

Reduction of acrylamide formation in potato slices during frying

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Abstract

Reduction of acrylamide formation in potato chips was investigated in relation to frying temperature and three treatments before frying. Potato slices (Tivoli variety, diameter: 37 mm, width: 2.2 mm) were fried at 150°C, 170°C and 190°C until reaching moisture contents of ~1.7 g water/100 g (total basis). Prior to frying, potato slices were treated in one of the following ways: (i) soaked in distilled water for 0 min (control), 40 min and 90 min; (ii) blanched in hot water at six different time–temperature combinations (50°C for 30 and 70 min; 70°C for 8 and 40 min; 90°C for 2 and 9 min); (iii) immersed in citric acid solutions of different concentrations (10 and 20 g/l) for half an hour. Glucose and asparagine concentration was determined in potato slices before frying, whereas acrylamide content was determined in the resultant fried potato chips. Glucose content decreased in ~32% in potato slices soaked 90 min in distilled water. Soaked slices showed on average a reduction of acrylamide formation of 27%, 38% and 20% at 150°C, 170°C and 190°C, respectively, when they were compared against the control. Blanching reduced on average 76% and 68% of the glucose and asparagine content compared to the control. Potato slices blanched at 50°C for 70 min surprisingly had a very low acrylamide content (28 µm/kg) even when they were fried at 190°C. Potato immersion in citric acid solutions of 10 and 20 g/l reduced acrylamide formation by almost 70% for slices fried at 150°C. For the three pre-treatments studied, acrylamide formation increased dramatically as the frying temperature increased from 150°C to 190°C.

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1. Introduction

Frying is a widely used cooking method that creates unique textures and flavors in foods. Potatoes (*Solanum tuberosum*), one of the world's major crops, is consumed daily by millions of people from diverse cultural backgrounds. Potato chips, have been popular salty snacks for 150 years and its retail sales in US are about \$6 billion/year representing 33% of the total sales on this market (Garayo & Moreira, 2002; Clark, 2003).

Reports of the presence of acrylamide in a range of fried and oven-cooked foods have caused worldwide concern because this compound has been classified as probably carcinogenic in humans (Rosen & Hellenäs, 2002; Tareke, Rydberg, Karlsson, Eriksson, & Tornqvist, 2002). In April 2002, Swedish researchers shocked the food safety world when they presented preliminary

findings of acrylamide in some fried and baked foods, most notably potato chips and French fries, at levels of 30–2300 µm/kg. As acrylamide has not been detected in unheated or boiled foods, it was considered to be formed during heating at high temperatures. They attributed this fact to the higher temperatures reached in Maillard nonenzymatic browning reactions required for desirable color, flavor and aroma production (Coughlin, 2003). The data published so far indicate that a temperature >100°C is required for acrylamide formation (Becalski, Lau, Lewis, & Seaman, 2003). Tareke et al. (2002) showed that acrylamide was formed by heating above 120°C certain starch-based foods, such as potato chips, French fries, bread and processed cereals.

Recently, research has focused on possible mechanisms of acrylamide formation in foods (Zyzak et al., 2003). Some international research groups have separately confirmed a major Maillard reaction pathway for acrylamide formation (Coughlin, 2003). Mottram and

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Wedzicha (2002) showed how acrylamide could be formed from food components during heat treatment as a result of the Maillard reaction between amino acids and reducing sugars. Stadler et al. (2002) have shown also that acrylamide can be released by the thermal treatment of certain amino acids such as asparagine, particularly in combination with reducing sugars, and of early Maillard reaction products (*N*-glycosides). Weißhaar and Gutsche (2002) found from model experiments that the amount of acrylamide increases dramatically if asparagine was heated in the presence of glucose or fructose. Acrylamide formation in potatoes was significantly lower, if they were treated with asparaginase (*L*-asparagine amidohydrolase) before heating.

