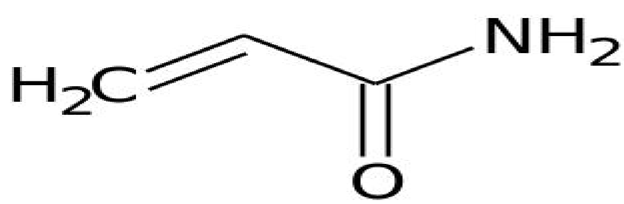
Acrylamide

Acrylamide is a crystalline white powder with a molecular formula of C_3H_5NO also been known as , ethylene carboxamide, acrylic acid amide or propenoic acid amide and the structure is presented in Figure below.



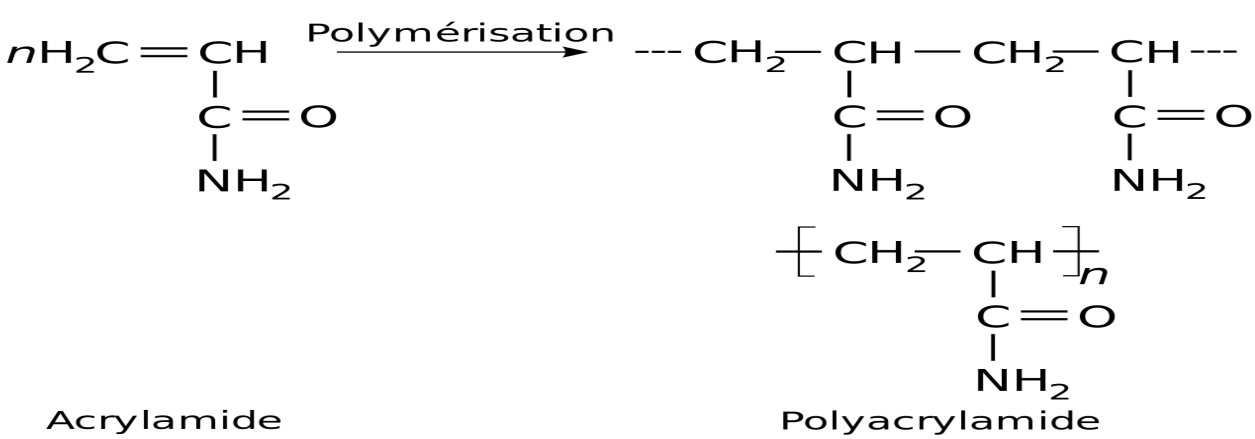
CH_2=CHCONH$_2$

structure of acrylamide

Acrylamide can undergo reactions both at the amide group and at the double bond (vinyl group) .

The solubility in polar and un-polar solvents varies considerably, but solubility in water is extremely high than other common solvents such as methanol, ethanol, and acetone.

Acrylamide exists in two forms; a monomer (single unit) and a polymer (multiple units joined together by chemical bond).



Polymerized acrylamide is not toxic, but monomeric is toxic form is neurotoxic Polymerized acrylamide used to produce polyacrylamide polymer, which find many uses as a coagulant in waste water treatment, clarifying drinking water, and electrophoresis gels. Also used in some food packaging materials such as paperboard, soil conditioning agents, plastics, and specialized grouting agents, but the single (monomer) form of acrylamide, is recently discovered to be present in food, which is toxic to the nervous system.

The International Agency for Research on Cancer has classified acrylamide carcinogenic to human and it is also known as **human neurotoxin**. A **carcinogen** in rats, and a suspected carcinogen in humans cause **gene mutation and DNA damage.** Earliest results from long term studies on acrylamide exposure of humans have shown that consumption of high acrylamide food is linked with a slightly higher occurrence of human ovarian, breast, and kidney cancer.

Acrylamide occurrence and dietary intake

People are exposed to different amounts of acrylamide drinking water, indoor air, or the environment and mainly **through the diet.** A.A 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 (120-170ºC)** by the reaction of the amino acid **asparagines** with a **reducing sugar** such as glucose.

Acrylamide primarily found in plant-based foods; heat treated starchy foods such as potato, cereal and bakery products contain high levels of acrylamide. The main precursor that **required in the production** of acrylamide is amino acid **asparagine** and **Carbonyl source (reducing sugars, glucose & Fructose).The formation of acrylamide in heat-processed foods occurs via the Millard reaction,**

. A.A is not found in foods that are **not fried or baked** (low heat treated) and found very low levels in animal-based food products such as **meat and fish**.

