AGRICULTURAL AND FOOD CHEMISTRY

Effective Ways of Decreasing Acrylamide Content in Potato Crisps during Processing

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The aim of this work was to examine the effect of blanching or soaking in different acid solutions on the acrylamide content in potato crisps. Furthermore, the effects of a shorter frying time and a lower frying temperature combined with a postdrying were investigated. Soaking or blanching of potato slices in acidic solutions decreased the pH of potato juice and increased the extraction of amino acids and sugars. Potato crisps obtained after such pretreatments were characterized by lower acrylamide content. The most effective extraction of free amino acids and sugars as well as the largest decrease of acrylamide content (90%) in crisps was obtained when potato slices were soaked in acetic acid solution for 60 min at 20 °C. Shorter frying time followed by postdrying resulted in low-moisture potato crisps. Furthermore, the postdrying treatment gave a decreases in acrylamide content of ~70% when potato slices were fried at 185 °C and ~80% when potato slices were fried at 160 °C. Effective ways of decreasing acrylamide content in crisps production have been found. Crisps with low acrylamide content and good sensory quality can be obtained either by blanching in acetic acid as pretreatment or by a short frying followed by postdrying.

KEYWORDS: Acrylamide; potato crips; soaking; blanching; postdrying

INTRODUCTION

Potato crisps are one of the most popular snack products in the world. They are also among the products that have been reported to have the highest levels of acrylamide. Because acrylamide is a potential carcinogen, several works have been devoted to the study of the mechanism of its formation and the factors influencing its formation (1-12). Still, there are few solutions on how to decrease acrylamide creation during processing (13, 14). One of the possibilities could be decreasing the content of acrylamide precursors: reducing sugars and asparagine by soaking or blanching of potato slices. When water has been used for that kind of pretreatment, the results have been inconclusive, having no, very little, or a significant effect on the amount of acrylamide formed during frying (13, 15). It has been suggested that lowering the pH during processing limits acrylamide formation. Jung et al. (14) found that blanching or soaking in a citric acid solution before baking or frying greatly reduced acrylamide formation in corn chips and French fries.

It is possible that such treatment could also be introduced in crisps production.

The critical point when acrylamide is formed during crisps processing is frying. It has been shown that the most important factors influencing acrylamide formation are temperature and time of frying (5, 8, 13). It is suggested that frying temperature should be below 175 °C and time of frying should be no longer than necessary to obtain the right quality parameters of fried products. However, a lower frying temperature will influence the fat content and the moisture of crisps (16, 17). The moisture is one of the critical quality factors of potato crisps because it affects the texture, which should be crispy not only after frying but also during several months of storage (18). In general, the moisture of crisps should be very low, not higher than 2%. This is easy to obtain when crisps are fried in hot oil (usually at 185–190 °C). Decreasing the frying temperature necessitates increasing the frying time, which could affect the acrylamide content. To limit acrylamide formation during relatively long frying times, we introduced a new step in crisps processingpostdrying (Figure 1).

The aim of this work was to examine the effect of blanching or soaking in different acid solutions. In addition, the effects of a reduced time and temperature during frying combined with

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Figure 1. Potato crisp processing steps—possibilities of decreasing acrylamide formation.

a postdrying step on the acrylamide content in potato crisps were investigated.

MATERIALS AND METHODS

Chemicals. Citric acid, acetic acid (98%), NaOH, glucose, fructose, sucrose, and mannitol were obtained from Merck (Darmstadt, Germany). Acrylamide was supplied by Sigma (Deisenhoffen, Germany) and deuterium-labeled d_3 -acrylamide by CIL (Cambridge Isotope Laboratories Inc., Andover, MA). All other solvents and chemicals used were of analytical grade.

Raw Material. For crisps production three different potato varieties were used: Tivoli and Saturna, stored for 1-2 months at 8 °C, and Asterix, stored at 4 °C for 1 month. All potatoes came from specialized farms in Norway. Storage was conducted in a storage room with monitored temperature and moisture.