Asparagine, a major amino acid in potatoes and cereals, is a crucial participant in the production of acrylamide by Maillard reaction at temperatures above 100°C (Friedman, 2003). Since potato products are especially high in asparagine, it is now thought that this Maillard reaction is most likely responsible for the majority of the acrylamide found in potato chips and French fries. Martin and Ames (2001) found that asparagine was the free amino acid present in the highest amount in potatoes (93.9 mg/100 g). Asparagine content in potatoes depends on factors like variety, location, fertilization, storage and processing (Davies, 1977; Hippe, 1988). Moreover, the fact that fried potato products are the food commodity with highest (detected to date) amounts of acrylamide might be related to the relatively high concentration of free asparagine in potatoes.

Potential of acrylamide formation is also related to the sugar content such as glucose and fructose (Biedermann, Biedermann-Brem, Noti, & Grob, 2002). For instance, some authors reported that the reduction of the sugar content by blanching or soaking could decrease acrylamide concentration by about 60% in potato chips (Haase, Matthäus, & Vosmann 2003). Wide variations of acrylamide concentration in foods are, at least partially, caused by different levels of precursors of acrylamide in various batches of raw materials (levels of asparagine and sugars fluctuate widely in raw potato tubers). Both potato variety and field site had a noticeable influence upon acrylamide formation. In addition to food composition, other factors involved in acrylamide formation are the processing conditions (pre-treatments, temperatures and times).

Jung, Choi, and Ju (2003) showed that lowering the pH with citric acid before frying was an efficient way to considerably diminish acrylamide formation in French fries. On the other hand, some authors reported that by lowering frying temperature of potato chips from 185°C to 165°C, it was possible to reduce the acrylamide formation to a half (Haase et al., 2003). These results suggest that there may be ways to reduce or prevent

acrylamide formation by changing production and preparation methods. The objective of this work was to study ways of reducing acrylamide formation in potato chips processed under different conditions and determine its relation to the frying temperature and the contents of some important acrylamide precursors such as glucose and asparagine.

2. Materials and methods

2.1. Materials

Potatoes (variety Tivoli, 20 g/100 g of dry solids, higher diameter ≥ 7 cm) and vegetable oil (Fritao) were the raw materials. Potatoes stored at 8°C and 95% of relative humidity were washed and peeled in an industrial peeler IMC (model M591E4, England). Slices (thickness of 2.2 mm) were cut from the pith of the parenchymatous region of potato tubers using an electric slicing machine Robot coupe (model CL50B, France). A circular cutting mold was used to provide chips with a diameter of 37 mm.

2.2. Pre-treatments

Slices were rinsed immediately after cutting for 1 min in distilled water to eliminate some starch material adhering to the surface prior to frying. Then, 60 potato slices were soaked in 1 l of distilled water for the following times: 40 min and 90 min before frying. Rinsed slices in water without soaking treatment were considered as the control.

Blanching was accomplished by immersing 60 raw potato slices in 10 l of distilled water (ratio of potato to water (g/g) of ~ 0.015). The following temperature–time blanching treatments were applied over the potato slices: (i) 50°C for 30 min, (ii) 50°C for 70 min, (iii) 70°C for 8, (iv) 70°C for 40 min, (v) 90°C for 2 min, (vi) 90°C for 9 min.

Additionally, 60 raw potato slices were immersed in one liter of citric acid (J.T. Baker, Deventer, Holland) solution. The acid concentrations tested were 10 and 20 g/l, and the immersion time was 30 min.

All experiments were run in duplicate.

2.3. Frying conditions

Thirty slices of each pre-treatment were fried in an industrial fryer containing 100 l of oil at the following temperature–time conditions: (i) 150°C for 7 min, (ii) 170°C for 5 min, (iii) 190°C for 3.5 min. These frying conditions allowed the chips to reach final moisture contents of ~ 1.7 g water/100 g (wet basis). Frying temperature was maintained constant since the potato

mass to oil mass ratio (g/g) was kept very low (~ 0.00083).

2.4. Analysis

pH of the citric acid solutions and potato samples before and after the immersion of the slices was measured using a pH meter Metrohm (Model 691, Switzerland).

