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Acrylamide in Foods: Causes, Health effects and Reduction strategies

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Abstract: **Acrylamide, a proven rodent carcinogen, was reported to have been found in commonly consumed carbohydrate-rich foods by Swedish National Food Association in 2002. The alarm raised escalated a lot of concern in public health. Acrylamide is a chemical compound formed in potatoes, cereals and bakery foods when processed by frying, baking or roasting at temperature above 120^{o}C and at low moisture condition. The reducing sugars or its carbonyl derivatives and amino acid Asparagine are known to play important roles in its formation. Due to its high solubility in water, acrylamide is readily absorbed in the gastrointestinal tract, and can be metabolized in the body through conjugation with glutathione or biotransformation with Cytochrome P450 metabolic enzyme. The toxicity of acrylamide to health has been extensively studied. The neurotoxic, carcinogenic, genotoxic and effects on reproductive health are evident with symptoms ranging from central and peripheral neuropathy to anomalies caused in the genome of animals as well as human subjects. Available studies are not enough to conclude that acrylamide is carcinogenic in humans although in animals, cases of several types of cancer had been documented. The mitigation strategies of reducing acrylamide in foods include: the use of asparaginase, addition of antioxidant, increase in water activity of the food product, storing at 8 ^{o}C, baking at high relative humidity, blanching at 70 ^{o}C for 10 -15mins, and frying under low pressure conditions. This review covers acrylamide's occurrence in various food products, dietary intake, formation, absorption, metabolism, health effects and its reduction strategies.**

Keywords: **Acrylamide, asparagine, reducing sugars, neurotoxic, carcinogenic, glycidamide.**

1. INTRODUCTION

Public health concern about acrylamide escalated after the provocative announcement of the presence of acrylamide in a host of commonly consumed foods particularly in fried, roasted and baked starch-based goods [1].

Acrylamide (ACR) is a reactive, highly water-soluble vinyl monomer. It is an industrial chemical used in the manufacture of polyacrylamides that are common to personal care and grooming products, such as lotions, cosmetics and deodorants.

In addition to Industrial and laboratory uses, it has been reported that the formation of ACR is associated with high-temperature (> 200°C) cooking process in certain carbohydrate-rich foods, especially when asparagine reacts with sugar [2].

Acrylamide has been found in a wide variety of fried, baked or roasted foods; it is found in both foods processed by manufacturers and foods that are cooked in the home. Although the presence of acrylamide in food has been discovered comparatively recently, it has probably been present for many years, in staple foods forming a significant part of the human diet. Acrylamide has not been found in foods that are not fried or baked, such as boiled potatoes [3].

According to YuZhang *et al*. (2009) as cited in Ubaoji and Orji (2016 p.4), the mechanism for acrylamide formation in starchy foods involves two components of these foods namely reducing sugars and amino acid asparagine.

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Factors affecting acrylamide formation and degradation in foods are acrylamide precursors such as free amino acids (mainly asparagine), reducing sugars and processing conditions, that is, baking time and temperature, moisture content and matrix of product [4].

This review covers the occurrence, exposure, absorption, metabolism, formation, health effects of acrylamide in foods as well as possible reduction and recommendations to food consumers, food manufacturers and food regulatory agencies as regards this subject matter.

2. OCCURRENCE, FORMATION, DIETARY EXPOSURE AND FATE OF ACRYLAMIDE IN FOODS

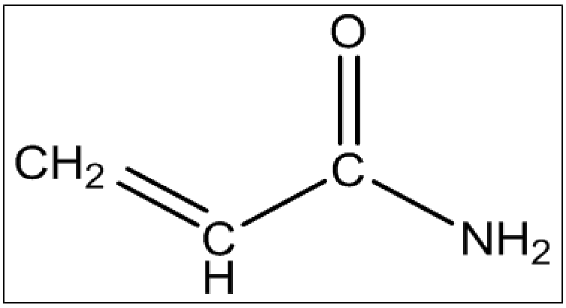
What Is Acrylamide?