Soaking or Blanching in Acid Solutions. Potato tubers of the varieties Tivoli and Asterix were washed, peeled, and sliced (1 mm) (slicer machine Crypto Peerless Ltd.). After a rinse in water, 500 g of potato slices was soaked (1 min at 20 °C or 60 min at 20 °C) or blanched (1 min at 70 °C or 3 min at 70 °C) in water, 0.05 M citric acid solution, and 0.15 M acetic acid solution (both acid solutions having the same concentration of acidic protons) (all experiments with solution/potato = 20:1). In addition, soaking in a 1% NaOH solution was used. The slices were dried using paper towels, and 100 g samples were fried for 4 min in 10 L of palm oil heated at 175 °C in an electric frying pan (Masterline). After soaking or blanching, the pH in potato juice and sugars and amino acids contents in freeze-dried material were measured. In crisps, acrylamide content was measured. All experiments were run in duplicates.

Postdrying of Potato Crisps. Potato tubers of the variety Saturna were washed, peeled (carborundum peeler, Millert B.V., Ulft, Holland), and sliced (1.5 mm) (slicing machine, Brown). After rinsing in water and drying (paper towels), 100 g of potato slices was fried in a 10 L electric frying pan (Elframo) for 3-7 min in palm oil at 160 °C and for 2-5 min in palm oil at 185 °C. After frying, potato slices were dried in a hot air oven (105 °C) (WTB Binder) for 30-120 min. After frying and postdrying, the moisture and acrylamide contents were measured. The experiment was conducted according to a central composite design.

Sugars Analysis. The concentrations of sucrose, fructose, and glucose in potatoes were quantified using an HPLC technique based on that of Coop et al. (19) with a few modifications. A 5 g sample of freeze-dried potato tubers was shaken with 25 mL of 50% methanol with 1.5 mg/mL mannitol as an internal standard. Activated carbon (2.5 g) was added, and the suspension was shaken for 100 min at room temperature. The samples were filtered by paper filters, and the filtrate

Table 1. Sugars and Amino Acids Contents in Potato Tubers

	potato variety				
	Tivoli ^a (mg/kg)	Asterix ^a (mg/kg)			
sucrose	1405 a	1440 a			
glucose	270 a	2040 b			
fructose	79 a	1200 b			
aspargine	3168 b	2661 a			
glutamine	4423 b	3115 a			

^a Different letters in the same row indicate significant differences ($P \leq 0.05$).

Table 2.	Effect	of	Soaking	or	Blanching	in	Acid	Solutions	on	pН	of
Potato Ju	uice										

soaking/ blanching	soaking/ blanching	soaking/ blanching	р	рН ^а		
solution	temp (°C)	time (min)	Tivoli	Asterix		
raw material			6.05 c	6.10 c		
water	20 70	1 60 1 3	6.05 c 5.95 c 6.05 c 6.00 c	6.10 c 6.10 c 6.10 c 5.95 c		
citric acid	20 70	1 60 1 3	4.95 b 4.15 a 4.60 ab 3.85 a			
acetic acid	20	1 60	4.95 b 3.70 a	4.90 b 3.85 a		
	70	1 3	4.25 ab 4.00 a	4.60 ab 4.20 a		
NaOH	20	1 60		11.40 d 12.00 d		

^a Different letters indicate significant differences ($P \le 0.05$).

was collected. Five milliliters of the filtrates was incubated at 35 °C for 16 h, and precipitates were removed by centrifugation. One milliliter of filtrate was evaporated by vacuum centrifugation (ISS110 SpeedVac, Termo Savant) and redissolved in 1 mL of distilled water. After filtration through Millex-HV (0.45 μ m, 13 mm), the samples were analyzed by HPLC on a Shimadzu pump (LC-10AD) controlled by Class VP software. Twenty microliters of sample was injected with an SIL-10 autoinjector into a Varian Carbohydrate PB column (300 × 7.8 mm) eluted with water (0.4 mL/min) at 80 °C and equipped with a refractive detector (RID-6A). The sugars were quantified on the basis of their areas relative to the internal standard, corrected for their individual response factors. All samples were analyzed in duplicates.