For sugar analysis, pre-treated samples (soaked in water, immersed in acid or blanched) of 40 g of randomly selected potato slices were frozen in a freezer at -24°C and then freeze-dried at 22°C in a Martin Christ freeze-drier (γ 1–20, Osterode, Germany). The dried material was treated in a micro hammer mill (Culatti, Bie and Berntsen, Rødovre, Denmark) equipped with a 1 mm sieve. Sugars were extracted from 100 mg freeze-dried material by adding 50 ml ultra pure boiling water generated by an Elgastat Maxima Analytica water purification system (Elga Ltd., England). The extracts were kept at room temperature for 3 h and then filtered through a $0.45\ \mu\text{m}$ AcetatePlus Cameo filter and diluted with water. Separation, identification and quantification were carried out as described by Kaack, Christensen, Hansen, and Grevsen (2004) using analytical high performance anion exchange chromatography (HPAEC) according to the method described by Campbell et al. (1997) with a few modifications.

Amino acids were extracted with an acetate buffer at pH 7.0 in water, derivatization of the amino acid hydrolysate with 6-aminoquinoline-hemi-succinylcarmin and quantification using reverse phase HPLC and gradient elution according to Cohen and Michaud (1993). Measurement of sugars and amino acids were carried out in two replicates.

For acrylamide analysis, acrylamide (2-propene amide) [CAS No. 79-06-1] ($>99.5\%$) was obtained from Sigma-Aldrich (St. Louis, MO, US). Labelled d3-acrylamide ($>98\%$) was from Polymer Source Inc. (Dorval, Quebec Canada). The SPE columns were Isolute Multimode 300 mg from International Sorbent Technology (Hengoed, Mid Glamorgan, UK). Mini uniprep Teflon filter vials $500\ \mu\text{l}$, filter pore size $0.45\ \mu\text{m}$, Whatman Int. Ltd (Kent, UK). The water used was MilliQ water (Millipore Corp., Bedford, MA, USA). The acetonitril was of HPLC grade from Rathburn Chemicals (Walkerburn, Scotland). Formic acid for the eluent (0.1% in water) was from Merck (Darmstadt, Germany). All stock solutions of acrylamide and d3-acrylamide (1000 and $10\ \mu\text{g/ml}$) as well as calibration standards (2–30 ng/l) were prepared in water and kept at -18°C until use.

4.00 g of homogenized potato were extracted with 40.0 ml MilliQ water by an Ultra-turrax mixer (Janke & Kunkel, Staufen, Germany) (after addition of $200\ \mu\text{l}$ d3-

acrylamide $10\ \mu\text{g/ml}$ as internal standard). Each analytical batch included 1–2 spiked samples for recovery measurements. The samples were centrifuged for 10 min. at 3500 rpm (Hereaus Sepatech Megafuge 3.0R (Osterode, Germany)). The clean up was made on 300 mg Isolute Multimode SPE columns (IST), using an ASPEC TM XLI automatic SPE clean up system (Gilson Inc., Middleton, WI, US). The SPE columns were conditioned with acetonitrile (1 ml) and water ($2 \times 2\ \text{ml}$). The first $500\ \mu\text{l}$ was discharged and the following $400\ \mu\text{l}$ of sample was collected in Mini uniprep Teflon filter HPLC vials.

A HP1100 HPLC system (Agilent Technologies, Palo Alto, CA, USA) was used for acrylamide separation on a Hypercarb column, $5\ \mu\text{m}$, $50\ \text{mm} \times 2.1\ \text{mm}$ (Thermo-Hypersil, Cheshire, UK, www.thermohypersil.co.uk) after a guard column (Phenomenex SecurityGuardTM, C18 ODS, $4\ \text{mm} \times 2.0\ \text{mm}$, Cheshire, UK). $10\ \mu\text{l}$ was injected and eluted with 0.1% formic acid in water at a flow of $250\ \mu\text{l/min}$. The MS/MS detection was performed on a Quattro Ultima triple quadrupole instrument with masslynx software (Micromass Ltd., Manchester, UK). The electrospray was operated in the positive ion mode, and the capillary was set to 3.0 kV, the cone voltage was 31 V, and the collision energy 10 eV. The source temperature was set at 120°C and the desolvation temperature at 400°C . Nitrogen was used as nebulizer gas (flow 500 l/h) and desolvation gas (flow 150 l/h), and argon was used as collision gas at a pressure of $2.3\text{e}-3\ \text{mbar}$. The multiple reaction monitoring (MRM) mode of the degradation patterns $m/z\ 72 \rightarrow 55$ (acrylamide) and $m/z\ 75 \rightarrow 58$ (d3-acrylamide) were used for quantification. Acrylamide analyses were done in a laboratory accredited for acrylamide analysis in foods by The Danish Accreditation Body.