Acrylamide (or acrylic amide) is a chemical compound with the chemical formula C_3H_5NO and has a molecular weight of 71.08 g. Its IUPAC name is 2- propenamide. It is a white odourless crystalline solid, soluble in water, ethanol, ether, and chloroform [5].

According to European Food Safety Authority, EFSA (2015), acrylamide is a chemical that naturally forms in starchy food products during every-day high-temperature cooking (frying, baking, roasting and also industrial processing at +120°C and low moisture). It mainly forms from sugars and amino acids (mainly one called asparagine) that are naturally present in many foods. The chemical process that causes this is known as the Maillard Reaction; it also 'browns' food and affects its taste.

Acrylamide can also be generated from food components during heat treatment as a result of the maillard reaction between amino acids (mainly asparagine) and reducing sugars or reactive carbonyls [6]. Most people are exposed to acrylamide through food consumption and environmental pollutants [7].

Krishnakumar and Visvanathan (2014) explained that, Acrylamide exists in two forms: monomer and polymer. Polyacrylamide and acrylamide copolymers are used in many industrial processes, such as the production of paper, dyes, and plastics, and in the treatment of drinking water and wastewater, including sewage. Acrylamide is considered as the important heat-induced process contaminants formed mostly in potatoes, cereals, and bakery products.



Chemical formula: $CH_2{=}CH\text{-}CONH_2$

Figure 1: Structure of Acrylamide

Source: Ubaoji and Orji (2016)

Occurence And Dietary Exposure:

Acrylamide primarily found in plant based foods; heat treated starchy foods such as potato, cereal and bakery products, contains high levels of acrylamide [1], [8], [9].

As released by Agency for Toxic Substances and Disease Registry, ATSDR (2012) in its Public Health Statement on Acrylamide:

Drinking water can sometimes contain acrylamide. It can enter drinking water from the treatment process of municipal supplies as well as from substances used to construct dams and wells. Acrylamide breaks down quickly in water and soil, but there is still a chance of exposure if you live near a plastics or dye plants (p.2).

ATSDR (2012) further explained that People involved in the production or use of acrylamide and acrylamide-containing products are exposed if they breathe in air that contains acrylamide. They may also be exposed by coming into skin contact with acrylamide. Also, Acrylamide is formed in foods that are rich in carbohydrates (particularly potatoes) when they are fried, grilled, or baked at normal cooking temperatures. Levels of acrylamide in these foods increase with higher temperatures and longer cooking times. Protein-based foods (such as meats) probably contain low amounts of acrylamide. Ingestion of foods that contain acrylamide is a primary source of exposure.

Acrylamide is not found in foods that are not fried or baked such as boiling or microwaving [10], [11] 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 analyse the acrylamide presence in diet, different dietary exposure databases consisting 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 [12], [13], [14]. 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 as shown in figure 2 below:

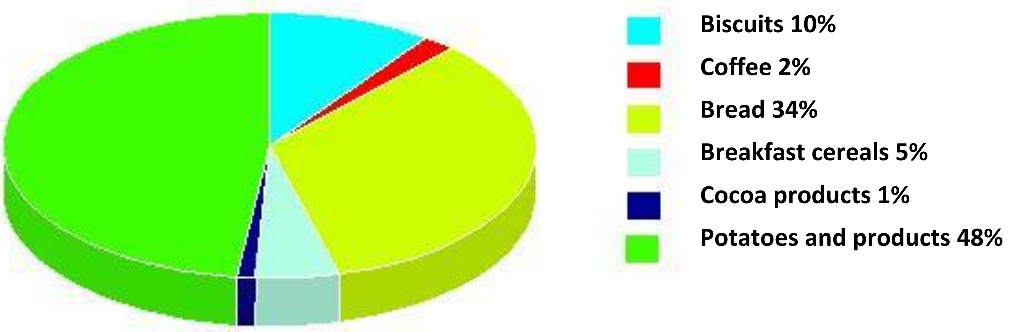


Figure 2: Percentage contribution to mean μg/kg body weight of Acrylamide exposure (total population)

Source: Food Safety Authority of Ireland (2009).

Concentration and dietary intake of food have significant variations, which depends upon cooking methods [12], [15], [16]. 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 [17].

