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A CASE STUDY ON MITIGATION STRATEGIES OF ACRYLAMIDE IN BAKERY PRODUCTS

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Abstract

Acrylamide is a chemical compound first detected in food in 2002 by the Swedish National Food Administration (NFA) and the University of Stockholm. Acrylamide was added on the list of substances of very high concern and was also classified as a probable carcinogenic substance to humans.
Acrylamide is mainly formed in the Maillard reaction when asparagine reacts with the reducing sugars, especially glucose and fructose that are present in food. This usually takes place during high temperature processing of food: frying, baking, roasting and grilling.
This work presents a review of scientific literature published between 2003 and 2014 presenting different methodologies and experimental approaches to reduce acrylamide levels in bakery products. The main pathways for acrylamide mitigation in bakery products take into account three important issues: raw materials, recipes and food processing conditions.

***Key words**: acrylamide, asparagine, bakery products, mitigation strategies.*

INTRODUCTION

Acrylamide (acrylic acid amide, 2-propen-amide) is a colorless to white and odorless chemical compound having molecular weight 71.08 g/mol (Lewis, 2000; WHO, 2003; Lewis, 2007; HSDB, 2009; Zhang et al., 2009). Its physical state is crystalline solid (WHO, 2003; Lewis, 2003). After publishing the information announcing the presence of acrylamide in some food products processed at high temperatures in 2002 (Sweedish National Food Administration, 2002), and being already known the classify-cation of acrylamide as "probably carcinogenic to humans" made by the International Agency for Research on Cancer (IARC) (IARC, 1994), the interest of scientific community all over the world increase significantly (Ahn et al., 2002; Becalski et al., 2003; Hartig et al., 2002; Hofler et al., 2002; Nemoto et al., 2002; Tareke et al., 2002; Biedermann et al., 2002; Tateo et al., 2003; Clarke et al., 2002).
During the last years researches were conducted in the field of finding new pathways for the reducing of acrylamide content and developing mitigation strategies (Zhang et al., 2009; Amrein et al., 2007; Sadd et al., 2008; Claus et al., 2008).

MATERIALS AND METHODS

Data from specialized literature regarding acrylamide formation and available mitigation strategies for reducing acrylamide levels was used in this work.

RESULTS AND DISCUSSIONS

Acrylamide formation

Asparagine is the only amino acid capable of directly generating acrylamide; consequently it is considered the main source of acrylamide in food. The studies related to the detailed me-chanism of this transformation have indicated that sugars and other carbonyl compounds play a specific role in the decarboxylation process of asparagine - a necessary step in the generation of acrylamide.
Mass spectral studies showed that the three C atoms and the N atom of acrylamide were all

derived from asparagine (Zyzak, D.V, 2002). In several studies (Stadler et al., 2002, Zyzak, 2002, Mottram et al., 2002, Becalski et al., 2003) it was also found that reducing sugars containing an aldehyde group such as glucose react with asparagine above 100 °C to form an N-glycoside, which is then cleaved at the C-N bond to an intermediate that can be transformed to acrylamide (Figure 1)

