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CONDITIONS OF ACRYLAMIDE SYNTHESIS IN FOOD AND ITS EFFECTS ON LIVE ORGANISMS

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Acrylamide is an important industrial chemical used since the 1950-ies as chemical intermediate in production of polyacrylamides. The neurotoxicity of acrylamide in humans is well-known from occupational and accidental exposures. The occurrence of acrylamide in tobacco smoke, which could be observed in smokers as an increased level of the corresponding Hb adduct. Experimental study with acrylamide in animals shown reproductive, genotoxic and carcinogenic properties. The International Agency for Research on Cancer (IARC) has classified acrylamide as a potential human carcinogen. Studies conducted in 2002 and 2003 showed that a high level of acrylamide was formed during the frying or baking of a variety of foods. Acrylamide is generated in food as a result of the Millard reaction between asparagine and carbonyl groups of reducing sugars.

INTRODUCTION

Acrylamide (2-propenamide) is an organic compound, an amide characterised by a simple structure, synthesized on the industrial scale from acrylnitrile. It is well soluble in water, methanol, ethanol and other organic solvents, which determines its high mobility in water and relatively fast biodegradation. Under UV rays or once heated, acrylamide readily undergoes polymerization [JECFA/64/SC; Bekas *et al*., 2006]. It is a component of tobacco smoke which, in turn, is a significant source of human body contamination since acrylamide is relatively easily absorbed by the respiratory system. It is also well absorbed by the alimentary tract and, to a weaker extent, by skin. In the body, in reactions catalysed in liver by isoenzyme CYP2E1, it is subject to changes mainly to a very strongly reactive glycidamide. Acrylamide may also be coupled with glutathione and both in the intact form and in the form of metabolites it is excreted with faeces (90%) and urine (10%). Its half-life period spans for 2–7 h. It penetrates to placenta and milk of a mother [Dybing *et al*., 2005].

Application of acrylamide, both in the form of polymers and copolymers, is quite common in various branches of industry. It is applied, among others, for treatment of drinking water, in the production of packages, cosmetics used for hair care, fabrics, and as a component of fertilizers preventing soil erosion [Bekas *et al*., 2006]. From the onset of acrylamide application as a component of packages coming into contact with food, investigations have begun on its toxicity. Already in the 1990-ies, its permissible level in products stored in plastic packages was stipulated at a level below 10 mcg/kg. In 1994, the IARC Committee acknowledged acrylamide as a substance with potentially carcinogenic effect on humans and classified it to a group 2A. In a number of countries, its permissible levels in drinking water have been stipulated as well at a level below 0.5 mcg/kg. In 2003, the Member States of the European Union accepted its lower permissible content in drinking water at a level below 0.1 mcg/kg [Ahn *et al*., 2002].

CONDITIONS OF ACRYLAMIDE SYNTHESIS IN FOOD AND METHODS OF ITS LIMITATION

In the years 2000–2002, Tareke *et al*. [2000, 2002] detected acrylamide in a number of food products, especially in those being a rich source of monosaccharides and those subjected to culinary and industrial treatment at high temperatures. Investigations have then begun into conditions facilitating its synthesis. They have demonstrated that acrylamide synthesis was enhanced by: concentration and type of amino acids and carbohydrates (reagents in the synthesis of acrylamide are: carbonyl groups of monosaccharides, mainly of glucose, and amine groups of free amino acids, mainly of asparagine), temperature of the process (the highest quantities of that compound are produced at a temp. of 120 –180°C), time of exposure to those temperatures, the surface area of a product subjected to heating, pH of medium, water content of the heated product, a degree of dish browning, and the method of culinary treatment. An intensive increase in the content of acrylamide has been observed in the processes of grilling, baking, frying, and roasting, whereas no intensification of such a synthesis was found during cooking.

A linear dependency has been observed between temperature increase from 120 to 175°C in potato products and up to 180°C in cereal products and elevated concentration of acrylamide. Above those temperatures, its content in food products

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was found to decrease considerably due to its decomposition, the course of which has not be exactly recognized yet [Gökmen *et al*., 2006]. The synthesis reaction of acrylamide is a reaction proceeding on the surface of a heated product and is strictly linked with its browning under the influence of temperature [Ahn *et al*., 2002].

The value of pH facilitating that synthesis reaches 7-8, and its decrease inhibits the production of acrylamide. It has been found that at this pH reactivity of amine groups of free amino acids and carbonyl groups of monosaccharides is the highest. The intensification of acrylamide synthesis has also been observed in potato products at moisture content of 10–20%. In other products its concentration increased at the end of frying and grilling processes when moisture content of the product was already very low [Yung *et al*., 2003; Claeys *et al*., 2005].