Dietary acrylamide intake may increase the risks of kidney and breast cancer [18], [19]. The daily intake of acrylamide in human diets was estimated to be 0.3 to 0.8 μg per kg body weight [16]. At normal conditions, the average total daily intake of acrylamide is about 0.85μg per kg body weight [20].

Generally, the darker the colour of food product, the higher the acrylamide content. Acrylamide formation increases drastically towards the end of the frying process [21].

Formation Of Acrylamide In Foods:

Acrylamide is not a substance that is added to food, but it is formed in food during thermal processing. Studies have indicated that heating of food could be an important source of acrylamide formation. Acrylamide formation takes place in a wide variety of foods, particularly carbohydrates (reducing sugars) rich foods cooked above 120^0C upon frying, baking and roasting [22], [23].

At low moisture in potatoes, acrylamide is formed at below 120^0C and prolonged heating condition. Therefore, the formation of acrylamide in food products follows different pathways, the major pathway being Asparagine route as shown in figures 3 and 4.

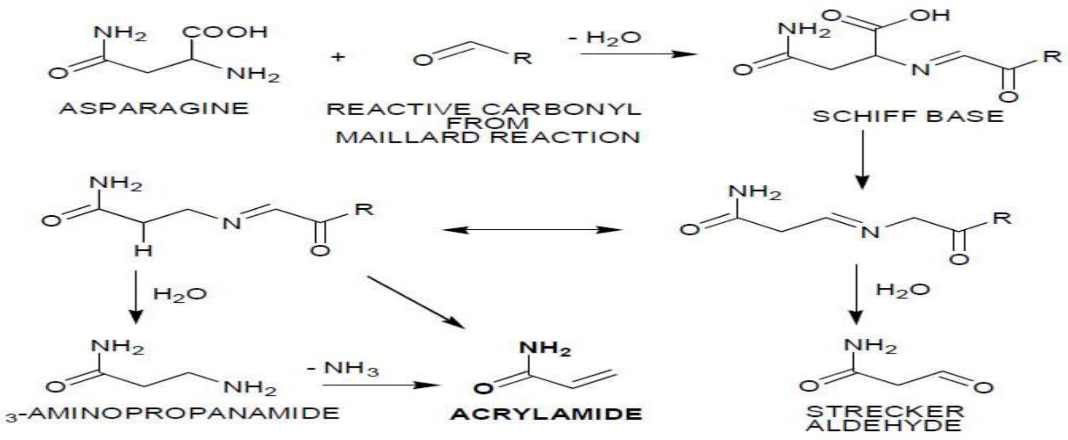


Figure 3: Mechanism of Acrylamide Formation

Source: Krishnakumar and Visvanathan (2014)

Formation Through Asparagine Route:

The major pathway leading for acrylamide formation in food products is a part of the Maillard reaction with free amino acid (asparagine) and reducing sugars (mainly glucose and fructose). Asparagine, the free amino acid present in potatoes in high amount, needs carbohydrates to form acrylamide [24].

It has also been reported that the reducing sugars are the major limiting factors in potatoes [25], while asparagine (mainly in cereal bran) is the major limiting factors in cereal products [26].

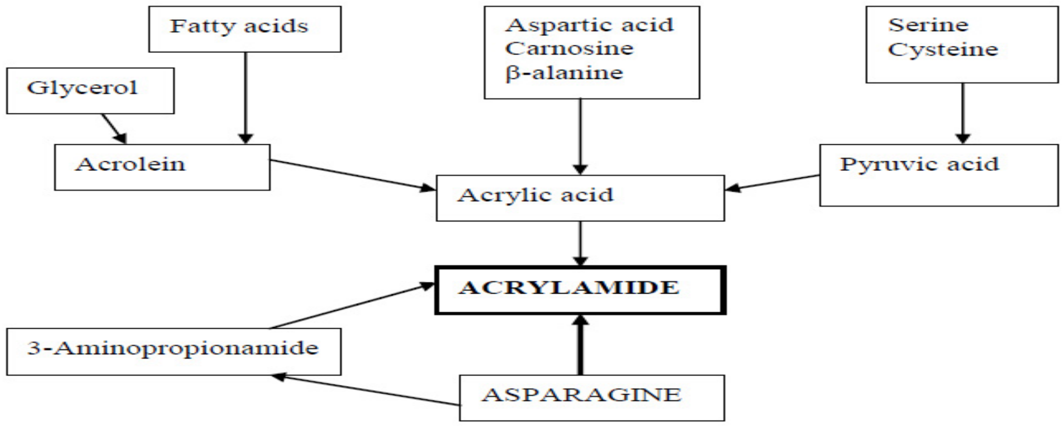


Figure 4: Major Route of Acrylamide Formation (Asparagine route)