Amino Acids Analysis. Amino acids were analyzed using an HPLC (series 410) pump, an ISS 200 autoinjector (series 200) column oven, an LC240 fluorescence detector, a Turbochrom version 4.1 LC terminal, and a 900 series interface (Perkin-Elmer, Norwalk, CT) equipped with a Hypersil ODS 4 \times 4 mm precolumn and a 250 \times 4 mm column, both with a particle size of 5.0 μ m (Agilent, Wilmington, DE). The precolumn derivatization method of Bütikofer and Ardö (20) with O-phthaldialdehyde (OPA) and fluorenylmethyl chloroformate (FMOC) was used, but the internal standard contained 0.5 µmol/mL L-norvalin and 0.5 µmol/mL piperidine-4-carboxylic acid (PICA) (Merck). Extraction, deproteination, and derivatization of the amino acids were made by dispersing 1 g of freeze-dried potatoes in 10 mL of 0.1 M HCl containing the internal standards mentioned above, according to the method of Ardö and Polychroniadou (21). The amino acid standards were delivered by Pierce (Erembodegem, Aalst, Belgium), the L-amino acid kit was from Sigma (St. Louis, MO), OPA, FMOC, and borate buffer were from Agilent, and sodium acetate trihydrate, tritriplex III, and tetrahydrofuran were from Merck.

Acrylamide Analysis. Crisps were ground by a c-mill electrical coffee grinder (Bodum, Switzerland) and stored at -20 °C until

Table 3. Extraction of Asparagine and Sugars from Potato Slices: Percentages Related to the Initial Content

					extr	action (%)		
soaking/blanching	soaking/blanching	soaking/blanching time (min)	asparagine		sucrose		glucose	fructose
solution	temp (°C)		Tivoli	Asterix	Tivoli	Asterix	Asterix	Asterix
water	20	1	6	7	14	5	2	5
		60	9	40	16	17	22	17
	70	1	4	16	7	8	17	15
		3	11	34	15	18	35	32
citric acid	20	1	8		8			
		60	18		13			
	70	1	26		25			
		3	31		42			
acetic acid	20	1	22	30	14	0	19	9
		60	83	76	83	78	65	63
	70	1	19	22	31	14	21	20
		3	38	36	41	38	48	46
NaOH	20	1		38		78	99	99
		60		89		80	99	99

Table 4.	Acrylamide	Content in	Potato	Crisps	after	Soaking or
Blanching	Potato Sli	ces in Acid	Solution	ns		-

soaking/	soaking/	soaking/	acrylamide			
blanching	blanching	blanching	content ^a	reduction		
solution	temp (°C)	time (min)	(μ g/kg)	(%)		
water	20	1	550 d	10		
		60	438 c	24		
	70	1	472 c	19		
		3	428 c	26		
citric acid	20	1	399 b	31		
		60	289 b	50		
	70	1	438 c	24		
		3	293 b	49		
acetic acid	20	1	329 b	43		
		60	60 a	90		
	70	1	336 b	42		
		3	293 b	49		

^a Different letters indicate significant differences ($P \le 0.05$).

analysis. Two grams of the homogenized sample was defatted with 80 mL of *n*-hexane. To the residue were added and mixed 20 mL of water, 200 μ L of internal standard, *d*₃-acrylamide (10 μ g/mL). Acrylamide was extracted by sonication for 30 min. The sample was purified by adding 500 μ L of Carrez I and Carrez II, respectively. The samples was centrifuged at 4000 rpm for 10 min, and the supernatant (3 mL) was filtered through SPE columns Isolute Multimode 300 mg (ITS, Hengoed, U.K.) pretreated with acetonitrile (1 mL) and water (2 × 2 mL). The first portion (1 mL) was discarded, and the remaining portion was collected and passed through a 0.22 μ m syringe filter Millex-GS (Millipore, Bedford, MA). The filtrate was frozen and stored for later analysis. Five hundred microliters of filtrate was passed through a centrifuge spin filter, Microcon YM-3 (Millipore) (13000 rpm, 10–20 min) until a sufficient volume had been obtained for analysis with LC-MS-MS.

