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Short communication

Acrylamide removal from heated foods

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ABSTRACT

The possibility to remove acrylamide from foods by exploiting its chemical physical properties was studied. Commercial biscuits and potato chips were subjected to vacuum treatments at different combinations of pressure, temperature and time. Results showed that acrylamide removal was achieved only in samples previously hydrated at water activity values higher than 0.83, and that, a maximum of acrylamide removal was obtained between 5 and 15 min of vacuum treatment at 6.67 Pa and 60 °C. By applying these process conditions, it was possible to remove 43% and 18% acrylamide from the biscuits and the potato chips, respectively. It was hypothesised that the vacuum treatment could favour acrylamide formation by promoting the decarboxylation of the Schiff base, a key intermediate of acrylamide formation. Although further research is needed to find out for each food category the process conditions that can maximise acrylamide removal while minimising its formation as well as to evaluate the effects on the sensory properties, this technology would represent a promising and alternative strategy to mitigation interventions aimed at reducing acrylamide levels in foods.

1. Introduction

Acrylamide is a probably human carcinogen molecule (IARC, 1994), which can form in heated foods. In fact, acrylamide can form during intense heat treatments as a consequence of the reaction between asparagine and a carbonyl source *via* Maillard-type reactions (Becalski, Lau, Lewis, & Seaman, 2003; Mottram, Wedzicha, & Dodson, 2002; Stadler et al., 2002; Yaylayan & Stadler 2005; Zyzak et al., 2003). According to one of the most reliable mechanisms, the α-amino group of free asparagine reacts with a carbonyl source, forming a Schiff base, that, under heat, decarboxylates. The decarboxylated Schiff base can further hydrolyse to form 3-aminopropionamide and subsequently degrade to form acrylamide, or decompose directly to form acrylamide *via* elimination of an imine (Zyzak et al., 2003).

The presence of acrylamide in foods was first detected in 2002 (Tareke, Rydberg, Karlsson, Eriksson, & Törnqvist, 2002) and the most important dietary sources include potato chips, French fries, roasted coffee and bakery products such as bread, crisp bread, biscuits, crackers, breakfast cereals (FDA, 2006; IRMM, 2005). Due to the great consumption of dietary sources of acrylamide among people of different ages and in different countries, worldwide efforts have contributed to identify potential routes to reduce acrylamide levels in foods and consequently consumer exposure. These are relevant to mitigations strategies, which include agronomical interventions (i.e. selection of raw materials with low sugar and asparagine contents), and technological strategies (e.g. chemical and biotechnological pre-treatments, thermal input and moisture control, formulation changes) (CIAA, 2007; Claus, Carle, & Schieber, 2008; Friedman & Levin, 2008; Stadler & Scholz, 2004; Taeymans et al., 2004; Zhang & Zhang, 2007).

The physical removal of acrylamide from the finished product can be regarded as an innovative approach, which has not been fully investigated. With respect to the mitigation strategies, acrylamide removal is conceptually different. In fact, while the former are aimed at lowering possible acrylamide formation during heating, the objective of acrylamide removal is to physically remove the molecule after the heat process has been completed. By virtue of its low molecular weight (71 Da), one can plausibly think that acrylamide can be removed from foods by exploiting its physical chemical properties (Budavari, O'Neil, & Smith, 1996). In principle, acrylamide can be removed from the food as vapour by choosing suitable temperature and pressure conditions. The possibility to reduce acrylamide levels in foods by means of its physical removal has been already investigated (Zhaoyang, 2003). Potato chips, introduced in an apparatus where a vacuum of 1.33 Pa was applied for one hour at 85 °C, had a reduced (not specified) level of acrylamide as compared to that prior to treatment. Further experiments on model systems confirmed these results (Nicoli & Anese, 2006).

The aim of the present study was to investigate the possibility to physically remove acrylamide from finished products (i.e. biscuits and potato chips), by considering different combinations of pressure, temperature and time.

