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Acrylamide in Food Products: A Review

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Abstract

Acrylamide or 2-propenamide an industrial chemical formed in some foods particularly starchy foods during heating process such as baking, frying and roasting. Acrylamide is proven to be carcinogenic in animals and a probable human carcinogen mainly formed in foods by the reaction of asparagine (free amino acid) with reducing sugars (glucose and fructose) as part of the Maillard reaction during heating under high temperature and low moisture conditions. The main aim of this review is to summarize the results of academic and industrial research on occurrence, dietary exposure, formation mechanism and mitigation measures of acrylamide in bakery, cereal and potato food products.

Keywords: Acrylamide; Asparagine; Maillard reaction; Bakery; Cereal; Potato products

Introduction

Acrylamide (C_3H_5NO; 2-propenamide), is a colourless, non-volatile crystalline solid, soluble in water and has a molecular weight of 71.08 kDa [1,2]. It is produced commercially by hydrolyzing acrylonitrile using nitrile hydrase and exists in two forms: monomer and polymer. It is used to produce polyacrylamide polymer, which find many uses as a coagulant in waste water treatment and clarifying drinking water, grouting agents for the construction of dam foundations and tunnels and as electrophoresis gels. In 1994, the International Agency for Research on Cancer (IARC) classified acrylamide as a potential carcinogen to humans (Group 2A) based on its carcinogenicity in rodents. This classification was endorsed by the WHO Consultation in 2002. The single (monomer) form of acrylamide, is recently discovered to be present in food, which is toxic to the nervous system. A carcinogen in rodents, and a suspected carcinogen in humans cause gene mutation and DNA damage [2,3-12]. It is probably always been present in cooked foods and cigarette smoke. However, the presence of acrylamide in foods was first reported by the Swedish National Food Administration (SNFA) in 2002. It is considered as the important heat-induced process contaminants formed mostly in potato, cereal and bakery products, respectively by the heat treatment.

Occurrence and Dietary Intake

People are exposed to different amounts of acrylamide mainly through the diet. Acrylamide occurrence in foods is being studied intensively since the original report of high levels of acrylamide found in food that are subjected to high temperature [6,13,14]. Acrylamide primarily found in plant based foods; heat treated starchy foods such as potato, cereal and bakery products contains high levels of acrylamide [6,13,15-19]. Acrylamide is not found in foods that are not fried or baked such as boiling or microwaving (Eriksson, 2005; Törnqvist, 2005) [2,20] and found very low levels in animal based food products such as meat and fish. To date, there is no permissible limits have been set worldwide for acrylamide consumption in diet. To analyze the acrylamide presence in diet, different dietary exposure databases consist of different food groups have been prepared by the European Union's acrylamide monitoring database, the United States Food and Drug Administration's acrylamide survey data and the WHO's summary information and Global Health Trends database. Estimation of acrylamide occurrence in food commodities is a great concern in many countries. Moreover, the predictions of dietary acrylamide intake have been made for populations in many countries consist of different dietary records [21-33]. These studies found that the amount of acrylamide was extremely higher in fried potato products (such as French fries and potato chips) followed by cereals, crisp breads, biscuits and other bakery products. Concentration and dietary intake of food have significant variations, which depends upon cooking methods [21,34-42]. Factors such as difference in food composition, high temperature (more than 120°C), and high carbohydrate, free asparagine, reducing sugars, pH, water content, ammonium bicarbonate and high concentration of competing amino acids could be the sources for variation in acrylamide level [43-47]. Dietary acrylamide intake may increase the risks of kidney and breast cancer [48,49]. The daily intake of acrylamide in human diets was estimated to be 0.3 to 0.8 µg per kg body weight [42]. At normal conditions, the average total daily intake of acrylamide is about 0.85 µg per kg body weight [50]. The total macro and micro nutrient composition of the diet is mainly obtained from acrylamide containing foods [51]. Foods that are contributing most dietary intake of acrylamide differ from country to country [52]. Foods with high acrylamide levels contribute to 38% of daily calories, 36% of fibre and greater than 25 % of micronutrients [53].Generally, darker the colour of food product, higher the acrylamide content. Acrylamide formation increases drastically towards the end of the frying process [54]. The amounts of acrylamide in different food and food product groups are summarized in Table 1.

