

# Formation of Acrylamide Compounds in Food Products from Maillard Reactions: A Review Article

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**Abstract.** The process of heat treatment is commonly used in food processing to improve colour, flavour, nutrition, and safety from microorganisms, while also reducing the potential of toxic chemical risks. However, researchers have identified a potential risk associated with the Maillard reaction in food products that occurred during in food heating process. The Maillard reaction occurs in three stages: the initial stage (such as in milk and UHT milk), the intermediate stage (as in lager beer and bakery products), and the advanced stage (as in stout beer, coffee, and chocolate). The Maillard reaction is influenced by both physical variables (such as temperature and time of treatment) and chemical variables (including pH, water activity, and substance). Acrylamide is one of the toxic chemical risks that can be formed during the Maillard reaction. This occurs when through the major pathway involving asparagine and carbonyl groups specifically, leading to the formation of N-glycoxy-asparagine. Additionally, acrylamide can also be formed through oxidized acrolein and lipid oxidation. This review article used online search engines such as ScienceDirect, Google, and ResearchGate as literature research method.

## 1 Introduction

Heating food improves its properties by altering molecules with high temperatures, resulting in better shelf life and organoleptic properties, such as colour, texture, and flavour. This process is used in various food products such as fried, baked, roasted, dried, pasteurized, sterilized, and ultra-high temperature-treated foods [1–5].

When heating certain foods, such as bakery products, roasted coffee, snacks, baby porridge, and refined oils, chemical reactions, such as the Maillard reaction can produce harmful substances, such as acrylamide, furans, and chloropropanol. Maillard's discovery in 1912 demonstrated that amino acids and reducing sugars create pigments. This is commonly observed in food production for shelf-stable foods with specific nutritional properties [1,6,7].

Acrylamide was discovered in 2002 by Tareke, a Swedish researcher in fried and baked products, and was a major breakthrough in food science due to the Maillard reaction [8–10].

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Acrylamide has been classified as a Group 2A carcinogen by the International Agency for Research on Cancer (IARC) and a Category 2 carcinogen and Category 2 mutagen by the European Union. This compound has sparked global interest as it is considered a "probable human carcinogen", "likely to be carcinogenic to humans", and "reasonably anticipated to be a human carcinogen". The WHO recommends a maximum daily acrylamide intake of 1 µg/kg of body weight. In Addition, acrylamide is known to be a neurotoxin [11–13].

The Acrylamide compounds found in food products can threaten public health. Therefore, it's essential to conduct research in public health nutrition, including food heating, the Maillard reaction, and the total quantity of acrylamide compounds found in food [14]. This review article provides a comprehensive overview of various studies conducted on these topics. Virtually everyone has been exposed to these compounds based on their dietary habits, emphasizing the need for research to be conducted in this area.

## **2 Methods and literature research**

This article review used secondary research methods that utilize prominent search engines, including ScienceDirect, Google, and ResearchGate. The literature search was conducted using the keywords 'heat treatment', 'Maillard reaction, and 'acrylamide'. The gathered data was then meticulously analyzed and categorized to correlate with the formation of acrylamide compounds in various food products resulting from Maillard reactions.

## **3 Results and discussion**

### **3.1 Heat treatment for foods**

Food heating methods depend on various factors such as food type, microbial content, heating medium, and desired product characteristics. Different techniques such as pasteurization, canning, blanching, preheating, ultra-high temperature treatment, ohmic heating, radio-frequency heating, microwave heating, pressure heating, infrared heating, pH heating processes, and novel drying methods are used [4,15–18].

Heating food is an effective way to enhance its shelf life, taste, and safety by eliminating enzymes and microorganisms and reducing water activity. However, this process can also change the chemical components of food, including hydrolysis decomposition, oxidation rancidity, protein denaturation, molecular level modification, colour degradation, enzymatic degradation, carbohydrate caramelization, the formation of neo-formed contaminants (NFC), and interactions between proteins and organic compounds that may have mutagenic, carcinogenic, and cytotoxic effects [4,15,19–21].