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2. Materials and methods

2.1. Sample preparation

Commercial short dough biscuits and potato chips were chosen for experiments on acrylamide removal, due to them being representative of food categories significantly different in terms of chemical composition. Their average composition, as reported on their respective labels, is shown in Table 1.

Previously ground samples were subjected to the vacuum treatment. Also, aliquots of the ground samples were hydrated before the vacuum treatment. Weighed Petri dishes containing approximately 5 g of sample were introduced in vacuum desiccators saturated with water vapour. Samples were left in the desiccators for the time (varying from 1 to 24 h) necessary to reach different water activities, covering almost all the range of values. The initial water activity values of the biscuits and potato chips were 0.12 and 0.2, respectively. After hydration, samples were immediately subjected to the experiments at low pressure.

2.2. Vacuum treatments

Experiments of acrylamide removal were made by using an apparatus consisting of an oven (5Pascal, VS-25 SC, Trezzano S/N, Milano, Italy), connected to a rotary vacuum pump (BOC Edwards, E2M40, Crawley, West Sussex, UK) able to achieve a pressure of 0.133 Pa in few seconds when the oven was empty.

The samples, previously weighed (approximately 5 g) in Petri dishes, were introduced into the oven once the desired temperature was reached. Afterwards, the rotary pump was immediately switched on. The time needed to achieve the desired vacuum ranged from 2 to 15 min depending on the set pressure value and the water content of the samples. In all cases, computation of treatment duration started once the set pressure value was achieved. Different combinations of pressure, temperature and time were considered. These were chosen on the basis of literature data relevant to the physical properties of acrylamide as well as the results of preliminary trials. In particular, treatments were carried out at pressures ranging from 2.67 to 66.67 Pa at 60 °C for 1 h; at a constant pressure of 2.67 Pa and temperature values from 20 to 80 °C for 1 h; at 6.67 Pa and 60 °C up to 120 min. After the treatments, samples were immediately removed from the oven, wrapped in aluminium foil and stored in desiccators until analyses were performed. In all cases, the time between the end of the vacuum treatment and analytical determinations never exceeded 24 h.

2.3. Analysis of acrylamide

Acrylamide determination was carried out following the method of Anese et al. (2009). Briefly, 1000 μl of an aqueous solution of 2,3,3[$^2H_3$] acrylamide (d_3-acrylamide) (0.20 μg/mL) (Isotec, Sigma–Aldrich, Italy) as internal standard and 15 ml of water Milli Q (Millipore, Italy) were added to 1 g of finely ground sample. The extraction was carried out at 60 °C, for 30 min, under magnetic stirring. The mixture was then centrifuged at 12000*g* for 15 min at 4 °C (Beckman, Avanti Centrifyge J-25, Palo Alto, CA, USA). The clarified aqueous extract was cleaned-up by solid phase extraction (SPE) on an Isolute Env+, 1 g (Biotage, Sweden). The volume of the purified sample was reduced, under vacuum, to about 1.5–2 ml by using a rotary evaporator at a temperature of 70 °C and filtered through a 0.45 μm membrane filter before the HPLC–MS analysis. LC–ESI–MS–MS in positive ion mode analyses were performed by a Finnigan LXQ linear trap mass spectrometer (Thermo Electron Corporation, San Josè, CA, USA) coupled to a Finnigan Surveyor LC Pump Plus equipped with a thermostated autosampler and a thermostated column oven. The analytical column was a Waters Spherisorb ODS2 (250 × 2.0 mm, 5 μm). Elution was carried out at a flow-rate of 0.1 ml/min, in isocratic conditions, at 30 °C using as mobile phase a mixture of 98.9% water, 1% methanol and 0.1% formic acid (v/v/v). In these conditions the retention time of acrylamide and d_3-acrylamide was about 10 min. A time programmed valve was used to discard the eluate from the column for the first 7.5 min in order to eliminate the compounds with retention times shorter than acrylamide. At 12.5 min the column flow was again diverted and the mobile phase changed to 100% methanol in order to clean the column from strongly retained compounds. Full scan MS/MS was carried out by selecting the ions at *m/z* 72 and *m/z* 75 as precursor ions for acrylamide and d_3-acrylamide respectively. The area of the chromatographic peaks of the extracted ion at *m/z* 55, due to the transition 72 > 55, and at *m/z* 58, due to the transition 75 > 58 were used for the quantitative analysis. The quantitative analysis was carried out with the method of the internal standard. The relative response factor of acrylamide with respect to d_3-acrylamide was calculated daily by analysing a standard solution.