Immediately after detection of acrylamide in food products rich in monosaccharides and amino acids as well as after identification of conditions facilitating that synthesis, researches have been undertaken into mechanisms of reactions proceeding in products rich in carbohydrates and subjected to baking or grilling. The fact that this synthesis intensifies during processes of browning, in the course of which there proceed numerous reactions referred to as Maillard's reaction, has given rise to the most important hypothesis elucidating the mechanism of acrylamide formation. During Maillard's reactions there proceed, among others, reactions of asparagine with carbonyl groups of monosaccharides that result in the formation of first N-glucosylasparagine which is then transformed into the Schiff's basis. From that basis, there are simultaneously produced the so-called Amodari's products, simple and reduced ones, and oxazolidine-5-1 derivative of Schiff's basis, whose degradation products are acrylamide and amino sugars [Stadler *et al*., 2002]. Another hypothesis on acrylamide generation is based on the reaction of glycerol degradation during heating, production of acrolein and its transformation into acrylic acid which, after linking with an amine group of asparagine, leads to the production of acrylamide [Gertz *et al*., 2002]. Bęcalski *et al*. [2003], in turn, explains that synthesis by a direct reaction proceeding at an elevated temperature, with the omission of acrolein production, between nitrogen-containing compounds (amino acids) and glucose. It seems that the synthesis of acrylamide is the most probable when linked with the Maillard's reactions. It is indicated by the type of products in which higher contents of acrylamide were detected. Concentrations of acrylamide determined in the same product by various centres are often very diversified. It results, among other things, from the application of different analytical methods, diversified composition of raw materials and conditions of heating. Determinations of acrylamide in food products are carried out in renowned laboratories using GC/MS, HPLC/MS and HPLC/MS/MS methods. Some research works addressed verification of the results of assays performed with various methods and confirmed their sensitivity and accuracy [Ahn *et al*., 2002; Hoenicke *et al*., 2004].

The highest contents of acrylamide are detected in French fries and chips – up to 12000 mcg/kg (Table 1). Its high concentrations (400–1660 mcg/kg) are also found in: crackers, biscuits, gingerbread, dry biscuits, toasts, cracknels, bread and coffee [JECFA/64/SC]. Bekas *et al*. [2006] analysed acrylamide contents in potato chips produced and sold in Poland. These contents, from 380 mcg/kg to 861 mcg/kg, fall into range reported in literature and being rather on its lower edge.

In recent years studies have been undertaken with the aim to reduce the quantity of available acrylamide in food products. It has been demonstrated that this can be obtained by reducing the number of acrylamide precursors in a product or by changing technological parameters of the culinary process [Kita, 2006].

The first aspect requires the selection of potato cultivars suitable for processing of French fries and chips. Such potatoes should be characterised by a very low content of monosaccharides – below 0.5% – which should not increase during storage. Potatoes intended for food processing should be stored at a temp. of 7–8°C to prevent excessive accumulation of reducing sugars in tubers. Attempts are also made to eliminate asparagines as a reagent in acrylamide synthe-

TABLE 1. Content of acrylamide in selected food products subjected to culinary or industrial processing (2002 – 2004) acc. to JECFA/64/SC.

Products	Mean content (mcg/kg)	Maximal content (mcg/kg)
Cereals seeds and cereal products(after processing)	343	7834
Bread	446	3436
Biscuits (USA)	350	7834
Corn flakes	96	1346
Pizza	33	763
Fish and sea fruits	25	233
Meats and meat products	19	313
Milk and dairy products	5.8	36
Nuts and seeds of oil plants	84	1925
Potatoes – puree	16	69
Cooked potatoes	169	1270
Potatoes-French fries	752	4080
Potatoes – chips	334	5312
Coffee – infusion	13	116
Instant coffee	288	1291
Coffee extract	1100	4948
Cocoa – powder	220	909
Green tea – powder	306	660
Sugar and honey	24	112
Fresh vegetables	4.2	25
Roasted, fried, grilled vegetables	59	202
Fresh fruits	<1	10
Dried, frozen fruits	131	770
Alcohol beverages	6.6	46
Modified milk	<5	15
Children formulas (powdered)	16	73
Crackers, sponge fingers	181	1217
Dried food products	121	1184

sis through its decomposition with asparaginase [Durston, 2004]. It seems, however, that future belongs to methods of reducing acrylamide concentration through modification of conditions of the culinary process, mainly by means of decreasing the temperature of frying to 165°C and re-drying the product to a desired temperature. It has been demonstrated that in this way the quantity of produced acrylamide can be decreased by 80%. Even higher activity inhibiting the production of that compound (*ca*. 90%) has been obtained after initial soaking of French fries in 0.15 mol/L acetic acid, yet the fried product was gaining sour aftertaste [Kita *et al*., 2004; Bräthen *et al*., 2005].