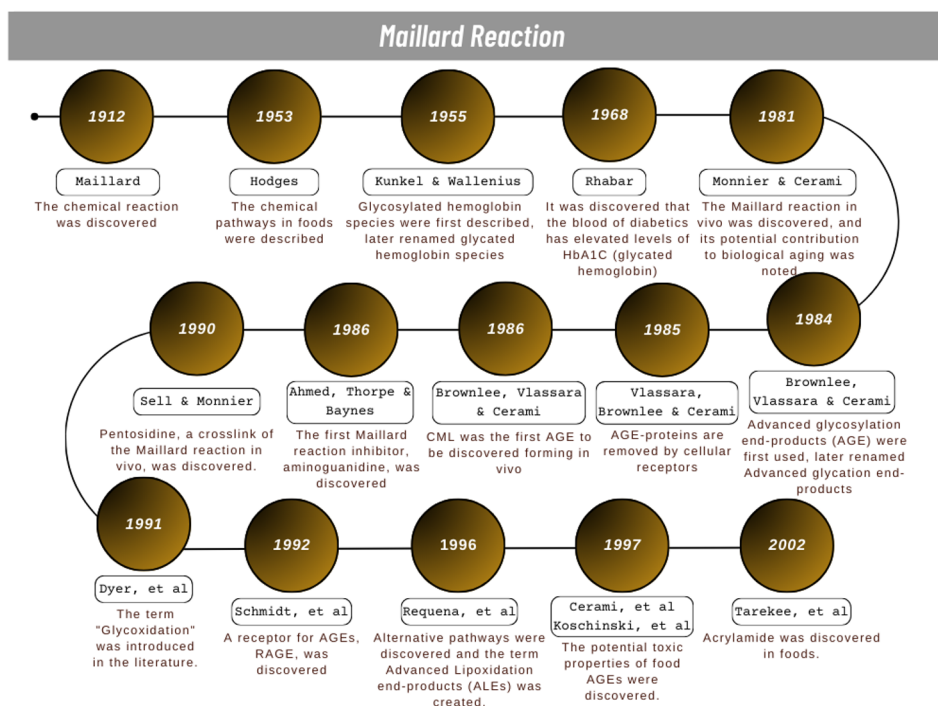
The food industry faces challenges in developing heating processes that can produce foods with desirable qualities while maintaining their stability. Heating food during processing or storage triggers the Maillard reaction, this reaction leads to the formation of various compounds called Maillard Reaction Products (MRPs), which can have both positive and negative effects on food products. To achieve desirable qualities products, several parameters must be considered to control the Maillard reaction rate. However, modifying this rate can be difficult because of the chemical complexity of food. Lowering the pH, temperature, and water activity can inhibit the reaction, but it may not always be feasible. Comprehending the nuances of this reaction and its impact on food preparation is crucial for the food industry to fine-tune processing techniques and minimize the formation of unpalatable compounds [22–27].

### 3.2 Maillard reaction

The Maillard reaction has been a significant subject of research for a long time. This has helped us understand biological aging and diseases, such as diabetes. Figure 1 shows the major research timeline since 1912 to 2002 about Maillard Reaction. The reaction was first discovered in 1912, and subsequent research has shown its relevance to biological aging. AGEs (Advanced Glycation End-products) are the end products of the Maillard reaction, and their impact on human health has become a major area of research.

Research has uncovered various types of AGEs generated within the human body, including N-(carboxymethyl)lysine (CML) and Advanced Lipoxidation End-products (ALEs). Additionally, a Receptor for AGEs, known as RAGE (Receptor for AGEs), has been identified and shown to play a crucial role in the pathophysiology of diseases linked to AGE accumulation. These studies provide a scientific basis for understanding the influence of Maillard reaction on human health. Recent studies have revealed that acrylamide, a potentially harmful substance, is present in food [9,11].

The Maillard reaction also called non-enzymatic browning reaction is a chemical process that occurs when carbohydrates react with amino acids during the heating of food. This reaction creates unique colours, aromas that enhance the taste of food, safety, and health-promoting properties by forming flavour-enhancing Maillard reaction products (MRPs). Factors such as protein source, temperature, and pH affect this reaction, which is also significant in the taste of processed foods [1,11,23,28–30].



**Fig. 1.** Major research timeline on the Maillard reaction.

The Maillard reaction is complex and can produce multiple compounds depending on the reactants used. It is initiated by the combination of amino groups on proteins and carbonyl groups on reducing sugars, resulting in the formation of Schiff bases and rearrangements of Amadori and Heyns compounds [31,32]. The Maillard reaction has various stages according to Hodge: initiation, intermediate, and final.