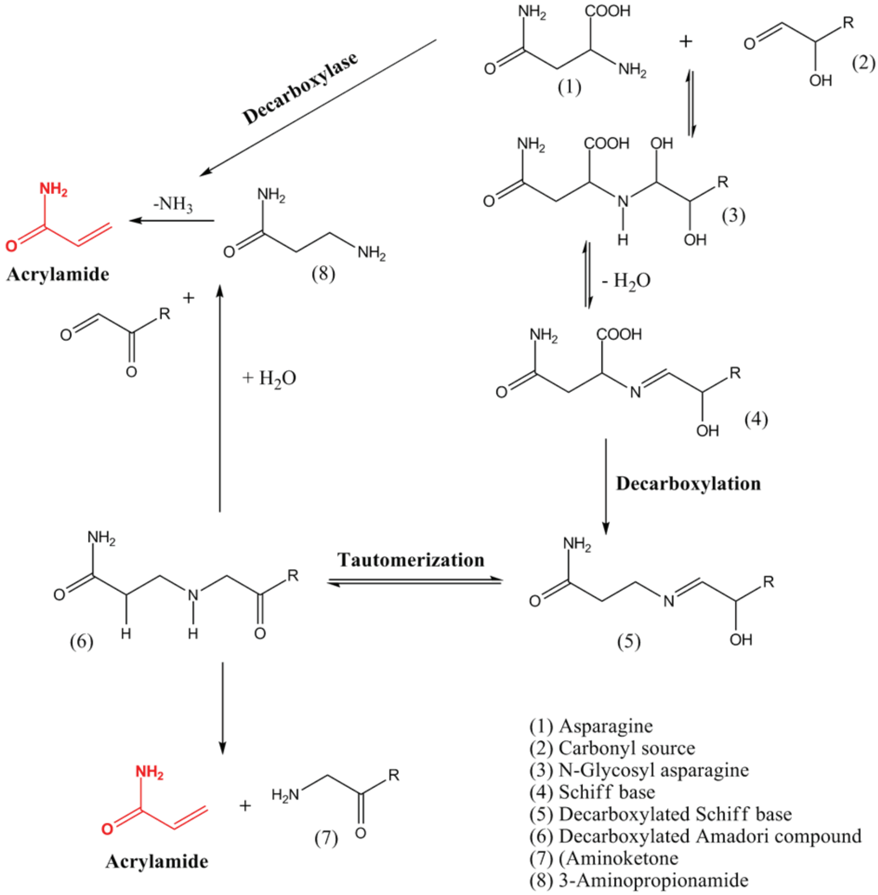

Figure 1. Acrylamide formation via asparagine route

It is well known that recent studies had clarified the formation mechanism of acrylamide via asparagine and carbohydrate route, but is also necessary to refer strictly to a certain food matrix to investigate corresponding factors influencing acrylamide generation.

In bakery products, the most important source of high amounts of acrylamide are bread, biscuits and cookies (Brathen et al, 2005; Konings et al., 2003; Amrein et al., 2004; Fink et al., 2006; Gokmen et al., 2007; Gokmen et al., 2008).

In Table 1 are presented some of acrylamide formation conditions in cereals and bakery products, including acrylamide analysis determination method and acrylamide content.

Table 1. Acrylamide formation conditions

Product	Frying/baking conditions	Pretreatment	Acrylamide determination method	Acrylamide content	Reference
Cereals	Baking at 190 °C for 9 min.	--	-	Inorganic salts declined acrylamide content	Kukurova et al., 2009
Flours	Toasting at 180 °C for 22 min.	---	LC-MS/MS	260 – 300 µg/kg	Capuano et al., 2009
Wheat	Drying at 105 °C for 24 hours	---	GC-MS	-	Weber et al., 2008
Bread	Baking at 180-280 °C for 15-45 min. in a fan oven	One half-baked immediately and other freeze-dried prior to baking	HPLC	-	Brathen et al., 2005

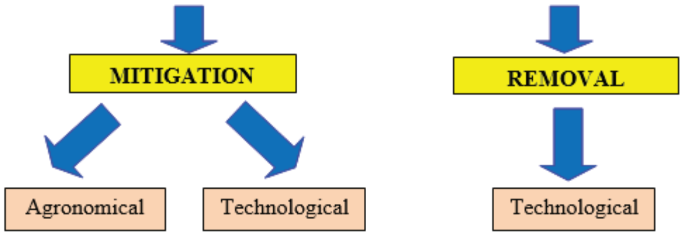

Figure 2. Strategies to reduce acrylamide levels

Mitigation

The possibilities of reducing acrylamide levels in food have to be regarded by two conceptually different approaches, as presented in Figure 2 (Anese et al., 2009): Mitigation strategies – used to keep as low as possible acrylamide formation

Removal strategies – used to move away the already formed acrylamide Based on Trade Guidelines on Reducing Acrylamide in Food, published by Centre for Food Safety – Food and Environment Hygiene Department in 2011 and revised in 2013, there are three main strategies for reducing acrylamide formation to be covered, which are applied to raw materials, recipes and food processing conditions.

The concentration of the precursors in the raw materials is the essential factor in acrylamide formation. Free asparagine and reducing sugars, the main precursors of acrylamide formation, are essential compounds in several biochemical pathways (Matthaus and Haase, 2014). In cereals, the reducing sugars concentration is much higher than asparagine (Muttucumaru et al., 2006; Granvogl et al., 2007; Curtis et al., 2009) meaning that asparagine content is the limiting factor to form acrylamide. Taking this into account, in order to reduce acrylamide level in bakery products, you have to consider replacing proportion of high asparagine level cereals with those with low asparagine. Asparagine level in commonly cereals used in bakery is presented in Table 2.

Table 2. Asparagine level in cereals

Cereal	Asparagine level, mg/kg
Wheat	75 – 2200
Oat	50 – 1400
Maize	70 – 3000
Rye	319 – 880
Rice	15 – 25

Another promising strategy for acrylamide mitigation is asparaginase pre-treatment. The main role of asparaginase is to convert asparagine in aspartic acid with maintaining intact the sensorial attributes of the final product (Pedreschi et al., 2014). Asparaginase can achieve a 60 to 90% reduction level (Kukurova et al., 2009).