2.5. Statistical analysis

Multiple analysis of variance was carried out using Statgraphic Statistical Package (Statistical Graphics Corporation, Version 4, Rockville, USA) including multiple range tests ($P > 0.05$) for separation of least square means.

3. Results and discussion

3.1. Soaking in water

Glucose content in potato slices decreased slightly as the soaking time in water increased due to the water extraction of this component (Fig. 1A). Other reducing sugars such as fructose and sucrose followed the same trend of glucose (results not shown). On the other hand, asparagine content tended to remain constant even for 90 min of soaking time. As shown in Fig. 1B there was

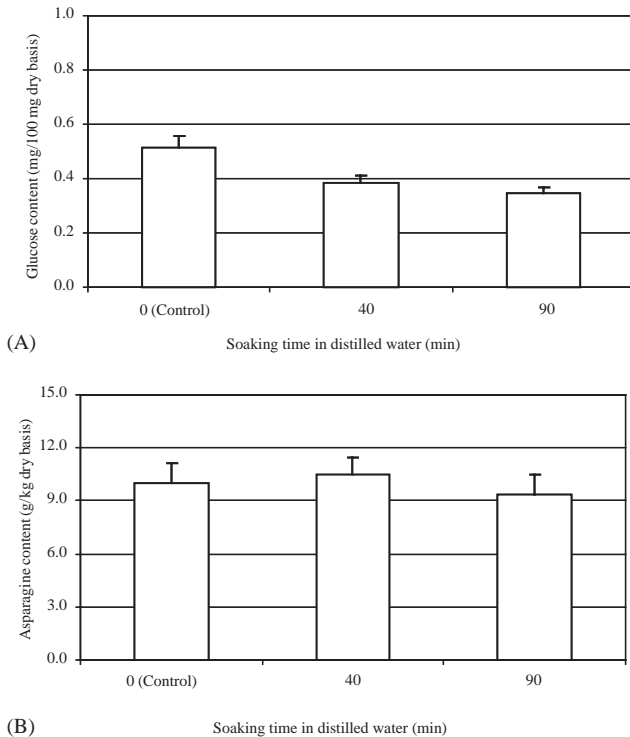


Fig. 1. (A) Glucose content of potato slices soaked 0 min (control), 40 min and 90 min in distilled water before frying. (B) Asparagine content of potato slices soaked 0 min (control), 40 min and 90 min in distilled water before frying.

no significant difference between the control and the soaked samples ($P < 0.05$). When comparing the control (no soaking in water) with samples soaked in water for 40 and 90 min, the decrease in glucose content was 25% and 32%, respectively, while asparagine content remained almost constant in 9.95 ± 0.99 g/kg dry basis. Davies (1977) and Hippe (1988) reported that asparagine is present in potatoes in varying, relative high amounts of 0.5–3% of dry matter, depending on factors like variety, location, fertilization, storage and processing. Both the fried control and soaked samples, showed a marked increase in acrylamide formation as the frying temperature increased from 150°C to 190°C (Fig. 2). The reduction of the frying temperature from 190°C to 170°C and to 150°C, decreased acrylamide formation with 68% and 88%, respectively (average values for control and soaked samples).