### 3.2.1 Initiation stage

The product does not have any colour due to the absence of nutrients such as lysine, and it cannot absorb UV radiation. At this stage, two reactions occur - the condensation of sugar-amine and the rearrangement of Amadori compound.

In the initial stage of the Maillard reaction, sugar-amine condensation, the carbonyl group, and the amino group combine through nucleophilic condensation. An unstable Schiff base is produced as a result of dehydration. These Schiff bases can be transformed into N-substituted-glycosylamine or imines, which are commonly known as Schiff bases for glucose or fructose. Notably, the process is reversible because of the ability of sugars and amino acids to be reconstituted in highly acidic environments. Amino groups can originate from free amino acids, side chains of amino acids that have been incorporated into the protein (such as lysine), or amino groups in the final amino acid of each protein. Carbonyl groups can also originate from intermediate phases of the Maillard reaction; in this instance, they are typically reducing sugars and/or oxidized fats.

The next stage was the Amadori rearrangement mechanism. It is possible for imines (also known as Schiff bases) to undergo rearrangement through 1,2-eneaminol, resulting in 1,2-enediol owing to the presence of a hydroxyl group at the  $\alpha$ -position. In the case of N-substituted aldositylamine, this process leads to the formation of 1-amino-1-deoxy-2-ketose (also known as an Amadori compound) through Amadori rearrangement. Conversely, starting with N-substituted-ketosylamine results in Heyns rearrangement, leading to the formation of 2-amino-2-deoxy-2-ketose (also known as a Heyns compound). Amadori compounds are the first Maillard reaction compounds to be detected in food, and they are generally more stable than the parent Schiff base because of their cyclic chemical structure. This cyclic structure prevents them from being as unstable as imines, which can be converted into unstable cyclic hemiaminals owing to their tendency to rotate. However, the rearrangement of Amadori compounds results in the hemiacetal furanose being able to rotate, although it is still more stable than the carbohydrates.

### 3.2.2 Intermediate stage

Toxic substances are produced during this phase, resulting in the formation of colourless or yellow substances that strongly absorb UV light. This process occurs through the dehydration of sugars, fragmentation of sugars, and degradation of amino acids.

The sugar dehydration and sugar fragmentation stage influence the flavour and colour of food from several intermediate compounds produced during the decomposition of Amadori and Heyns compounds, which occurs due to the pH and temperature of the medium during heating. The Maillard reaction results in the formation of various osuloses, such as 1-, 3-, or 4-deoxyosones, and reductones. Deoxyosones can be formed at pH values ranging from 4 to 7. Amadori's 1-amino-1-deoxy-2-ketose can be converted into 2,3-eneaminol and 1,2-eneaminol, which then decomposes into deoxyosone. Hydrolysis of imine cations produces 3-deoxyosone, and the removal of  $\beta$ -2,3-eneaminol can occur via retro-Michael reaction, resulting in 1-deoxyosone synthesis, or by removing water from carbon 4 of 2,3-eneaminol to generate 4-deoxyosone.

Upon subjecting 3-deoxyosones to low pH conditions, they undergo further decomposition via 1,2-enolization, leading to the formation of furanic compounds, including 5-hydroxymethylfurfural (HMF), hexose, and pentose furfural, at a later stage. Conversely, the 2,3-enolization compounds are produced under basic pH conditions, resulting in pyrrole and pyranones.

The process that comes between sugar dehydration and sugar fragmentation stages is known as the Amadori compound stage. During this process, Amadori compounds separated

into fission products such as acetal or acetaldehyde. The amino acid degradation (Strecker degradation) stage follows this process.

Strecker degradation is a chemical process that occurs when amino acids react with dicarbonyl substances such as dehydrereductones or fission products. This reaction can lead to a loss of amino acids in the diet. During this process, a new aldehyde is formed with one less carbon atom, which is then released as CO<sub>2</sub>. Strecker degradation is more such asly to occur in foods with higher concentrations of free amino acids and under extreme conditions such as high temperature or pressure. The resulting aldehydes, such as methional, phenylacetaldehyde, and 3-methylbutanal, can have a potent aroma depending on the type of amino acid that is degraded.