Foods which are rich in precursors are **fried potatoes, bakery products, and roasted coffee**. The range of acrylamide varies from one type to another type of food due to the differences in **composition** and **processing techniques**. The Concentration and dietary intake of food have significant variations, which depends upon cooking methods. Factors such as difference in food composition, high temperature (more than 120°C), and high carbohydrate, free asparagine, reducing sugars, pH, water content and high concentration of competing amino acids could be the sources for variation in acrylamide level.

However, A.A intakes have been estimated for populations of a number of countries based on the approach of using dietary records and the results of acrylamide analysis of foods. Calculated A.A intakes range from 0.3 to 0.6 µg/kg body weight per day for adults and 0.4 to 0.6 µg/kg for children and adolescents.

There is a great deal of data on A.A concentration in different foodstuffs which presented by many research and review papers.

Acrylamide levels in processed foods

Foods	Concentration (µg/kg=ppb)
Almonds, roasted	260
Baked products: bagels, breads, cakes, cookies, pretzels	70–430
malt, and whey drinks	30–70
Biscuits, crackers	30–3,200
Cereals, breakfast	30–1,346
Chocolate powder	15–90
Coffee powder	170–351
Corn chips, crisps	34–416
Crispbread	800–1,200
Fish products	30–3 9
Meat and poultry products	30–64
Nut butter	64-457
Potato boiled	48
Potato chips, crisps	170–3,700
Potato puffs, deep-fried	1,270
Soybeans, roasted	25

Sunflower seeds, roasted	66

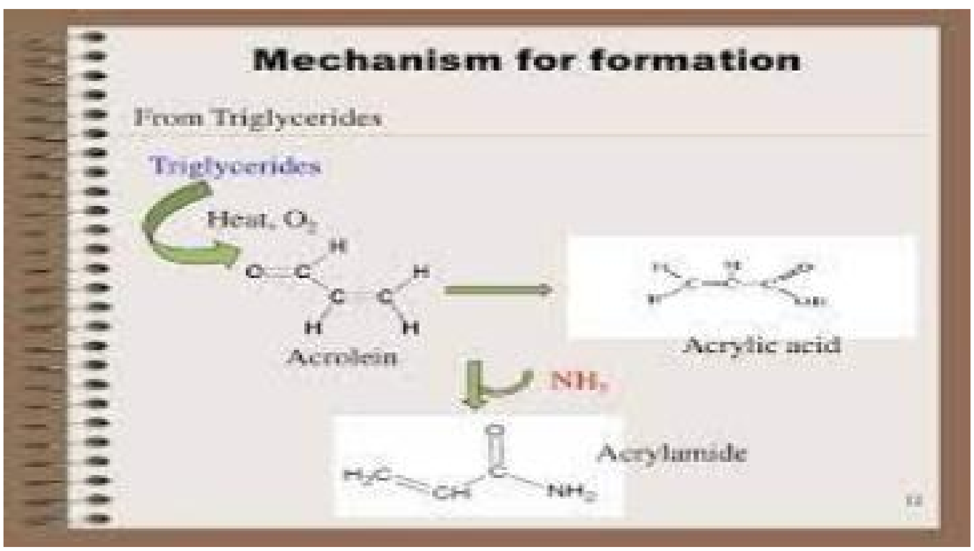
Mechanisms of Acrylamide Formation

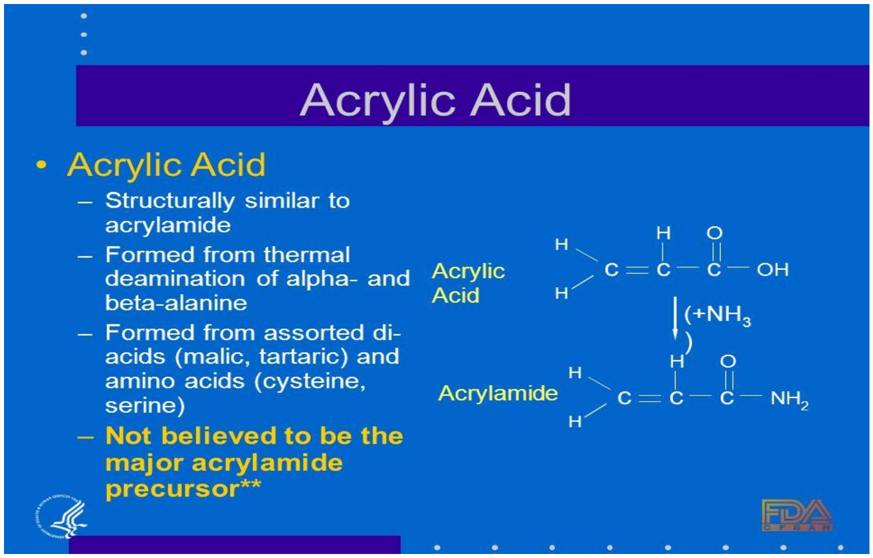
Researchers identified several mechanisms by which the toxin might form in foods and these potentially involved carbohydrates, proteins, amino acids, lipids as well as other food components. Some of the more likely pathways suggested were:

• Formation via acrolein or acrylic acid; acrylic acid is a possible intermediate to acrylamide and would involve reaction with a source of ammonia.

• Formation via the dehydration/decarboxylation of organic acids such as malic acid, lactic acid and citric acid.

• Direct formation from amino acids via degradation of a α-amino acid initiated by carbonyl compounds.





The last of these three is an example of the group of reactions in foods known as Maillard reactions. These are widely recognized as a type of **non-enzymatic browning.**

However the basic formation routes of acrylamide in foods is shown in Figure below 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.

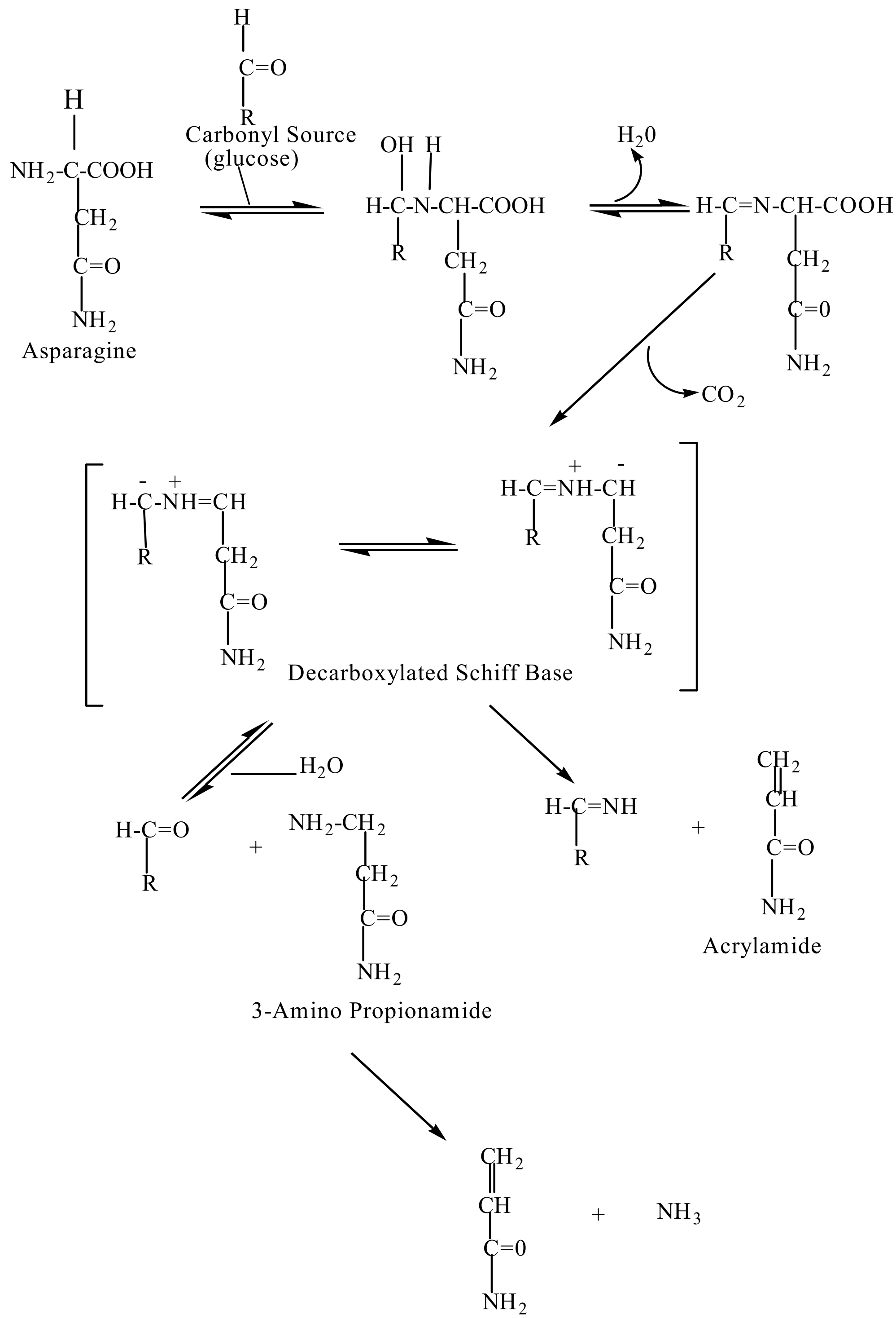
During the Millard reaction,

1- the **amino group** of **asparagine** reacts with a **carbonyl source** to form **imines**, known as a **Schiff base**.

2- **Heat** causes **decarboxylation** of the base,

3- which is followed by the **loss of amine group** to form acrylamide.

A secondary pathway involves **hydrolysis of the decarboxilated Schiff base,** forming **3-aminopropionamide** as an intermediate. This intermediate is **degraded** by **heat** to form acrylamide via the **elimination of ammonia.**

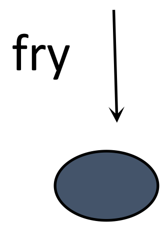


Mechanism of the formation of acrylamide from asparagine via the Millard reaction.