Table 1
Average composition of commercial biscuits and potato chips, as reported in the respective labels.

Food component	Cookies (g/100 g)	Potato chips (g/100 g)
Protein	7	5
Carbohydrate	65	72
of which sucrose	25	3
Fat	21	12
Water	2	2

2.4. Determination of water activity

Water activity was determined by means of a dew-point measuring instrument (AQUA LAB, Decagon, Pullman, WA, USA) at 25 °C.

2.5. Determination of total solid content

Total solid content was determined by a gravimetric method by drying the samples under vacuum (1.32 kPa) to a constant weight, according to AOAC (1995). With respect to the official method, drying was carried out at 75 °C instead of 100 °C, to avoid losses due to non-enzymatic browning and pyrolysis reactions.

2.6. Statistical analysis

Analyses were carried out at least twice on two replicated experiments. Coefficients of variation, expressed as the percentage ratio between the standard deviations and the mean values, were lower than 10 for acrylamide and water activity, and five for total solid content.

One-way analysis of variance was carried out and differences among means were assessed by using the Tukey test (STATISTICA for Windows, 5.1, Statsoft Inc., Cary, NC, USA). Means were considered significantly different at $P < 0.05$.

3. Results and discussion

Table 2 shows acrylamide concentrations of biscuits and potato chips subjected to treatments at 6.67 Pa and 60 °C for increasing lengths of time. Unexpectedly, the treatments did not cause any significant change in acrylamide concentration. Acrylamide was not removed from the product even when the treatments were

Table 2
Acrylamide concentration of cookies and potato chips subjected to treatments at 6.67 Pa and 60 °C for increasing lengths of time.

Food	Time (min)	Acrylamide (ng/g_{dm})
Cookies	0	1166 ± 30[a]
	2	1230 ± 8[a]
	10	1216 ± 29[a]
	30	1158 ± 82[a]
	120	1222 ± 113[a]
Potato chips	0	366 ± 4[b]
	5	323 ± 10[b]
	15	340 ± 23[b]
	30	335 ± 5[b]
	60	345 ± 12[b]

Different letters within each food category indicate significant difference ($P < 0.05$) by Tukey test.

carried out at different pressures (ranging from 2.67 to 66.67 Pa) at 60 °C for 1 h, or at 2.67 Pa and increasing temperatures (from 20 to 80 °C) for 1 h (data not shown). These results differed from those of Zhaoyang (2003), who, however, performed experiments at a lower pressure (1.33 Pa) and higher temperature (85 °C). The mechanisms of release of low molecular weight compounds have already been discussed in the literature (Flink & Karel, 1970a, 1970b; Rifa & Voilley, 1991). According to these studies, the high degree of volatile retention in low moisture foods contrasts with the expected behaviour for highly volatile organic compounds. Such a high degree of retention has been regarded as a physically and structurally based phenomenon (Flink, 1975). Based on this theory, volatile compounds are entrapped into the low moisture matrix and are released during moistening due to structural collapse of the matrix itself. In order to investigate a possible role of water on acrylamide removal, further experiments were carried out on the food matrices previously hydrated at different water activity values. The hydrated samples were treated at 6.67 Pa and 60 °C for 1 h. As shown in Table 3 the percentage of acrylamide removal from the biscuits and potato chips increased with the increasing of water activity, suggesting that water plays an important role in influencing acrylamide removal. It can be hypothesised that hydration could lead to the formation of water-food interactions, while weakening those between acrylamide and food. Alternatively, as, at the experimental pressure and temperature conditions adopted in the above experiment, water evaporates faster than acrylamide (data not shown), a water stripping effect can be suggested.