### 3.2.3 Final stage

The formation of advanced glycation ends (AGEs) is responsible for various skin aging effects, including coloured products, melanoidins, and aromatic compounds. These reactions involve aldol condensation, aldehyde-amine condensation, and the formation of heterocyclic nitrogen compounds. Table 1 provides insight into the contribution of Strecker degradation and amino acid involvement in the formation of odours.

The first reaction is aldehyde-amine condensation. Amadori compounds alone cannot produce volatile aromatic compounds without the presence of free amino groups. However, when 2-deoxyglucose interacts with amino acids, it results in the formation of 1% of the total volatile chemicals produced. This process is similar to Strecker degradation and produces a range of chemical odour, such as pyrazines, pyrroles, thiazoles, and thiophenes. For instance, the primary flavour of roasted meat is alkylpyrazine, while braised meat produces different compounds such as 2,4,5-trimethyl-3-thiazoline.

After the aldehyde-amine condensation, heterocyclic nitrogen is the next reaction. Melanoidin is a polymeric chemical with a brown color that is formed through the condensation of laminated mid Maillard reaction products, such as N-substituted-pyrrole, N-substituted-2-formylpyrrole, and 2-furaldehyde. Melanoidins have various molecular weights and absorbance spectra, making them quite diverse. When the melanoidin core is generated by carbohydrates, such as coffee and balsamic vinegar, they are referred to as melanosaccharides, while melanoproteins are used when the melanoidin core is formed by proteins, such as bakery products.

Some melanoidins, such as N- $\epsilon$ -fructosyllysine (FL) and N-(carboxymethyl)lysine (CML), are used to measure protein glycation in food heating, which can indicate a loss of nutritional value. Other Maillard reaction products, such as acrylamide and furfurals, can pose food safety risks during heating, as they have potential adverse effects on human health. Melanoidin is the end product of non-enzymatic browning and is believed to be superior to melanin, which is the end product of enzymatic browning.

To optimize Maillard reactions in food preparation, it's essential to consider physical variables such as heating temperature and time, as well as chemical variables, such as pH, water activity, and substrate. Understanding these stages is crucial for controlling and optimizing Maillard reactions [1,22,31,33,34].

## 3.3 Acrylamide

Asparagus shoots were discovered to contain asparagine in 1806. Its importance in regulating basic cellular processes led to growing interest in the fields of chemistry, biology, and medicine.

Asparagine is a non-essential amino acid, synthesized by living organisms. The catabolism and anabolism of amino acid formation share similar characteristics and use

coenzymes. The end products of the catabolic pathway and the metabolic precursors of the anabolic pathway include glycolysis intermediates, the citric acid cycle, and the pentose phosphate pathway. Some amino acids, such as asparagine and aspartate, yield only one intermediate end product (oxaloacetate), while others such as lysine and leucine yield acetyl-CoA [35].

**Table 1.** The formation of odour is influenced by the involvement of amino acids and the Strecker degradation process.

Compound	Molecular mass (g)	Odour	Amino-acid involved	Detection threshold in water (ppb)
Acetaldehyde	44	Yogurt, fruity	Alanine	15–120
2-mercaptoacetaldehyd	76	Cabbage	Cysteine	5–500
2-metilpropanal	72	Malt, baked potato, banana	Valine, threonine, Serine	0.1–2.3
3-metilbutanal	86	malt, almond, chocolate, cheese, malt	Leucine	0.2–2
2-metilbutanal	86	Burned, almond, cocoa	Isoleucine	1–10
Methional	104	Boiled potato	Methionine	0.2
Methanethiol	48	Cabbage, egg	Methionine	0.3–1
Dimethyl disulfide	94	Gasoline, sulfur, cabbage	Methionine	0,16–12
Dimethyl trisulfide	126	Gas	Methionine	0,005–0.01
Phenylacetaldehyde	120	Honey	Phenylalanine	4
Furaneol	128	Caramel, strawberry	Proline	0.03
2-furaldehyde	96	Baked bread	Isoleucine, leucine	3000–23000
2-furanmethanol	98	Burned	Isoleucine, leucine,	5000
5-methylfurfural	110	Caramel, almond,		–
Maltol	126	Baked bread, caramel,		35000
2,5-dimethylpyrazine	108	Roasted meat, cacao	Phenylalanine, glycine,	800–1800
Tetramethylpyrazine	136	Roasted peanut	Valine, threonine, serine	1000–10000