The asparagine level can be decreased by using fermentation. Longer fermentation time may reduce acrylamide formation as shown by Haase et al., 2012. Yeast fermentation may assimilate up to 80% of asparagine in dough, while sourdough fermentation can only assimilate only up to 17% of asparagine (Pedreschi et al., 2014).

The type of flour to be used is also important because high extraction flours contain less asparagine than whole meal flour. However, reducing whole meal content will decrease the nutritional benefits of the final product.

Reducing the use of ammonium bicarbonate as raising agent also reduce acrylamide level. Other alternatives are: sodium bicarbonate + acidulants, disodium diphosphate + sodium bicarbonate + organic acids, potassium bicarbonate + potassium bitartrate or sodium bicarbonate + sodium acid pyrophosphate (Biederman and Grob, 2003; Weisshaar, 2004; Amrein et al., 2004, 2005; Sadd et al., 2008).

Fermentation time and addition of cysteine decrease acrylamide level in bread. Claus et al., 2008, conducted an experiment in which breads were brushed with an aqueous solution of cysteine prior to and after baking. Obtained results were in agreement with those obtained by Clayes et al., 2005, who also reported a significantly decrease in acrylamide level when cysteine was used.

pH modification is also a way to reduce acrylamide formation in food (Zhang et al., 2009). Several studies were conducted in order to explain how a lower pH can mitigate acrylamide level. It was found that citric acid can be used to modify pH (Low et al., 2007).

Addition of NaCl as well as $CaCl_2$ seems to have also mitigation effect in acrylamide generation. Ou et al., 2008, tested the effect of $CaCl_2$ on mitigating acrylamide and found that Ca^{2+} prevent acrylamide formation completely.

In Table 3 are presented recent studies regarding acrylamide mitigation in several food matrixes (bread, cereals, and bakery products). Information in Table 3 is adapted from Zhang et al., 2009, and completed with other recent studies.

Table 3. Studies on mitigation of acrylamide in different food matrix

Food matrix	Mitigation recipe and acrylamide reduction percentage	Reference
Bread	Long time fermentation - 87% and 77% reduction in whole grain and rye bran bread	Friedriksson et al., 2004
Baked, fried and roasted products	Addition of asparaginase - Significant reduction of acrylamide	Hendriksen et al., 2005
Wheat	Agronomic and genetic approaches - Reducing acrylamide precursors	Muttucumaru et al., 2008
Bakery products	Removing ammonium-based raising agents, long yeast fermentation, fortification of flour with $CaCO_3$ and lowering the dough pH - Summarizing the effectiveness of mitigation methods	Sadd et al., 2008
Wafers	When increasing extraction rate from type 550 to 1050, acrylamide level is almost doubled	Haase et al., 2003
Wheat crackers	Replacing invert sugar syrup by sucrose - 60% reduction	Vaas et al., 2004
Gingerbread	Replacing NH_4HCO_3 with $NaHCO_3$ - Acrylamide is significantly reduced when using $NaHCO_3$	Amrein et al., 2004
Wheat bread	Different baking temperatures - Linear increasing of acrylamide with time and temperature	Surdyk et al., 2004
Wheat crackers	Changing linear temperature profile (220 °C) to a gradient temperature profile (230 – 190 °C) – up to 60% reduction	Vaas et al., 2004
Breakfast cereals	Direct expansion extrusion cooking process gives raise to acrylamide content compared to pellet-to-flaking extrusion cooking	Rufian-Henares et al., 2006
Crisp bread	Lactic acid fermentation – 70% reduction	Baardseth et al., 2004
Wheat bread	Addition of glycine (high doses) – more than 80% reduction	Brathen at al., 2005
Cereals	Addition of legume proteins reduces acrylamide level	Vattem et al., 2005

CONCLUSIONS

The aim of this review is to summarize the studies regarding mitigation of acrylamide in bread and bakery products published in the last 12 years. Three main strategies for acrylamide mitigation are covered: raw materials, recipes and processing conditions.

The main precursors in acrylamide formation are asparagine and reducing sugars. Thus, strategies regarding possibility of reducing the content of these acrylamide precursors are taking into account.

By reducing time and temperature during baking the acrylamide content can be significantly reduced.

Among other mitigation strategies, asparaginase was extremely effective at different formulation and temperatures.

Fermentation time and addition of cysteine significantly lowered acrylamide in bakery products.

Replacing ammonium bicarbonate as raising agent, modifying pH, adding NaCl or $CaCl_2$, or adding legume proteins are other mitigation strategies for reducing acrylamide in bakery products.

A lot of works has been done in the last 12 years to mitigate acrylamide formation in bakery products. Nevertheless, this problem is not solved, yet.

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