The analysis of acrylamide was done by the Norwegian Air Research Institute (NILU), using a method similar to that of Rosén and Hellenäs (7), using high-resolution time-of-flight mass spectrometry instead of tandem mass spectrometry. Acrylamide was separated from the sample matrix by using a high-performance liquid chromatography (HPLC) Agilent HP-1100 system. The chromatographic separation was performed with a Waters Atlantis precolumn in front of an analytical column (3.9 mm × 20 mm, 3 μ m, no. 186001313, and 3.9 × 150 mm, 3 μ m, no. 186001317, respectively). The injection volume was 100 μ L, and the mobile phase was 100% water at a flow rate of 0.8 mL/ min up to 6 min with a subsequent column flushing (100% acetonitrile).
 Table 5. Most Effective Ways of Decreasing Acrylamide Content in

 Potato Crisps during Processing

treatment	decrease (%)
soaking in citric acid solution (60 min/20 °C)	50
soaking in acetic acid solution (60 min/20 °C)	90
blanching in citric acid solution (3 min/70 °C)	49
blanching in acetic acid solution (3 min/70 °C)	49
frying for 2 min/185 °C and postdrying for 75 min/105 °C	69
frying for 3 min/160 °C and postdrying for 75 min/105 °C	83

The detector was a Micromass LCT orthogonal time-of-flight (TOF) mass spectrometer equipped with a Z-spray ion source operated in the atmospheric pressure chemical ionization positive mode APCI(+). The cone voltage was 15 V, and the monitoring ions were m/z 72 and 75 for acrylamide and the internal standard, respectively, with a signal peak width of typically 30 mDA. The limit of detection (signal-to-noise ratio of 3) depends on instrument tuning and ion source contamination and corresponds typically to $10-30 \mu g/kg$ acrylamide in the sample.

Statistical Analysis. Statistical analysis of the data was performed using Minitab, version 14. Tukey's multiple-range tests were performed to determine significant differences ($P \le 0.05$) among treatment means.

RESULTS AND DISCUSSION

Soaking or Blanching in Acid Solutions. The potato varieties used for crisps production varied in sugars and amino acids contents (**Table 1**). In the first experiment only Tivoli was used. Soaking in acid decreased the pH of the potato juice (**Table 2**). However, due to the low reducing sugars contents in Tivoli, soaking and blanching were repeated with the potato variety Asterix. Only water and acetic acid were used in this case because acetic acid was more effective in reducing the pH in the first experiment.

As shown in **Table 2** there were no changes in the pH of potato juice when water was used for soaking or blanching. Most effective in decreasing pH was soaking for 1 h at 20 °C in acetic acid solution (pH <4). Quite satisfactory results (pH <4.2) were also obtained after blanching for 3 min at 70 °C in both acids. Soaking or blanching changed the chemical composition of the potato slices by removing reducing sugars as well as amino acids (**Table 3**). When pure water was used, the most efficient extraction of reducing sugars was observed after 3 min of blanching at 70 °C.



Figure 2. Effect of frying time on moisture of potato crisps.



Figure 3. Response surface plot of moisture in potato crisps after frying at 160 °C (a) and at 185 °C (b) followed by postdrying: (•) measured values.

Similar results have been obtained by other authors (13, 15) after soaking or blanching potato slices for different periods of time at different temperatures.

Much more interesting results were observed when acids or bases were used for pretreatment. The most efficient extraction of sugars (60-80%) as well as of asparagine (80%) was observed after soaking of potato slices in acetic acid or NaOH solutions for 60 min at 20 °C. Citric acid reduced the content of these components by <20%. However, in citric acid efficient extraction of sugars and asparagine (~40%) was obtained after blanching for 3 min at 70 °C.