Mechanisms of Formation

Acrylamide is not a substance that is added to food, but it is formed in food during heat processing. Research indicates that heating of food could be an important source of acrylamide formation. Acrylamide formed in a wide variety of foods, particularly carbohydrate (reducing sugars) rich foods cooked at above 120°C upon frying, baking and roasting [55-57]. However, acrylamide formation in potato fries taken place at below 120°C at low moisture content and prolonged heating

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Product/ Product group	Acrylamide range (µg kg^{-1})
Bakery products and biscuits	18-3324
Breads	<10-3200
Bread (toast)	25-1430
Breakfast cereals	<10-1649
Chocolate products	<2-826
Coffee substitute	80-5399
Dairy products	<10-130
French fries/chips	59-5200
Meats	<10-116
Potatoes (raw)	<10-<50
Potato chips/crisps	117-4215
Roasted coffee	45-9359

Table 1: Amounts of acrylamide in different foods and food product groups. Adapted from Peterson [150].

conditions [58]. The basic formation routes of acrylamide in foods in shown in Figure 1. Acrylamide formation follows different routes in conjunction with the Maillard reactions system in food products, where the asparagine route is the major one for the formation of acrylamide [2].

Formation via Asparagine Route

The major pathway leading for acrylamide formation in foods is a part of the Maillard reaction with free amino acid (asparagine) and reducing sugars (mainly glucose and fructose) [59-66] (Figure 2). Maillard reaction is a non-enzymatic browning reaction occurring in foods during baking or frying. This happens at proper combination of carbohydrates, lipids and proteins for desirable colour, flavour and aroma [61,67]. Asparagine, is the free amino acid present in potatoes in high level (93.6 mg per 100 g) [68], needs carbohydrates to form acrylamide [69]. The potential of acrylamide formation is strongly related to glucose and fructose content [70,71]. Free asparagine concentration to be the main determinant of acrylamide formation in rye varieties [72] and in cooked flours and doughs (mainly rye and wheat) [73]. Research has shown that the reducing sugars are the major limiting factors in potatoes [74-77], while asparagine (mainly in the cereal bran) is the major limiting factors in cereal products [78-81].

Formation via Alternative Routes

Although formation of acrylamide in foods has its major routes through asparagine and reducing sugars, several other formation routes suggested via. Acrolein and ammonia (Figure 3). In the absence of asparagine, acrolein and ammonia to play a role in lipid rich foods to form acrylamide. It is known that acrolein and acrylic acid are produced by degradation of lipids (triglycerides) in subject to high temperature [83,84]. Degradation of amino acids with ammonia can give rise to acrylamide formation by thermal decomposition [85-89]. Amino acids such as glutamine, cysteine and aspartic acid have also been found to produce low amounts of acrylamide [90,91]. However, stated that this mechanism might be irrelevant for acrylamide formation in foods [74,79].

Mitigation Strategies for Acrylamide

Significant efforts have been undertaken in order to develop appropriate strategies that reduce acrylamide in foods. Reducing acrylamide content in foods at household and industrial level can help the public not only from food hazards but also to create perception about the food safety. A number of mitigation strategies have been focused so far regarding acrylamide formation at different stages of food production are discussed in the following sections.

Effect of Raw Materials

The influence of variety, harvest year, fertilization and storage conditions on acrylamide formation have been studied in potato products [92-97] and also in cereal products [98-102]. The composition of potatoes vary with variety to variety [103,104] and it relatively contains high amounts of reducing sugars, which is the major limiting factor in potato products for acrylamide formation of the positive influence of cereal varieties on precursors and acrylamide contents. Therefore, controlling reducing sugars and asparagine may be a better option to reduce acrylamide in potato and cereal products respectively (David et al., 2012) [56]. Potato varieties with low concentrations of reducing sugars can be an effective way to reduce acrylamide concentration [77,104,105].

Climatic condition such as harvest year has a significant impact on asparagine and reducing sugars in potatoes. The asparagine content was significantly lower in all the samples from the 2004 harvest as compared to 2003 [106]. This study concluded that an extremely hot summer will result in lower acrylamide generation. Fertilization is considered to be a key factor in crop production. A decrease in nitrogen fertilization enhanced reducing sugars concentrations, resulting in an increase of acrylamide formation in potato products [107]; whereas