Source: Emmanuel B, et al [36]

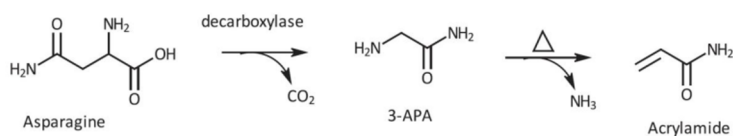
Acrylamide is formed in starch-based foods such as potatoes, bread, and cereals because of the reaction between amino acids and reducing sugars during heating, known as the Maillard reaction. Various carbonyl compounds, including fructose, glucose, glyoxal, methylglyoxal, and 5-hydroxymethylfurfural (HMF), contribute to its formation. Bioactive carbonyls, such as curcumin, ascorbic acid, dehydroascorbic acid, silymarin, and vanillin can also participate in the Maillard reaction, leading to the formation of acrylamide. The Carbonyls present in the heating process form a pool that contributes to the formation of acrylamide. The degree of fat oxidation can also affect the formation of carbonyl group in high-fat systems [37].

Acrylamide compounds are formed when asparagine reacts with reducing sugars or cleavage products at high temperatures and low moisture content. The reaction occurs because of the reaction between the  $\alpha$ -amino group of asparagine and the carbonyl group,

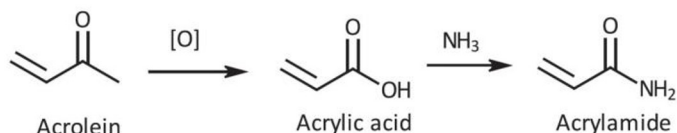
forming N-Glycosyl-asparagine (carbinolamine), which then produces a Schiff base through the removal of one water molecule when heated. Acrylamide precursors include cysteine and methionine in the presence of reducing carbonyls, and acrolein in the presence of ammonia.

3-APA (3-amino propionamide) is the primary pathway for the reaction mechanism that leads to the hydrolysis of imine II, which can potentially cause the formation of acrylamide. 3-APA is also generated during the enzymatic digestion of asparagines and can rapidly convert to acrylamide, even at low temperatures. An azomethine ylide is formed through hydrolysis or direct decomposition of the Schiff base. It undergoes intramolecular cyclization and produces acrylamide and 1-amino-2-hexulose upon cleavage of C-N bond. Acrylamides with acryloyl groups are highly reactive and can polymerize or form Michael adducts with nucleophiles.

Acrylamide formation in food is a complex process involving the transformation of acrolein into acrylic acid and subsequent reaction with ammonia generated from  $\alpha$ -amino acid degradation. Acrolein, being highly reactive, is more such likely to react with food components than acrylic acid. Additionally, acrylic acid may arise from the breakdown of aspartic acid, carnosine, and  $\beta$ -alanine. While the main pathway for the formation of acrylamide is well-known, Figure 2 and figure 3 illustrate alternative pathways.



**Fig. 2.** Minor pathways of acrylamide formation [36]



**Fig. 3.** Fat oxidation pathway of acrylamide formation [37]

Research indicates that acrylamide can bind to hemoglobin and convert it to the reactive epoxide glycidamide, making it imperative to maintain its concentration in water below 0.1 mg/L. This compound can also form in foods during high-heat cooking processes that involve significant levels of carbohydrates. To reduce acrylamide production, it is crucial to control precursor concentrations such as fructose, glucose, and asparagine, as well as varying cooking times. Effective reduction strategies may involve enzymatic hydrolysis of asparagine using asparaginase, addition of specific additives, lowering of pH levels, or reducing thermal exposure [11,37].

### 3.4 Acrylamide in food products

Acrylamide is a potentially carcinogenic compound that forms naturally during the heating process of certain foods, particularly at high temperatures (above 120°C/248 °F) and low humidity conditions, although it can even be present in fruits and vegetables under certain circumstances. Acrylamide levels in food vary according to regional diet. In the US, French fries account for 35% of the intake, whereas coffee and bread are low (7% and 11%, respectively). It is challenging to compare the intake across populations owing to the different preparation methods. Southern and Western Europeans consume more bread, breadcrumbs, and toast (24-50%), while Northern Europeans consume more coffee (33-40%), followed by

bread, crispbread, and toast (20-35%). Table 2 shows the total acrylamide content of the various food products.