Effectiveness of Amino Acids and Dextrose to Form Acrylamide

<u>Model System</u>

(Potato Starch ● + water) + Amino acid .Reducing sugar .Variety of ingredients



Measure Acrylamide

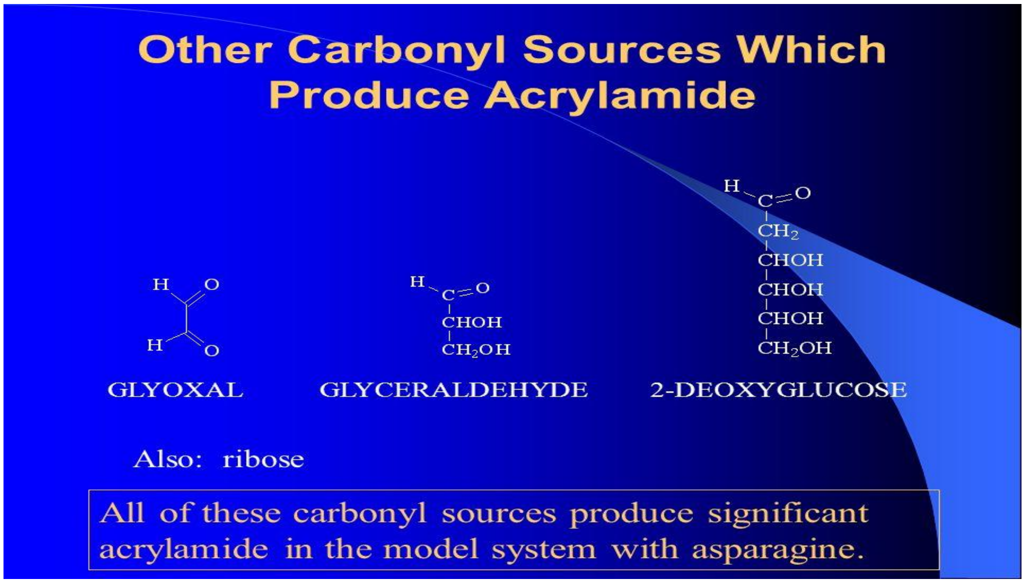
- Acrylamide Formation

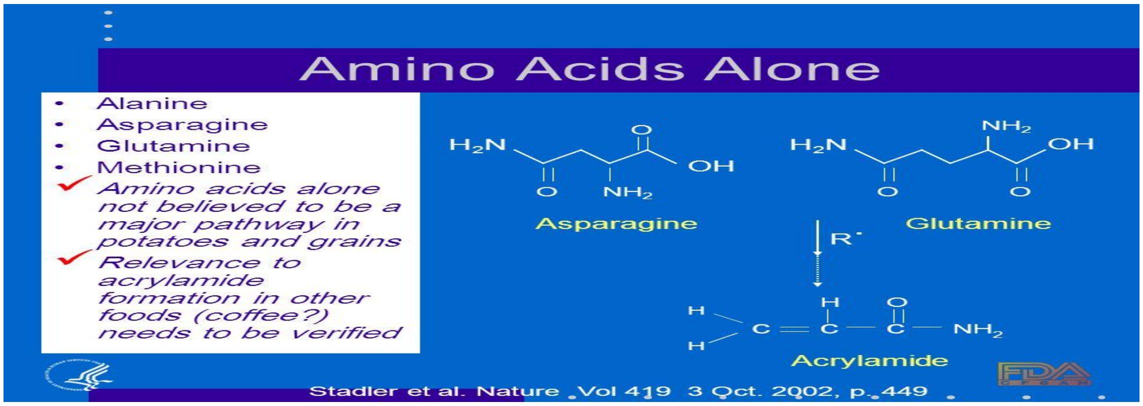
– Potato starch	<50 ppb
– Potato starch + dextrose	<50 ppb
– Potato starch + asparagine	117 ppb
– Potato starch + dextrose + asparagine	**9270 ppb**

- Other Amino Acids

– Alanine	<50 ppb	Arginine	<50 ppb
– Aspartic A	<50 ppb	Cysteine	<50 ppb
– Lysine	<50 ppb	Methionine	<50 ppb
– Threonine	<50 ppb	Valine	<50 ppb
– Glutamine	156 ppb	**Asparagine**	**9270 ppb**

- **Asparagine is the main source of acrylamide formation in foods.**
- **Carbonyl source (reducing sugars) is required in the reaction.**
- **Starch do not appear to be significant factors in a crylamide formation.**
- Formation of Acrylamide from Asparagine and Various Carbonyl Compounds in a Model Heated Food System
- *a* carbonyl source acrylamide (**µg/kg**)
- D-glucose **1454*b***
- 2-deoxyglucose 1036*b*
- ribose 2425
- glyceraldehyde 2669