The different treatments of potato slices before frying influenced acrylamide content in crisps (**Table 4**). Soaking or blanching of potato slices in all solutions used decreased the acrylamide content. The highest decrease (90%) was observed after soaking of potato slices in acetic acid solution (60 min/20 °C). Furthermore, a 50% decrease of acrylamide content in crisps was obtained after only 3 min of blanching at 70 °C in both acid solutions. Due to variability known to be present between potato tubers, exact reductions are impossible to give, but on the basis of our results the reduction should be in the range of 40–60% in a real situation. Such results suggest that it is possible in an easy way to decrease acrylamide creation during crisps production.

However, a sour taste was detected with the citric and acetic acid when slices were soaked in those solutions for 60 min (data not presented). A slight sour taste was detected also in crisps blanched for 1 or 3 min at 70 °C in citric acid solution, but no detectable taste differences were observed when acetic acid was used. This suggests that acetic acid could be a better acidulant for the pretreatment for potato crisps.

A large decrease of acrylamide content (74%) was also observed after soaking of potato slices in 1% NaOH solution (results not shown), but the base solution influenced the appearance as well as the taste and flavor of crisps, which were not sensorially acceptable. The results show that it is possible to decrease acrylamide content also with an increase of pH, most probably due to the removal of sugars and amino acids. However, more investigations with respect to which actual base or its concentration are needed to define a process.

Postdrying of Potato Crisps. The moisture content of crisps depended on frying temperature as well as on frying time



Figure 4. Acrylamide content in potato crisps fried at 160 and 185 °C.



Figure 5. Decrease of acrylamide content in potato crisps produced with postdrying.

(Figure 2). It was possible to obtain a low-moisture product after frying at 185 °C for 4.5 min, whereas when the frying temperature was lower (160 °C), the minimum frying time was 2.5 min longer. After a longer or shorter postdrying step, there was no problem in obtaining low moisture in the final product (Figure 3). The apparent increase in dry matter at long frying and drying times probably is a result of the second-order regression and is probably not real.

At both frying temperatures decreased frying times followed by postdrying resulted in a decrease in acrylamide content in the crisps (**Figure 4**). When crisps were fried in oil at 185 °C, it was possible to obtain a 70% decrease of acrylamide content after 2 min of frying and 75 min of postdrying. An even larger decrease was observed after frying at 160 °C. In this case it was possible to decrease acrylamide content in crisps by >80% if, after 3 min of frying, the crisps were dried for 75 min (**Figure 5**). This shows that it is possible to decrease acrylamide content by postdrying during crisps prodution.

The products had taste and mechanical properties (data not presented) comparable to those of regular processed products. A full sensory evaluation will be performed after a pilot-scale processing, taking advantage of the findings obtained by the postdrying procedure in the present work.

LITERATURE CITED

- (1) Amrein, T. M.; Bachman, S.; Noti, A.; Biedermann, M.; Ferraz Bardosa, M.; Biedermann-Brem, S.; Grob, K.; Keiser, A.; Realini, P.; Escher, F.; Amado, R. Potential of acrylamide formation, sugars, and free asparagine in potatoes: a comparison of cultivars and farming systems. *J. Agric. Food Chem.* **2003**, *51*, 5556–5560.
- (2) Becalski, A.; Lau, B. P. Y.; Lewis, D.; Seaman, S. W. Acrylamide in foods: occurrence, sources, and modeling. J. Agric. Food Chem. 2003, 51, 802–808.
- (3) Biedermann, M.; Biedermann-Brem, S.; Noti, A.; Grob, K. Methods for determining the potential of acrylamide formation and its elimination in raw materials for food preparation, such as potatoes. *Mitt. Lebensm. Hyg.* **2002**, *93*, 653–667.
- (4) Friedman, M. Chemistry, biochemistry, and safety of acrylamide. A review. J. Agric. Food Chem. 2003, 51, 4504–4526.
- (5) Gertz, Ch.; Klostermann, S. Analysis of acrylamide and mechanisms of its formation in deep-fried products. *Eur. J. Lipid Sci. Techonol.* 2002, *104*, 762–771.
- (6) Mottram, D. S.; Wedzicha, B. L. Acrylamide is formed in the Maillard reaction. *Nature* 2002, *419*, 448–489.
- (7) Rosen, J.; Hellenäs, K. E. Analysis of acrylamide in cooked foods by liquid chromatography tandem mass spectrometry. *Analyst* 2002, *127*, 880–882.