These results agree with those of Haase et al. (2003) who reported that by lowering the frying temperature from 185°C to 165°C, and from 190°C to 150°C, it was possible to reduce the acrylamide formation to a half and to a third, respectively. Average acrylamide contents for control and soaked samples were 552, 1530 and 4724 $\mu\text{g}/\text{kg}$ (ppb) after frying at 150°C, 170°C and 190°C, respectively. For the three temperatures tested, acrylamide formation was higher in the control than in soaked samples suggesting that the soaking

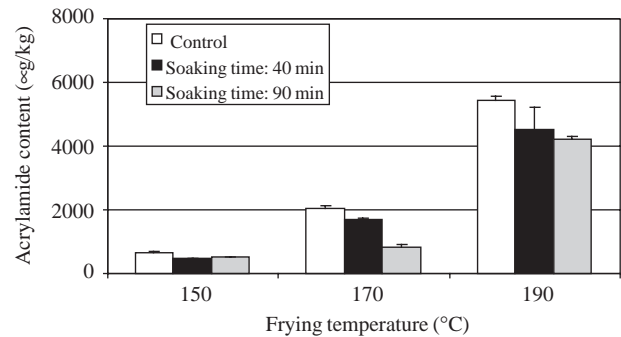


Fig. 2. Acrylamide content of potato slices soaked 0 min (control), 40 min and 90 min in distilled water after being fried at 150°C, 170°C and 190°C.

process leads to a higher leaching of one important acrylamide precursor such as glucose that finally results in lower acrylamide formation. Soaked samples (average values) showed a reduction in acrylamide formation of 27%, 38% and 20% at 150°C, 170°C and 190°C, respectively, when they were compared against the control. These results are coincident with those of Jung et al. (2003) who reported that dipping potato strips in distilled water for 1 h induced almost 25% reduction of acrylamide formation in French fries after frying at 190°C.

3.2. Blanching

Blanching was effective in removing not only glucose but also asparagine from potato slices (Figs. 3A and B). Blanching treatments reduced on average the glucose and asparagine content with 76% and 68% compared to the control (unblanched potatoes). The asparagine content in potato slices blanched at different time–temperature conditions before frying followed the same trend as the glucose content. Glucose and asparagine contents correlate well with acrylamide formation after frying for each of the temperatures tested (Fig. 4). As with the soaking treatment, acrylamide formation increased considerably in blanched samples when the frying temperature was increased. For instance, acrylamide contents were 306, 2197 and 3562 $\mu\text{g}/\text{kg}$ after frying at 150°C, 170°C and 190°C, respectively, in the case of potato slices blanched at 70°C for 8 min.

Long time blanching treatments such as that of 50°C for 70 min and 70°C for 40 min resulted in the lowest levels of acrylamide formation (18 and 60 $\mu\text{g}/\text{kg}$ as average values for the three frying temperatures). Surprisingly these two treatments, even at 190°C, lead to very low acrylamide contents (28 and 116 $\mu\text{g}/\text{kg}$, respectively). A reduction of the glucose and asparagine content by blanching potato slices at 50°C for 70 min and 70°C for 40 min could dramatically reduce the acrylamide content of potato slices with 97% and 91%,