- *a* The model system contained the following: asparagine (10 g); emulsifier (2.4 g);potato starch (400 g); water (400 g); and carbonyl source (D-glucose, 0.49 g;2-deoxyglucose, 0.45 g; ribose, 0.37 g; glyceraldehyde, 0.225 g; glyoxal, 0.175 g).
- *b* Average of results





Factors Affecting Acrylamide Formation in food

- reactant concentration in raw materials.
- Type of reducing sugar.
- reactant ratio
- Temperature.
- pH
- Storage conditions
- water content
- inhibitors

Methods for Reduction of acrylamide formation in food

A-Reducing levels of precursors

Reactants:

1-Soking of raw materials.

2-Blanching

3-selection of raw materials low in asparagine and/or reducing sugar

Impact of Potato variety on AA Levels

Impact of Potato variety on AA Levels (from D. Mottram, U. Reading)

Sample	Acrylamide concentration (µg/kg) GC-MS	Acrylamide concentration (µg/kg) LC-MS-MS	SNFA result (µg/kg)
Baking potatoes			
raw	<10	nd	<30
Boiled	<10	nd	
Chipped & fried	310	350	
King Edward potatoes			
raw	<10	Nd	
boiled	<10	Nd	
Chipped & fried	2800	3500	
Frozen frying chips			
as sold	200	100	
Cooked	3500	3500	
Over cooked	12800	12000	