In the aspect of risk posed to health, it is of great significance to estimate the mean supply of acrylamide with daily food rations. Investigations carried out in 2002 by FAO/WHO and in 2003 in the Netherlands demonstrated that children were exposed to a twofold higher intake of acrylamide originated from food than the adults. The mean supply of that compound with a daily food ration, based on results of studies carried out in different countries, is estimated at a level of *ca*. 0.55 mcg/kg b.m./day in adults and 1.04 mcg/kg b.m./day in children under 6 years of age. The mean intake in the entire population is estimated at a level of 0.3–0.8 mcg/kg b.m./day. The major source of acrylamide are French fries that deliver 40% from the total pool of available compound irrespective of age, followed by chips, fried potatoes and coffee [JECFA/64/SC; Konings *et al*., 2003; Svensson *et al*., 2003].

TOXIC EFFECT OF ACRYLAMIDE ON ANIMAL AND HUMAN ORGANISMS

In the Member States of the European Union, acrylamide is classified as a carcinogenic, second category mutagenic, and third category toxic to production substance. Toxicity analyses enabled determining its LD^{50} – 150 mg/kg b.m. and NOAEL dose – 0.5 mg/kg b.m. [JECFA/64/SC; Report of a Joint FAO/WHO, 2002].

In rats, doses of 0.5 mg AA/kg b.m. evoked an increase in the incidence of carcinomas of thyroid gland, testicles and adrenal gland. In embryos of Syrian hamsters acrylamide has been observed to evoke a negative impact on neoplasmatic transformations. It induced morphological changes in those cells. Detrimental effect of that compound has also been observed in rats, in which it diminished fertility by changing properties of spermatozoons in males [JECFA/64/SC; Report of a Joint FAO/WHO, 2002].

In humans, acrylamide has been proved to exert a toxic effect on the nervous system, In China, people exposed to that compound at work were characterised by high blood concentrations of AA adducts with hemoglobin and symptoms of polyneuropathy when exposed to a dose of 1mg/kg b.m./day. Epidemiological assays carried out in the second half of the 1990-ies on a population of people exposed to that compound at work did not demonstrate its carcinogenic activity, except for single cases of pancreas carcinoma. No relationship was confirmed either between nutritional patterns, intake of products being carriers of acrylamide and tumors of intestine, urinary bladder nor kidney [JECFA/64/SC; Report of a Joint FAO/WHO, 2002].

SUMMARY

In summary, it should be stated that while working out technological conditions of culinary processes it is extremely important to anticipate acrylamide synthesis in products rich in monosaccharides and amino acids as well as to their modification aimed at limiting possibilities of acrylamide formation. In prophylaxis of nervous system affections and tumor diseases, due to potential carcinogenicity of acrylamide to humans, of great significance are: quitting smoking, and in nutrition of children, pregnant and breast-feeding women – limiting the intake of such food products as: French fries, chips, toasts, and crisps.