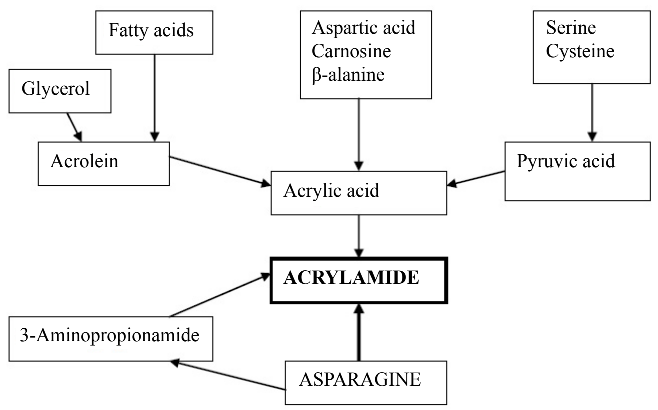

Figure 1: The basic formation routes of acrylamide in foods [2].

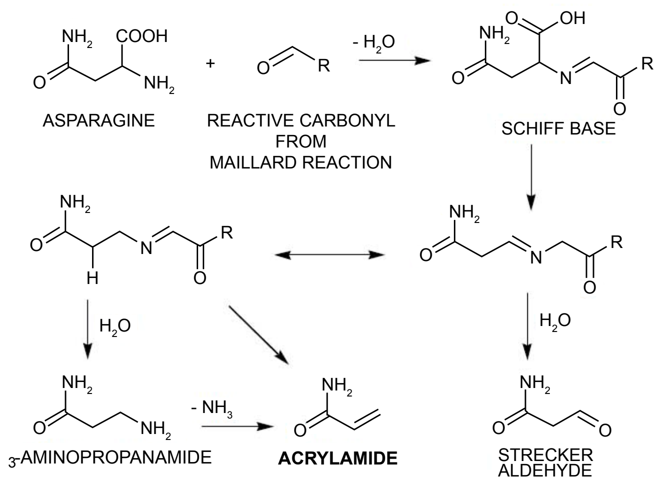

Figure 2: Proposed mechanism for formation of the acrylamide in heat treated foods [164].

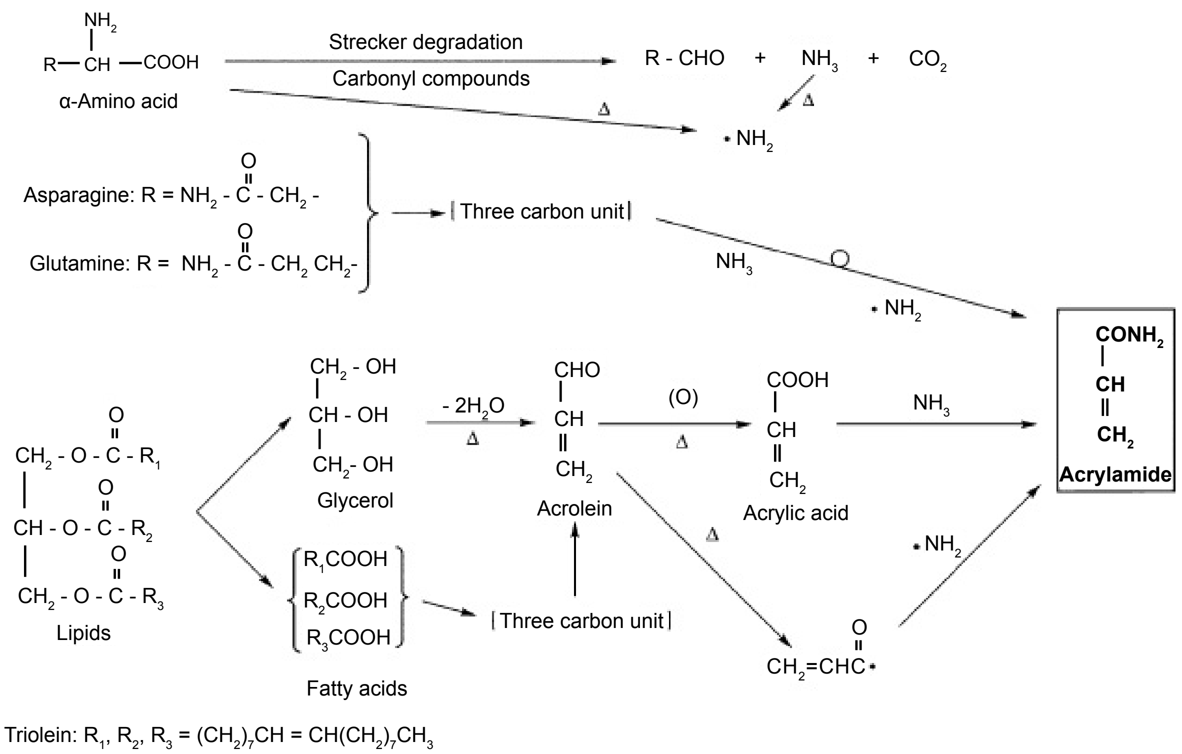

Figure 3: Hypothesized formation mechanism of acrylamide from an amino acid and a lipid.