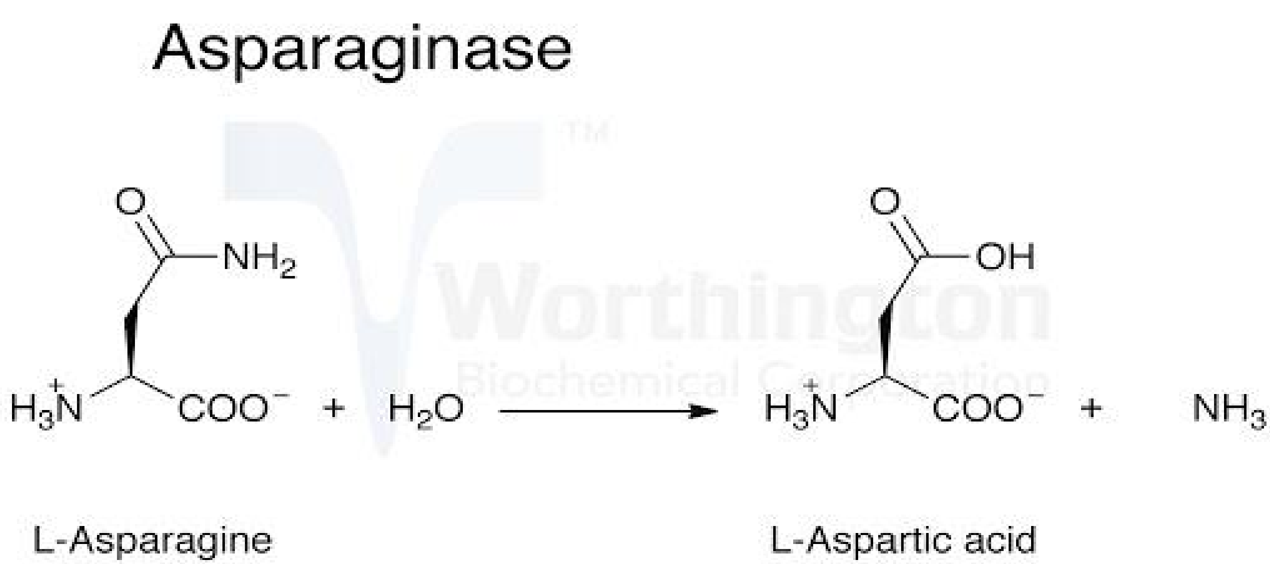
Acrylamide formation influenced by starting raw material

4-Use Selected Agronomic Methods

Selective breeding of crops to produced free asparagine, and to some extent of reducing sugar crops.

5- Enzymatically degrade reactants (asparagine, reducing sugar).

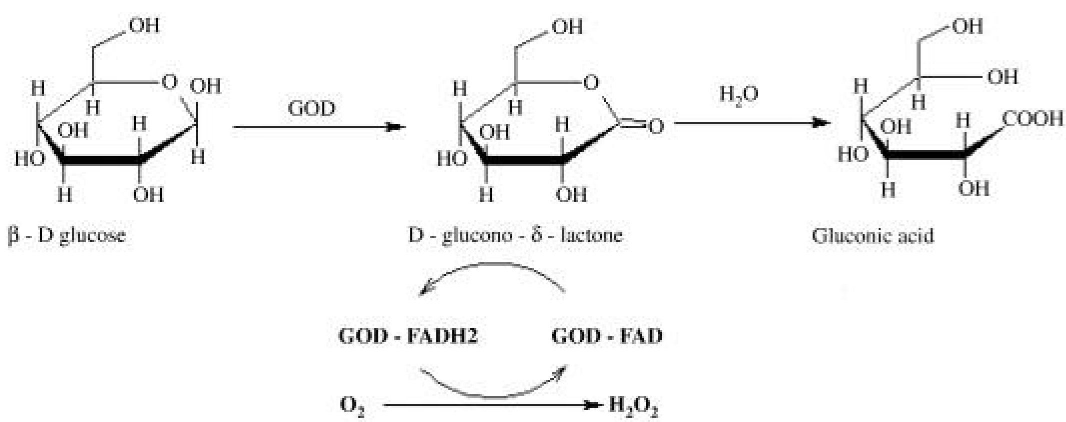
A-L-asparaginase (E.C. 3.5.1.1) catalyzes the irreversible deamidation of L-asparagine to L-aspartic acid and ammonia ions.



Potato Product	Acrylamide (ppb)		% Reduction[1]
Microwaved snack	Control	Asparaginase	>99
	20,500	164	

B-Glucose oxidase

The glucose oxidase enzyme (GOx or GOD) , (EC number 1.1.3.4) is an oxidoreductase that catalyses the oxidation of glucose to hydrogen peroxide and D-glucono-δ-lactone



6-Storage:-

In the case of potatoes, the storage temperature should not drop below 8 °C. the acrylamide formation during deep-frying will be higher when Potato tubers stored at 2°C than tubers stored at 20°C.because storage at low temperature cause the conversion of starch to glucose.

7-Cations treating

It was showed that by dipping French fries into calcium chloride, they were able to reduce acrylamide formation by up to 95%. the treatment did not affect final product quality. In similar manner, sodium ions were able to reduce acrylamide formation by as much as 50% in a model asparagine and fructose system.

8- Also, new production methods such as **vacuum frying** may lower the acrylamide formation.

9- pH controlling