine and reducing sugar than type 400. The content of sugars and free amino acids in cereal flour depends on the degree of extraction during milling, and thus the flour type can influence acrylamide formation in bakery [10]. The dough of the potato cracker contained about twice as much free asparagine than reducing sugars. Compared to the wheat cracker, it contained 49 times more of free asparagine which shows the different nature of the two products. The potato cracker resembles more a potato than a bakery product. This difference is also demonstrated by the acrylamide contents: On average, the wheat cracker contained 339 µg acrylamide per kg (relative standard deviation between batches: 9%) whereas the mean acryla-

mid content in the potato cracker was 833 µg/kg (relative standard deviation between batches: 55%). In overbaked potato crackers acrylamide contents exceeding 2000 µg/kg were determined. The higher acrylamide content and the stronger variation reflect the influence of the potato flakes and are typical for potato based products [1, 11, 12].

To reduce the acrylamide content of the wheat cracker, different approaches were made and the results are shown in Figure 1. If  $\text{NH}_4\text{HCO}_3$  in the baking agent was replaced by  $\text{NaHCO}_3$  the acrylamide content decreased by about 50% because the promoting effect of ammonia on acrylamide formation was eliminated [5, 6]. Replacing the inverted sugar syrup with sucrose decreased the acrylamide concentration by about 60% and a similar effect has also been observed in gingerbread [6]. The combination of these two approaches resulted in a 77% lower acrylamide content compared to the standard recipe and the product had good sensory properties and was well comparable to the standard product. The poorer leavening was corrected by

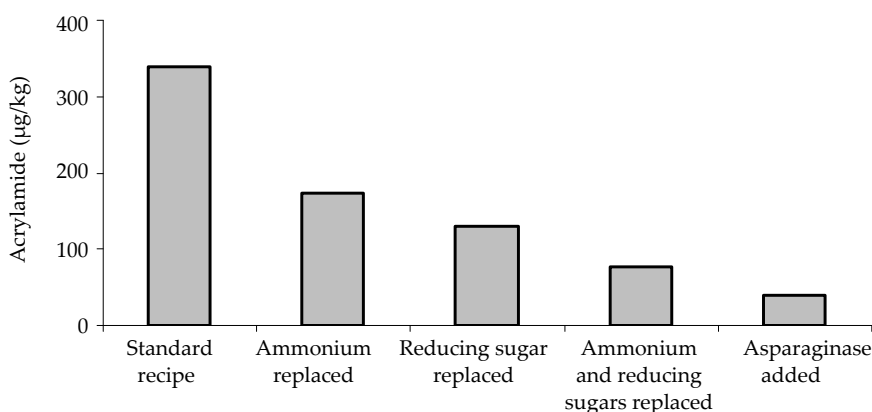


Figure 1. Effect of recipe changes on the acrylamide content of wheat cracker

adding some extra water to the dough which did not affect the acrylamide content.

In another experiment an asparaginase was added during the preparation of standard dough to decompose free asparagine and thus to eliminate the other crucial precursor for acrylamide formation. As a consequence, the product contained only little acrylamide (39 µg/kg), i.e. a reduction of 85% was achieved. Free asparagine was not fully hydrolyzed by this treatment which explains why still some acrylamide was formed. The efficacy and application of this enzyme was also shown in other matrices and deserves further investigation [4, 6]. Changes of baking conditions were not suitable to limit the acrylamide formation if a product with acceptable sensory properties was to be attained.

Due to the strong variation of the acrylamide content in the potato cracker a reference sample (standard recipe) had to be taken at the same time for every experiment to allow a correct interpretation. By inverting the ratio of potato flakes to wheat flour in the recipe the content of free asparagine was lowered by 40% and reducing sugars were decreased by 16%. As a consequence the acrylamide content decreased by 50% (from 557 to 274 µg/kg). The application of an asparaginase decreased free asparagine even more: The enzyme treated dough contained only 21 mg free asparagine per kg, i.e. 80 times less than the standard dough and thus, these baked potato crackers contained 70% less acrylamide (143 µg/kg; reference product: 489 µg per kg). The advantages of the use of asparaginase are: Recipe and process conditions remain the same and the product has virtually identical sensory properties. Another strategy for this product was to optimize baking conditions. If the baking profile was altered to decreasing temperatures, i.e. starting at 230°C and ending at 190°C, the acrylamide content decreased by 59% (reference: 1186 µg/kg; altered baking profile: 484 µg/kg). The end conditions during the heating process are a critical factor for acrylamide formation in the potato cracker which was also observed for French fries [13].

## CONCLUSIONS

The application of an asparaginase during dough preparation can reduce the acrylamide content of cracker products by at least 70% and thus deserves further investigations. The baking agent  $\text{NH}_4\text{HCO}_3$  promotes acrylamide formation and its replacement by  $\text{NaHCO}_3$  is another way to limit

the acrylamide formation in crackers. Minimizing reducing sugars in the ingredients or the use of a sucrose solution instead of inverted sugar syrup can also help to produce crackers with lower acrylamide content. For potato crackers the end temperature of the baking process should be lowered to contain the acrylamide formation. These strategies allow for the production of wheat and potato cracker products with lower acrylamide content and good sensory properties.

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