**Table 2** Total acrylamide in various food products

Food categories	Acrylamide (µg/kg)	References
French fries	338 (336–339)	[38,39]
French fries from fresh potatoes	325 (325–326)	[38,39]
Pre-cooked French fries	331 (329–333)	[38,39]
Oven French fries	690	[39]
Deep-fried French fries	198 (195–201)	[38,39]
Potato crisps	675 (674–676)	[38,39]
Potato crisp from fresh potatoes	758 (757–758)	[38,39]
Potato dough	435	[38,39]
Cereals	138 (132–144); 64.42	[39,40]
Processed cereal-based foods for infants and young children	51 (45–47)	[39]
Cereal bars	112.04	[40]
Biscuits	20–1514; 97.27	[40,41]
Crackers	178; 15-2017	[39,41]
Breads	5–116	[41]
Crisp breads	249 (248–250); 198.36	[39,340]
Ginger bread	415 (414–415)	[39]
Toasted bread	<10–1430; 48.45	[40,41]
Croissants	22–40	[41]
Muffins	12–100	[41]
Shortbread	341.25	[40]
Pastries and cakes	192 (189–194)	[39]
Wafer & waffle	389; 42–280	[39,41]
Wholemeal cookies	496.33	[40]
Dry cookies	63.16	[40]
Butter cookies	734.78	[40]
Roasted coffee	256 (255–257)	[40]
Instant coffee	1123	[40]
Green coffee	56	[42]
Roasted green coffee	681	[42]
Oolong tea	75	[42]
Black tea	21	[42]
Fermented soybean products	22.36–62.30	[40]
Commercial beer	0.52–72	[43]
Black ripe olive	10–600	[44]
Muesli dan porridge	80 (77–83)	[39]
Long-grain (LG) Rice	180	[45]
Wheat	298	[45]
Corn	378	[45]
LG + 10% pre-gelatin rice	319	[45]
LG + 5% pre-gelatin rice + 3% milk	336	[45]

Source: *Pieternel L.*, and *Maimunah S* [38], *Ayşegül Ç* [39], *Sladana Ž.* [40], *Marta M.*, and *Francisco J.M.* [41], *Fang C.*, et al [42], *Anna S-R.*, and *Magdalena S* [43], *Alfredo M.*, et al [44], and *Eduardo J. Guerra-Hernández* and [45]

## 4 Conclusion

Ensuring food safety is paramount to ensuring that food products available to the community are safe for consumption. One effective way to enhance food safety is through food heating,

which also has the added benefit of improving nutritional value, aroma, and flavor, while minimizing the risk of foodborne illness from harmful chemicals. Moreover, food heating can extend the shelf life of certain food items. A variety of heating methods are available, including pasteurization, canning, bleaching, preheating, ohmic heating, radio dielectric frequency heating, microwave heating, pressure heating, pH heating, roasting, and baking. This time-tested practice was used for generations.

When food is heated, a chemical reaction known as the Maillard reaction occurs. This reaction was first proposed by Louis-Camille Maillard in 1912 and has since been studied by researchers. It was not until 1997 that potentially harmful contents associated with aging were discovered. The Maillard reaction is a complex process that occurs in three stages. The first stage involves nutrient deficiency, such as lysine deficiency, and produces colorless products that do not absorb UV radiation, along with sugar-amine condensation and rearrangement of Amadori compounds. In the intermediate stage, toxic compounds are formed, resulting in colorless products or products with strong UV light absorption through sugar dehydration, sugar fragmentation, and amino acid degradation. The final stage involves the formation of AGEs responsible for skin aging, colored products, melanoidins, and aromatic compounds. This stage includes aldol condensation, aldehyde-amine condensation, and the formation of heterocyclic nitrogen compounds. The compounds produced in addition to acrylamide include heterocyclic amines, furan, furfural, and chloropropanol.

Acrylamide compounds can be produced via the Maillard reaction when asparagine and reducing sugars are combined. Although asparagine is not essential for daily life and can be synthesized by living organisms, it is present in various commodities created through anabolic pathways. The formation of acrylamide compounds is influenced by factors such as the temperature, heating time, and carbonyl groups. Additionally, acrylamide can be formed through minor pathways such as acrolein oxidation and fat oxidation. Typically, acrylamide formation occurs at temperatures above 120°C or 248 °F.

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