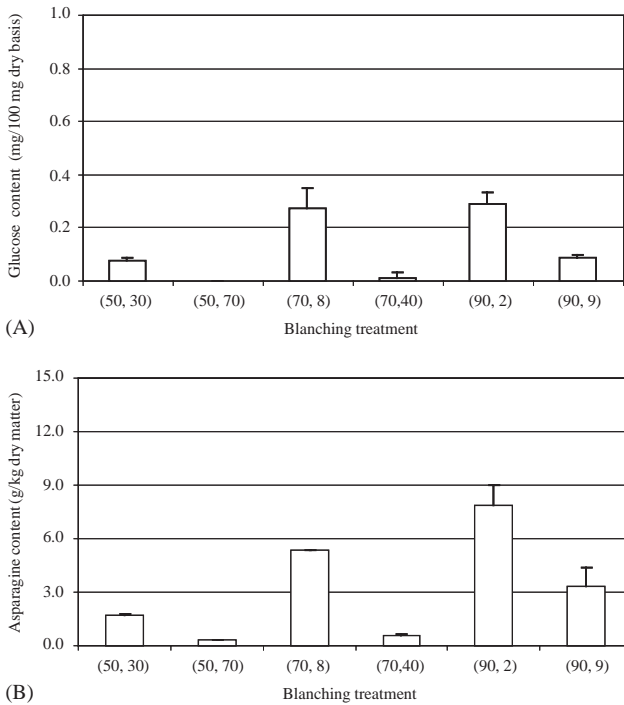


Fig. 3. (A) Glucose content of potato slices blanched in hot water at different temperature–time combinations before frying. (B) Asparagine content of potato slices blanched in hot water at different temperature–time combinations before frying. First numbers inside parenthesis indicate the blanching temperature (°C); second numbers indicate the blanching time (min).

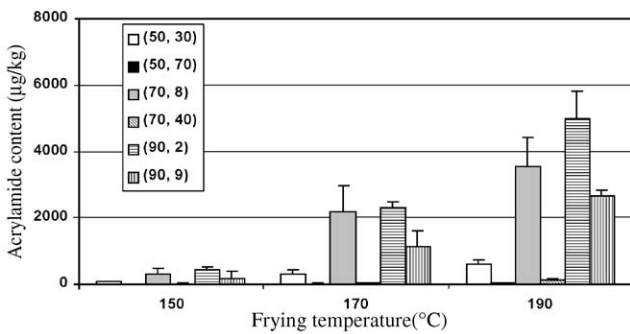


Fig. 4. Acrylamide content of potato slices blanched at different temperature–time combinations after being fried at 150°C, 170°C and 190°C. First numbers inside parenthesis indicate the blanching temperature (°C); second numbers indicate the blanching time (min).

respectively, compared to the control (average values for the three frying temperatures). Blanching in general, removes much more glucose and asparagine from the potato slices than the water soaking treatment consequently leading, to lower acrylamide formation in the resultant fried potatoes. Haase et al. (2003) reported that a reduction of the sugar content by blanching or soaking could reduce the acrylamide concentration by about 60% according to the raw material (potato variety and field site) and the production process variables (e.g. blanching conditions and frying tempera-

tures). Rydberg et al. (2003) showed that both addition of glucose and asparagine to the levels naturally occurring in potatoes would increase the acrylamide levels in fried potatoes. Blanched samples resulted in prepared potato chips lighter in color than those of the control or the samples soaked in water at ambient temperature (visual observations). Besides, as the frying temperature increased, the potato chips got darker as perceived by the naked eye.

3.3. Immersion in acid solutions

The effect of immersing potato slices in citric acid solutions of 10 and 20 g/l for 30 min on acrylamide formation after frying was also studied. pH of the 10 g/l citric acid solution before and after 30 min of slice immersion was 2.45 and 2.71, respectively. For the 20 g/l citric acid solution, the corresponding values were 2.25 and 2.50, respectively. pH of the potato slices decreased from ~6 to approximately 5 and 4.5 after being immersed 30 min in 10 and 20 g/l citric acid solutions, respectively (results not shown). Potato immersion in citric acid solutions of different concentrations (10 and 20 g/l) was not as effective as blanching in removing considerable amounts of glucose and asparagine from the raw slices before frying (Figs. 5A and B). There was no significant difference in the asparagine content