inverse effects have been noticed for bakery products. However, reducing sugars in wheat were not affected by fertilization. Generally, potato tubers are stored for several months in order to meet the supply throughout the year. Cold temperatures and senescent sweetening are the main causes of sugar accumulation in potatoes during storage [108]. Higher temperature storage (more than 8˚C), which results senescent sweetening is also related to sprout formation in potatoes [79]. Storing potatoes at low temperature (below 8°C) found to be an effective technique/tool to inhibit sprouting [108]; temperature below 4-6°C has a major effect on reducing sugar accumulation [109-111]. However, reducing sugars in potatoes are not significantly varied when potatoes are stored at 8°C [112-115] and no changes are found in asparagine contents in potatoes stored at different temperature and time [114-116]. In order to reduce acrylamide formation, potato tubers should be ideally stored at 8°C [117].

Effect of Additives

Asparaginase, an enzyme that converts precursor (asparagine) into ammonia and aspartic acid, can reduce acrylamide formation in foods [117-121]. It is commercially produced from *Aspergillus niger* (DSM's Preventase) or *Aspergillus oryzae* (Novozyme's Acrylaway) and found its most applications in potato and cereal products. Though it is a promising strategy for acrylamide reduction, it is rather expansive compared with other strategies.

The addition of amino acids or protein rich substances reduces the acrylamide content in foods [122,123]. Amino acids such as glycine, cysteine, methionine, glutathione and lysine on acrylamide formation and its elimination kinetics was assessed in several studies [124-134]. Formation of acrylamide decreased by 50% when cysteine and methionine were added to cracker [135] and potato dough [136]. On the contrary, Flückiger and Salih [137] studied the effect of cysteine on acrylamide formation in crisp bread and found that no such effects.

Addition of antioxidants has been found to influence the Maillard reaction, which results in acrylamide formation [138-145]. Antioxidants present in the rosemary extracts, bamboo leaves and green tea extract [146,147] could effectively reduce acrylamide presence in different heated foods. The exact mechanism on acrylamide formation is not yet understood, however it is proposed that it could interact with active aldehydes and block the oxidation of acrolein to a certain extent [148,149]. Moreover, most of these studies are based on *in vitro* or small scale conditions and ultimately may not provide the similar results on commercial or industrial conditions.

Mono and divalent cations (Na^+ and Ca^{2+} or Mg^{2+}) added to the dough showed a remarkable effect on acrylamide reduction [150]. In addition, polyvalent cations also capable to reduce acrylamide formation during heating [151]. These ions could interact with asparagine so that prevent the Schiff base intermediate formation and thus acrylamide generation [151-155].

A significant effect of NaCl on acrylamide reduction via polymerization was reported by several studies. However, the acrylamide content increased at higher NaCl levels, which was attributed to an inhibition of yeast growth by the salt [156]. Acrylamide formation in potato strips reduced by hydrocolloid coatings when alginic acid and pectin were used as coating agents [157], whereas carob gum, carrageenan, hydroxypropyl distarch phosphate and xanthan gum stimulated acrylamide formation.

Effect of Processing Conditions

Most of the strategies proposed to reduce the acrylamide are focused on the processing stage. The important factors that influence the process of acrylamide formation are: heating temperature and time, blanching and frying [116]. Several studies were conducted on the effects of baking temperature and time combination during baking and found strong correlation between baking temperature and time and acrylamide formation [158-162]. However, the prolonged baking temperature and time combination (260°C, 20 min) decreased the acrylamide content in foods. Biedermann and Grob found that acrylamide could also be formed at below 100°C. Compared with conventional baking conditions, optimized conditions such as temperature and relative humidity profile resulted in a 50% reduction of acrylamide formation. Conduction and radiation heat transfer are more effective in acrylamide reduction than convection baking ovens. Moreover, the combination of conventional and dielectric (microwave) heating found to be suitable for reduction of acrylamide in bakery products. Baking at high relative humidity proved to be effective for reducing acrylamide in bakery products [163,164]. This can be achieved not only by reducing the temperature, but also by using steam as heating medium during the final part of baking [164]. The reference baking temperature and time considered were 200°C for 20 min. Acrylamide formation mostly occurs in the outer crust than in the inner crust of bread, while only trace amount appears in the crumb [165,166].