Source: Krishnakumar and Visvanathan (2014)

Formation Through Alternative Routes:

In the absence of asparagine, acrolein and ammonia could both serve as starting materials in lipid-rich foods to produce acrylamide. At high temperature, lipid degradation yields acrolein and acrylic acid.

Furthermore, degradation of amino acids with ammonia can give rise to acrylamide formation by thermal decomposition [27], [28].

Amino acids such as glutamine, cysteine and aspartic acid have also been found to produce low amounts of acrylamide. Recent studies have indicated that 3-aminopropionamide (3-APA) is an important precursor leading to the formation of acrylamide. 3-APA occurs in food products and can generate high amount of acrylamide when heated [29]. This is referred to as Enzymatic Decarboxylation of Asparagine.

Fate Of Acrylamide In Foods:

Acrylamide is known to be a highly reactive molecule. It can react by ionic and by free-radical mechanisms and its presence, in free form, in food, was therefore unexpected. The observation of relatively high levels in certain foods rich in carbohydrates, and lower levels in protein-rich foods, may reflect the relative ease of formation in the former, or it may be due to volatilization or further reactions between acrylamide and food components in the latter. It is expected that acrylamide could react with any major or minor food component containing thiol, amino and, to a much lesser extent, hydroxyl groups. This complication, with the formation of acrylamide possibly being offset by disappearance pathways, means that it may be very difficult, if not impossible, to understand the mechanism(s) of formation based only on consideration of levels in foodstuffs. It will be necessary to conduct hypothesis-driven model studies, coupled with a systematic examination of the relationship between acrylamide levels and processing/cooking conditions [16].

3. HEALTH IMPLICATIONS OF FOOD ACRYLAMIDE

The health impairment caused by acrylamide hinges on its carcinogenic and genotoxic impact [29], [30].

Acrylamide is a compound, with a potential to cause a spectrum of toxic effects, including neurotoxic effects as has been observed in humans. Exposure to high levels of acrylamide in the workplace has been shown to cause neurological damage, e.g., among workers using acrylamide polymers to clarify water in coal preparation plants [4].

Toxic Effects:

Animal studies and human experience demonstrate that acrylamide is neurotoxic throughout postnatal life. Dysfunction of the central nervous system, especially the brain, dominates the acute toxic response to large single exposures. Brain dysfunction may present as seizures (overt poisoning only), or after prolonged exposure, in the form of sleepiness, changes in emotion and memory, hallucination, and tremor. These manifestations of acrylamide intoxication may precede and/or accompany signs of peripheral neuropathy (stocking-and-glove distribution of sensory loss, sweating, and muscle weakness) with or without the ataxia that characteristically results from repeated lower-level exposures to acrylamide. Peripheral neuropathy is a delayed response to acrylamide exposure and, depending on the dose received, may appear within weeks or months of daily exposures to small amounts, and up to several years in the event of chronic, low-level exposures. Rodent studies indicate that peripheral neuropathy develops more rapidly, and has greater severity and slower recovery in older versus young animals [14].

Carcinogenic Effect:

Available cohort mortality studies of occupationally-exposed workers have established any correlation between acrylamide and mortality from cancer. Available human data on cancer risk from acrylamide in food include case-control studies and reports from on-going prospective cohort studies. Most of these studies found no significant associations between dietary acrylamide and the risk of cancers; however, risks for selected cancers were slightly elevated in a few instances. Acrylamide has caused several types of cancer in animals. We do not know whether acrylamide causes cancer in humans. The EPA, International Agency for Research on Cancer (IARC), National Toxicology Program (NTP), and the Department of Health and Human Services has concluded that acrylamide is likely to be carcinogenic to humans [31].

