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A perspective on the evaluation of safety risks in thermal processing of foods with an example for acrylamide formation in biscuits

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REVIEW ARTICLE

Abstract

Thermal processing induces typical changes in foods such as enzyme inactivation, microbial destruction, as well as the development of desirable sensory characteristics. However, heating at elevated temperatures has been shown to generate potentially toxic compounds. In 2002, the discovery of acrylamide in fried potatoes caused a worldwide interest. It is a fact that numerous other toxicants can also be found in heated foods. Since safety remains as a primary objective, one of the challenges facing the food industry is to minimise these toxicants without adversely affecting desired attributes of thermal processing. To meet this challenge, it is essential to combine the knowledge on chemical mechanisms and process engineering. The Bigelow's procedure is used to evaluate a sterilisation process for the calculation of total lethality from the time-temperature history of food at the coldest point. This procedure could be successfully adapted to the baking process to evaluate acrylamide formation risk from the time-temperature history of biscuits recorded at the hottest point. Such an approach may provide a basis for thermal process safety calculations enabling better control of the risks associated with heat generated toxicants formed in foods during heating.

Keywords: acrylamide, safety evaluation, thermal process, thermal process contaminants

1. Overview of the safety risks associated with thermal processing of foods

Processing of foods is essential to improve microbiological safety, to increase nutritional quality, and to reduce the levels of potentially toxic compounds. The application of high temperatures, referred to as thermal processing, is the most commonly used method to kill or control the numbers of microorganisms present in high moisture foods (Tucker, 2008). In addition, thermal processing is indispensable for determining the specific nutritional and sensory properties, in particular texture, flavour and colour in fried, baked and roasted products. Previous studies have indicated that thermal treatment may induce the formation of health-promoting antioxidants in foods. On the other hand, it may lead to the formation of heat-induced toxic compounds, so called thermal process contaminants, such as heterocyclic amines, acrylamide, furan, furfurals and chloropropanols (Crews *et al.*, 2001; Maga, 1979; Skog *et al.*, 1998; Tareke *et al.*, 2012; Van Boekel, 1996). Thermally processed foods like bakery products, roasted coffee, snack foods, baby purees and refined oils may contain above-mentioned compounds at varying amounts as a result of heat induced conversions of certain compounds naturally available in food products (Figure 1). The final concentrations of thermal process contaminants in foods depend on the concentration of their corresponding precursors as well as the severity of process. Since these food products have to be heated to develop organoleptic profile and meet consumers' acceptance, optimised processing conditions need to be found for improving the formation of valuable compounds, while minimizing the harmful ones.

A firm mathematical approach is still lacking, but challenging for the evaluation of the success of thermal process like baking, frying and roasting. In the following sections, a process safety calculation approach is described taking into account the mechanism of formation, temperature

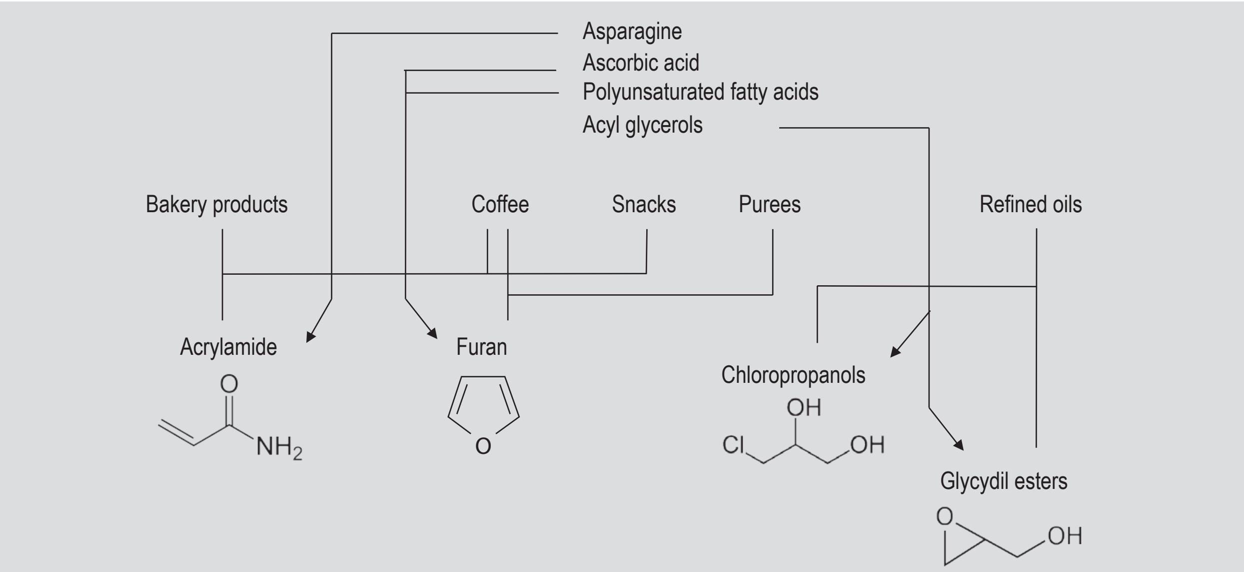

Figure 1. Occurrence of certain thermal processing contaminants and their potential precursors in common processed foods.