One aspect to take into consideration for a potential exploitation of such technology is represented by the time needed to achieve a satisfactory reduction of acrylamide levels in the food, which should be as low as possible. To this purpose, the biscuits and potato chips were hydrated at a water activity of 0.83 and subsequently treated at 6.67 Pa and 60 °C up to 1 h. Results, shown in Fig. 1, confirmed that the considered vacuum treatment resulted in

Table 3
Percentage of acrylamide removal from cookies and potato chips having different water activity values, subjected to treatment at 6.67 Pa and 60 °C for 1 h.

Food	Water activity	Acrylamide removed (%)
Cookies	0.12	12
	0.53	27
	0.83	32
Potato chips	0.26	0
	0.64	0
	0.74	4
	0.83	11
	0.95	20

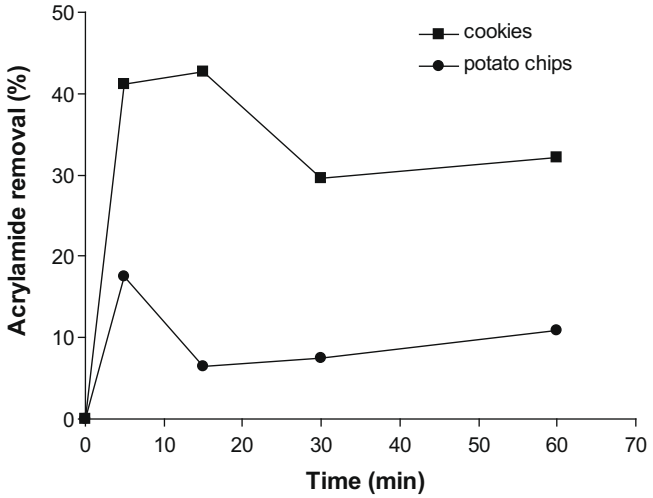

Fig. 1. Percentage of acrylamide removal from commercial biscuits and potato chips hydrated at a water activity of 0.83 and subsequently subjected to a treatment at 6.67 Pa and 60 °C as a function of time.

being effective in removing acrylamide. In particular, acrylamide removal was higher from the biscuits than from the potato chips, being 43% and 18% the maximum percentage of acrylamide removed from the bakery product and the potato derivative, respectively. Such a difference could be attributed to a matrix effect, e.g. interactions between acrylamide and other food components, and/or to a hurdle effect exerted by the superficial lipid film of the fried potatoes against acrylamide removal. A further consideration that can be drawn from Fig. 1 is that acrylamide removal is higher at shorter process times. In fact, in our experimental conditions, a maximum of acrylamide removal was achieved between 5 and 15 min of vacuum treatment for both foods. By contrast, less acrylamide was removed by increasing the duration of the vacuum treatment. According to the mechanism of acrylamide formation already mentioned (Zyzak et al., 2003), it can be hypothesised that the vacuum treatment of an acrylamide-containing food, by favouring carbon dioxide removal, may promote the formation of the decarboxylated Schiff base, that subsequently reacts to form acrylamide. According to this hypothesis, the pressure would play a dual role: it may favour acrylamide formation and/or removal, depending on the process conditions, as well as on the chemical and physical chemical properties of the food.

With respect to these preliminary results, further research is needed to understand the role of each variable to maximise acrylamide removal while minimising its formation by means of the vacuum process. Besides, based on preliminary sensory trials, showing that the product's volatiles profile was only slightly affected by the short times of the vacuum treatment at 6.67 Pa, more in-depth studies will focus on the impact of the removal technology on the sensory properties of foods.

Thinking to a possible industrial exploitation of this technology, it can be assumed that the finished product coming from the tunnel ovens with a low water activity is moved to a hydration step (e.g. carried out by means of a spray of pressurised water) followed by a vacuum step, where both acrylamide and the excess of water are removed. As acrylamide mainly forms in the product surface, it is likely that (but it should be confirmed by *ad hoc* experiments) the vacuum treatment can be carried out on the whole product instead of on the ground one.

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