Genotoxic Effect:

According to the FAO/WHO (2002) report, studies have shown that acrylamide does not induce gene mutations in bacteria, but the epoxide metabolite glycidamide does in the absence of metabolic activation. Acrylamide showed equivocal, negative, or weakly positive results when tested for the induction of gene mutations in mammalian cells. Acrylamide induces chromosomal aberrations, micronuclei, sister chromatid exchanges (SCE), polyploidy, aneuploidy and other mitotic disturbances (e.g. C-mitosis) in mammalian cells in the absence of metabolic activation [32]. Acrylamide was unable to induce Unscheduled DNA Synthesis (UDS) in rat hepatocytes. Glycidamide induced UDS in human mammary cells, with equivocal results in rat hepatocytes. For micronuclei induction, a mixed breakage (prevalent)-aneuploidy mechanism was shown.

In germ cells acrylamide produced several genetic effects such as chromosome aberrations, micronuclei (derived both by breakage and, to a lesser extent, by aneuploidy), SCE, UDS, single-strand breaks in DNA, dominant lethal mutations, specific locus mutations and heritable translocations. Glycidamide also induces dominant lethal mutations. Acrylamide is a germ cell mutagen in rodents, with the potential to induce heritable genetic damage at gene and chromosomal level

Neurotoxic Effect:

Acrylamide is a neurotoxin by either oral (in animals) or inhalation exposure (in humans and in animals). Toxic effects are central and peripheral neuropathy causing drowsiness, hallucinations, numbness in hands and feet, sweating and ataxia. However, most people are not exposed to acrylamide levels high enough to cause these effects and recovery is possible after cessation of exposure. So, this effect is not of major concern as compared to carcinogenic effect [31].

Effect On Reproductive Health:

Acrylamide reduces the ability of male animals to produce offspring and could cause similar effects in humans, but not likely at exposure levels experienced by most people. Effects such as decreased body weight, decreased startle responses, indicators of repressed learning ability and motivation, delayed development of motor skills, and decreased levels of some chemicals involved in transmission of brain signals were seen in some animals exposed to acrylamide before and after birth. There are no reports of acrylamide causing developmental effects in humans [31].

Acrylamide poses an elevated health risk to children [32]. The acrylamide in foods consumed by pregnant women has been shown to reduce birth weight and head circumference, key indicators of a child's future health. Critically, because of their smaller size and the types of foods they consume, young children are typically exposed to twice as much acrylamide, per kilogram of body weight each day, as adults [33], [4].

4. REDUCTION AND POSSIBLE CONTROL OF FOOD ACRYLAMIDE

Significant efforts have been undertaken in order to develop appropriate ways of reducing 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 below [34].

The Use of Additives:

The Use of Enzyme

Asparaginase, an enzyme that converts precursor (asparagine) into ammonia and aspartic acid, can reduce acrylamide formation in foods [35], [36]. 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 [34].

Addition of Amino Acids:

The addition of amino acids or protein rich substances reduces the acrylamide content in foods. Amino acids such as glycine, cysteine, methionine, glutathione and lysine on acrylamide formation and its elimination kinetics was assessed in several studies [37], [3], [39].

Formation of acrylamide decreased by 50% when cysteine and methionine were added to cracker and potato dough. On the contrary, Flückiger and Salih (2006) studied the effect of cysteine on acrylamide formation in crisp bread and found that no such effects [40].

Addition of Antioxidants:

Addition of antioxidants has been found to influence the Maillard reaction, which results in acrylamide formation [41], [42], [43]. Antioxidants present in the rosemary extracts, bamboo leaves and green tea extract [44] 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 [45]. 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.

Addition of Metallic ions:

Mono and divalent cations (Na^+ and Ca^{2+} or Mg^{2+}) added to the dough showed a remarkable effect on acrylamide reduction. In addition, polyvalent cations are also capable to reduce acrylamide formation during heating. These ions could interact with asparagine so that prevent the Schiff base intermediate formation and thus acrylamide generation [46], [47].