REFERENCES

1. Ahn J.S., Castle L., Clarke D.B., Lloyd A.S., Philo M.R., Speck D.R., Verification of the findings of acrylamide in heated foods. Food Add. Contam., 2002, 19, 1116-1124.
2. Bęcalski A., Lau B. P-Y., Lewis D., Seaman S.W., Acrylamide in food: occurrence, sources, and modeling. J. Agric. Food. Chem., 2003, 51, 802-808.
3. Bekas W., Kowalska D., Kowalski B., Acrylamide in commercial potato chips from Warsaw market. Pol. J. Food Nutr. Sci., 2006, 56, 391-394.ö
4. Bekas W., Kowalska D., Kowalski B., Acrylamide in food. Przem. Spoż., 2006, 6, 36-39 (in Polish; English abstract).
5. Bräthen E., Kita A., Knutsen S. H., Wicklund T., Addition of glycine reduces the content of acrylamide in cereal and potato products. J. Agric. Food Chem., 2005, 53, 3259-3264.
6. Claeys W.L., de Vleeschouwer K., Hendrickx E., Quantification of the formation of carcinogens during food processing: acrylamide. Trends Food Sci. Technol., 2005, 16, 181-193.
7. Durston J. The end of acrylamide?. Potato Buisnes World, 2004, 3, 2.
8. Dybing E., Farmer P.B., Andersen M., Fennell T.R., Lalljie S.P.D., Müller D.J.G., Olin S., Petersen B.J., Schlatter J., Scholz G., Scimeca J.A., Slimani N., Törnq vist M., Tuijtelaars S., Verger P., Human exposure and internal dose assessments of acrylamide in food. Food Chem. Toxicol., 2005, 43, 365-410.
9. Gertz Ch., Klostermann S., Analysis of acrylamide and mechanism of its formation in deep-fried products. Eur. J. Lipid Sci. Technol., 2002, 104, 762-771.
10. Gökmen V., Senyuva H.Z., Study of colour and acrylamide formation in coffee, wheat, flour and potato chips during heating. Food Chem., 2006, 99, 238-243.
11. Hoenicke K., Gatermann R., Harder W., Hartig L., Analysis of acrylamide in different foodstuffs using liquid chromatography – tandem mass spectrometry and gas chromatography – tandem mass spectrometry. Anal. Chim. Acta, 2004, 520, 207-215.
12. JECFA, Report of a Joint FAO/WHO Expert Committee on Food Additives 8 -17.02.2005. Rome. JECFA/64/SC.
13. Kita A., Bräthen E., Knutsen S. H., Wicklund T. Effective ways of decreasing acrylamide content in potato crisps during processing. J. Agric. Food Chem., 2004, 52, 7011-7016.
14. Kita A., Effect of selected technological parameters on the quality of fried snack products. Zesz. Nauk. A.R. we Wrocławiu, 2006, 537, Rozprawy CCXL (in Polish).

15. Konings E.J.M., Baars A.J., van Klaveren J.D., Spanjer M.C., Rensen P.M., Hiemstra M., van Kooij J.A., Peters P.W.J., Acrylamide exposure from food of the Dutch population and an assessment of the consequent risks. Food Chem. Toxicol., 2003, 41, 1569-1579.
16. Report of a Joint FAO/WHO Consultation WHO Headquarters" Health implications of acrylamide in food" Geneva, 2002.
17. Stadler R.H., Blank I., Varga N., Fabien R., Hau J., Guy Ph. A., Robert M., Riediker S., Acrylamide from Maillard reaction products. Nature, 2002, 419, 449.
18. Svensson K., Abramsson L., Becker W., Glynn A., Hellenäs K-E., Lind Y., Rosen J., Dietary intake of acrylamide in Sweden. Food Chem. Toxicol., 2003, 41, 1581-1586.
19. Tareke E., Rydberg P., Karlsson P., Eriksson S., Törnqvist M., Acrylamide: A cooking carcinogen? Chem. Res. Toxicol., 2000.13.517-22.
20. Tareke E., Rydberg P., Karlsson P., Eriksson S., Törnqvist M., Analysis of acrylamide, a carcinogen formed in heated foodstuffs. J. Agric. Food Chem., 2002, 50, 4998-5006.
21. Yung M.Y., Choi D.S.,Ju J.W., Novel technique for limitation of acrylamide formation in fried and baked corn chips and in French fries. J. Food Sci., 2003, 68, 1287-1290.

WARUNKI SYNTEZY AKRYLOAMIDU W ŻYWNOŚCI I JEGO WPŁYW NA ORGANIZMY ŻYWE

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Akryloamid jest substancją chemiczną stosowaną powszechnie w przemyśle chemicznym od lat 50 – XX wieku do produkcji poliakrylamidów. Neurotoksyczność akryloamidu obserwowano u ludzi przy narażeniu zawodowym i po przypadkowych zatruciach. Występowanie akryloamidu w dymie tytoniowym powoduje u palaczy wzrost stężenia w krwi adduktów hemoglobiny, które są wykorzystywane jako wskaźnik w ocenie narażenia na ten związek. Badania doświadczalne wykazały u zwierząt po podaniu im akryloamidu zahamowanie reprodukcji, genotoksyczność i rakotwórczość. Międzynarodowa Agencja Badań nad Rakiem (IARC) uznała ten związek za potencjalny rakotwórczy dla człowieka. Badania prowadzone w latach 2002 – 2003 wykazały wysoką zawartość akryloamidu w różnorodnych produktach spożywczych poddanych frytowaniu, smażeniu i pieczeniu. Akryloamid powstaje w żywności w wyniku reakcji Millarda zachodzących pomiędzy asparaginą i grupami karbonylowymi cukrów redukujących.