Blanching is an important unit operation in the prediction of French fries production. This reduces acrylamide formation mainly by leaching the precursors (reducing sugars) prior to frying [167-172]. Blanching conditions (temperature and time) can be varied in order to maintain the final product specifications constant . Blanching at 70°C for 10 to 15 min, reduced acrylamide formation of 65% and 96% for French fries and potato chips, respectively. Frying is used in food processing both at industrial and home levels. Acrylamide formation is correlated to colour development, which occurs in Maillard reaction during heating process, mostly at the end of the frying process [173,174]. Intensive frying conditions (temperature and time) lead to darker fries and higher acrylamide formation. Thus, two factors such as frying temperature (should not exceed 170-175°C) and time to be considered as important for acrylamide reduction. Frying under low pressure conditions using vacuum fryer results in higher acrylamide reduction [175].

Effect of PH, Water Activity and Fermentation

Maillard reaction has strong influence on pH. It is known that high pH affect nutrients in foods (Eriksson, 2005). Researchers showed that the reduced pH drastically reduces acrylamide content during frying and baking [176,177]. Any acid treatment reduces the pH of foods and results in formation of Maillard associated substances. Addition of different acids decreased the amount of acrylamide in bakery products such as corn chips, semi-finished biscuits and cracker models [177,178]. Reduced pH levels results in Maillard reactions, accompanied by reduced acrylamide formation [179,180]. Water activity in food plays a major role in reducing acrylamide formation. Acrylamide forms in food only when the water activity is below 0.8, whereas the acrylamide formation is high at water activity of 0.4 and below [181,182]. However, the removal of acrylamide from heated foods such as biscuits and potato chips increases with the increase of water activity. The percentage of acrylamide removal from cookies and potato chips having different water activity values is presented in Table 2. Fermentation controls the rate of acrylamide formation in food by maintaining precursor composition and pH. Prolonged fermentation time (at least an hour) was found to be suitable for acrylamide reduction in bread and fried potato products [183-186]. Combined lactic acid fermentation with blanching found suitable for higher acrylamide reduction in potato products [187].

Foods	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

Table 2: Percentage of acrylamide removal from cookies and potato chips having different water activity values, subjected to treatment at 6.67Pa and 60°C for 1 h [165].

Conclusions

The major limiting factors responsible for the formation of acrylamide in potato and cereal products are reducing sugars (glucose and fructose) and free asparagines (amino acids) respectively. For commercial production of potato products, select cultivars with low levels of reducing sugars taking into account seasonal and regional variability for high temperature processes such as frying and baking. Avoid using potato tubers stored below 6°C and maintain ideal storage temperature of about 8°C. However, retailers and consumers are unaware of the selection of cultivar and safe storage temperature. Therefore the advantages of these conditions have to be well informed to retailers and consumers through campaign by mass media and concerned food safety authority. Blanching in water followed by frying at controlled temperature-time combinations might be a better option to reduce the acrylamide formation in potato products. Use of additives such as amino acids, asparaginase enzyme, cations and antioxidants are reported effective for acrylamide reduction in bakery and cereal products. Nevertheless, the additives should not alter the quality and consumer acceptability of food products. Yeast fermentation is a promising technology, which will reduce the free asparagine precursor content in cereal products such as wheat bread. Combination of yeast fermentation and blanching will substantially reduce the acrylamide content in potato products. However, the strategy or approach developed for potato products are not applicable /transferable to other food products such as bakery and cereal products. A strong positive correlation exists between baking temperature and time and formation of acrylamide; whilst the use of flour with low asparagine content might decrease the content of acrylamide in bakery products. By introducing steam in conventional or traditional baking system, it is possible to reduce the acrylamide content in baked products. The strategies developed so far to mitigate acrylamide formation studied on lab conditions, which may not be suitable for commercial process. Therefore further work is necessary to explore different possibilities studied in the laboratories on industrial conditions. Reducing acrylamide in food products while protecting other quality aspects and reducing dietary acrylamide exposure still remains a major challenge.

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