- (8) Rydberg, P.; Erickson, S.; Tareke, E.; Karlsson, P.; Ehrenberg, L.; Törnqvist, M. Investigations of factors the influence the acrylamide content of heated foodstuffs. J. Agric. Food Chem. 2003, 51, 7012–7018.
- (9) Tareke, E.; Rydberg, P.; Karlsson, P.; Eriksson, S.; Törnqvist, M. Acrylamide: a cooking carcinogen? *Chem. Res. Toxicol.* 2002, 13, 517–522.
- (10) Tareke, E.; Rydberg, P.; Karlsson, P.; Eriksson, S.; Törnqvist, M. Analysis of acrylamide, a carcinogen formed in heated foodstuffs. J. Agric. Food Chem. 2002, 50, 4998–5006.
- (11) Yaylayan, V. A.; Wronowski, A.; Perez Locas, C. Why asparagine needs carbohydrates to generate acrylamide. *J. Agric. Food Chem.* 2003, *51*, 1753–1757.
- (12) Zyzak, D. V.; Sanders, R. A.; Stojanovic, M.; Tallmagde, D. H.; Ebenhart, B. L.; Ewald, D. K.; Gruber, D. C.; Morsch, T. R.; Strothers, M. A.; Rizzi, G. P.; Villagran, M. D. Acrylamide formation mechanism in heated foods. *J. Agric. Food Chem.* **2003**, *51*, 4782–4787.
- (13) Grob, K.; Biedermann, M.; Biedermann-Brem, S.; Noti, A.; Imhof, D.; Amrein, T.; Pfefferle, A.; Bazzocco, D. French fries with less than 100 μg/kg acrylamide. A collaboration between cooks and analyst. *Eur. Food Res. Technol.* **2003**, *271*, *3*, 185– 194.
- (14) Jung, M. Y.; Choi, D. S.; Ju, J. W. A novel technique for limitation of acrylamide formation in fried and baked corn chips and in French fries. J. Food Sci. 2003, 68, 1287–1290.
- (15) Haase, N. U.; Matthäus, B.; Vosmann, K. Acrylamide formation in foodstuffs—Minimizing strategies for potato crisps. *Dtsch. Lebensm,-Rundsch.* 2003, 99, 87–90.

- (16) Gamble, M. H.; Rice, P.; Selman, J. D. Relationship between oil uptake and moisture loss during frying of potato slices from cv. Record U.K. tubers. *Int. J. Food Sci. Technol.* **1987**, *22*, 233– 241.
- (17) Rice, P.; Gamble, M. H. Technical note: modelling moisture loss during potato slice frying. *Int. J. Food Sci. Technol.* **1989**, 24, 183–187.
- (18) Lisiñka, G.; Leszczyński, W. Potato Science and Technology; Elselvier Applied Science: London, U.K., 1989; pp 166–205.
- (19) Copp, L. J.; Blenkinsop, R. W.; Yada, R. Y.; Marangoni, A. G. The relationship between respiration and chip color during longterm storage of potato tubers. *Am. J. Potato Res.* 2002, 77, 279– 287.
- (20) Bütikofer, U.; Ardö, Y. Quantitative Determination of Free Amino Acids in Cheese. Chemical Methods for Evaluating Proteolysis in Cheese Maturation, Part 2; International Dairy Federation: Brussels, Belgium, 1999; pp 24–32.
- (21) Ardö, Y., Polychroniadou, A., Eds. Analysis of free amino acids and amines. In *Laboratory Manual for Chemical Analysis of Cheese*; Office for Official Publications of the European Communities: Luxembourg, 1999; pp 67–78.

Received for review May 7, 2004. Revised manuscript received August 26, 2004. Accepted September 5, 2004.

JF049269I