Addition of Sodium Chloride:

A significant effect of Sodium Chloride (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. Acrylamide formation in potato strips reduced by hydrocolloid coatings when alginic acid and pectin were used as coating agents [48], whereas carob gum, carrageenan, hydroxypropyl distarch phosphate and xanthan gum stimulated acrylamide formation.

pH, Water Activity And Fermentation

Potency of Hydrogen (pH)

Maillard reaction has strong influence on pH. It is known that high pH affects nutrients in foods [10]. Researchers showed that the reduced pH drastically reduces acrylamide content during frying and baking [49].

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. Reduced pH levels results in Maillard reactions, accompanied by reduced acrylamide formation [6], [50].

Water Activity (a_w)

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 [51], [52].

However, the removal of acrylamide from heated foods such as biscuits and potato chips increases with the increase of water activity [34].

Fermentation

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 [12]. Combined lactic acid fermentation with blanching found suitable for higher acrylamide reduction in potato products [53].

5. RAW MATERIALS

The influence of variety, harvest year, fertilization and storage conditions on acrylamide formation has been studied in potato products (and also in cereal products [54]. The composition of potatoes varies with variety to variety [55] 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 [22].

Potato varieties with low concentrations of reducing sugars can be an effective way to reduce acrylamide concentration [25].

6. STORAGE CONDITIONS

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 [56]. 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 [37]; whereas 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. Higher temperature storage (more than 8°C), which results senescent sweetening, is also related to sprout formation in potatoes. Storing potatoes at low temperature (below 8°C) found to be an effective tool to inhibit sprouting; temperature below 4-6°C has a major effect on reducing sugar accumulation [57], [58].

However, reducing sugars in potatoes are not significantly varied when potatoes are stored at 8°C [59] and no changes are found in asparagine contents in potatoes stored at different temperature and time [60], [59]. In order to reduce acrylamide formation, potato tubers should be ideally stored at 8°C.

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. 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, [61].

Baking:

Baking at high relative humidity proved to be effective for reducing acrylamide in bakery products [62]. This can be achieved not only by reducing the temperature, but also by using steam as heating medium during the final part of baking [63]. The reference baking temperature and time considered were 200°C for 20min. Acrylamide formation mostly occurs in the outer crust than in the inner crust of bread, while only trace amount appears in the crumb [64].

However, the prolonged baking temperature and time combination (260°C, 20 min) decreased the acrylamide content in foods. Biedermann and Grob (2007) 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 [66]. Moreover, the combination of conventional and dielectric (microwave) heating found to be suitable for reduction of acrylamide in bakery products [63], [64].

Blanching:

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 [68], [37], [66], [67].

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 [34]

Frying:

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 [69]. 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^{o}C) and time to be considered as important for acrylamide reduction. Frying under low pressure conditions using vacuum fryer results in higher acrylamide reduction [70], [71].

7. CONCLUSION

Direct exposure to pure acrylamide by inhalation, skin absorption, or eye contact irritates the exposed mucous membranes and can also cause sweating, urinary incontinence, nausea, myalgia, speech disorders, numbness, paresthesia, and weakened legs and hands. The mutagenic and carcinogenic properties of acrylamide can be strictly reduced, if people could limit their intake of processed foods, fried and fatty foods. Carbohydrates rich food should not be prepared at a temperature higher than 120^{o}C. Further epidemiological cohort studies are needed to help determine and explore the effects of dietary acrylamide intake on human cancer risk. Bio-specimen collections in cohort studies will provide an opportunity to avoid the limitations of interview-based dietary assessments by examining biomarkers of exposure to acrylamide and its metabolites in relation to the subsequent risk of cancer. The results of these various studies will help the industry to adopt practical effective and innovative ways to reduce the levels of acrylamide. The use of acrylamide in foods should not exceed 2% and up to 10mg polyacrylamide, 1L water can be used to wash or peel fruits and vegetables. Ameliorating acrylamide in food products while protecting other quality aspects and reducing dietary acrylamide exposure still remains a major challenge as complete acrylamide removal is probably not possible due to other, minor asparagine- independent formation pathways.

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