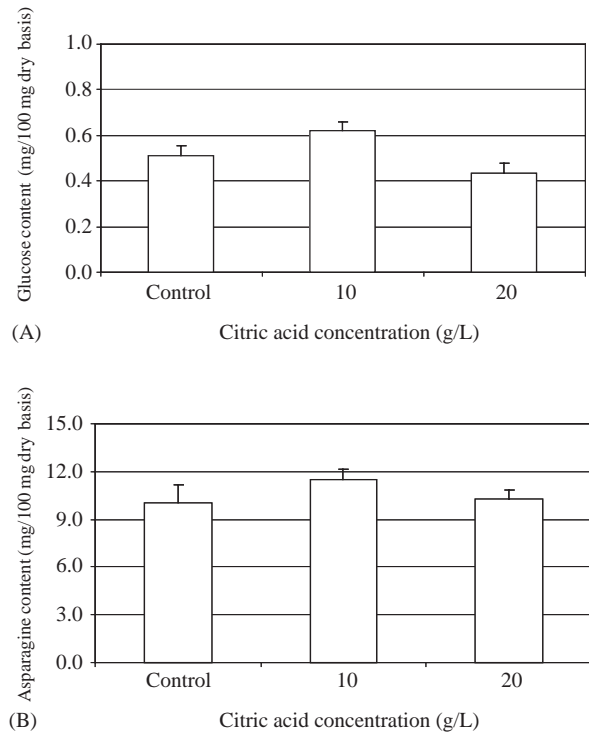


Fig. 5. (A) Glucose content of control and potato slices dipped in 10 and 20 g/l citric acid solutions for 30 min. (B) Asparagine content of control and potato slices dipped in 10 and 20 g/l citric acid solutions for 30 min. Control corresponds to potato slices not immersed in citric acid solutions.

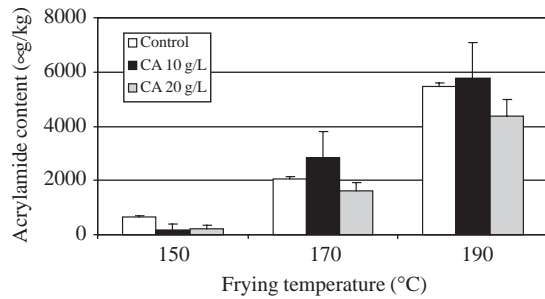


Fig. 6. Acrylamide content of control and potato slices dipped in 10 and 20 g/l citric acid solutions for 30 min after being fried at 150°C, 170°C and 190°C. Control corresponds to potato slices not immersed in citric acid solutions. CA: citric acid solution.

between acid immersed samples and the control ($P < 0.05$)—average value of 11 ± 0.79 g/kg dry solids. Glucose content of samples immersed in citric acid solutions was similar to that of the control (0.62 ± 0.04 and 0.44 ± 0.04 vs. 0.51 ± 0.04 mg/100 mg dry solids).

As in the previous pre-treatments studied, acrylamide formation increased drastically with increasing frying temperature—average values of 356, 2171 and 5198 µg/kg for 150°C, 170°C and 190°C, respectively (Fig. 6). At 150°C, slice immersion in citric acid solutions of 10 and 20 g/l reduced significantly acrylamide formation (~70%) with respect to the control. This result is coincident with that reported by Jung et al. (2003) who found that dipping potato strips in 10 and 20 g/l citric acid solutions induced 73.1% and 79.7% reduction of acrylamide formation in the resultant French fries when frying at 190°C. However in our frying experiments at 170°C and 190°C, this effect was not obvious since there was no detected significant difference ($P < 0.05$) in the acrylamide content between the acid immersed samples and the control. Jung et al. (2003) attributed the reduction of acrylamide formation in French fries by dipping the potato strips in citric acid solutions to both pH lowering and leaching out of free asparagine and the reducing sugars from the surface layer of potato cuts to the solutions. These authors also explain the mechanism by which lowering the pH of the potatoes reduces acrylamide formation after frying. Our results suggest that there was no significant removing of free asparagine and glucose that could explain the significant reduction of acrylamide formation in citric acid immersed samples after frying at 150°C. Finally, to the naked eye, fried samples previously immersed in acid solutions get as dark as fried unblanched samples previously soaked in water. Samples dipped in acid solutions after frying were much darker than fried blanched samples.

4. Conclusions

Soaking of potato slices in distilled water decreased their glucose content before frying and acrylamide

formation after frying. Most of the blanching treatments evaluated in this study diminished dramatically glucose and asparagine contents of potato slices leading to a significant reduction of acrylamide formation after frying. The previously reported citric acid immersion effect in acrylamide reduction after frying was not obvious in this investigation. There was no significant removing of glucose and asparagine by dipping the slices in 10 and 20 g/l citric acid solutions for half an hour. For the three pre-treatments studied, acrylamide formation decreased dramatically in potato chips as the frying temperature decreased from 190°C to 150°C.

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