dependence of formation, and time-temperature history of food. The validity of the approach is exemplified for the formation of acrylamide in bakery products.

Brief information about the chemistry of Maillard reaction

The chemical reactions that lead to the formation of thermal process contaminants in foods are diverse. They mainly involve lipids, carbohydrates and proteins and/or free amino acids as precursors. The formation of reactive intermediates from especially carbohydrates and lipids may play an important role. The reaction pathways are interrelated and strongly dependent on the size and composition of foods and processing conditions. Among the reactions occurring in food during heating, the reaction between reducing carbohydrates and free amino groups of proteins or amino acids is the major source of neo formed compounds. This reaction, so called the Maillard reaction, has three stages in which typical products are formed (Table 1). Some of them like N-ε-fructosyllysine and carboxymethyllysine have been using to evaluate the degree of protein glycation in heated foods that indicate the loss of nutritive value and the severity of thermal process (Gökmen *et al.*, 2008; Hodge, 1953; Wellner *et al.*, 2011). Some other Maillard reaction products like acrylamide and furfurals indicate the safety risks created in foods during thermal processing due to the potential adverse effects of these compounds on human health (Capuano and Fogliano, 2011; EFSA, 2011; IARC, 1994).

Facts on the occurrence of acrylamide in thermally processed foods

Swedish researchers have first reported the formation of acrylamide in foods processed at elevated temperatures (Tareke *et al.*, 2002). The main pathway of acrylamide

Table 1. Typical products formed during the stages of Maillard reaction.

Stage	Typical products formed
Initial stage	Early glycation Amadori products
sugar-amine condensation	N-ε-fructosyllysine
Amadori rearrangement (R-CHO + R-NH_2)	
Intermediate stage	Reductones and fission products, intermediates
sugar dehydration	hydroxymethylfurfual or furfural
sugar fragmentation	acrylamide
strecker degradation	
Final stage	Brown nitrogenous products
aldol condensation	melanoidins
aldehyde-amine condensation	Advanced glycation end products
	carboxylmethyllysine

formation in foods is linked to the Maillard reaction and, in particular, the amino acid asparagine (Mottram *et al.*, 2002; Stadler *et al.*, 2002; Yaylayan *et al.*, 2003). Since it is classified as a probable human carcinogen by the International Agency for Research on Cancer (IARC, 1994), presence of acrylamide in common heated foods is considered as one of the most important food safety concerns by international authorities. Acrylamide exposure varies depending upon the population's eating habits, and the way the foods are processed and prepared. Generally, fried potato products, bakery products and roasted coffee appear as the most important food categories that contribute most to acrylamide exposure. The resulting acrylamide concentration in thermally processed foods depends on certain recipe and process factors. The initial concentrations of precursors and processing temperatures are known to affect the rate of acrylamide formation in foods (Becalski *et al.*, 2003; Gökmen *et al.*, 2006; Matthäus *et al.*, 2004; Pedreschi *et al.*, 2005; Rydberg *et al.*, 2003).

During baking or frying of foods, the evaporation of water limits the amounts of acrylamide formed being an important barrier to internal energy increase. However, greater energy input to the food at higher temperatures will cause faster drying, and hence the temperature and moisture levels which favour the formation of acrylamide to set in early during the process (Gökmen *et al.*, 2006). Time-temperature history differs in different locations of food as a result of simultaneous heat and mass transfer. As shown in Figure 2, temperature rises much faster on the surface than the interior parts of cookies baked at 180 °C in a conventional oven (Açar and Gökmen, 2009). Obviously, the edge becomes the hottest point of cookie during baking process making it the most risky part from the viewpoint of chemical reactions leading to undesired toxic compounds. It is a fact that the formation of acrylamide takes place mainly at the surface and in near-surface regions, because during heating, the conditions in this part of foods become favourable (Gökmen *et al.*, 2006). As a result, there occurs a large difference between the acrylamide concentrations of the surface and the core regions of food as exemplified for a cookie in Figure 3 (Açar and Gökmen, 2009).

2. An approach to evaluate the process safety concerning thermal process contaminants

Thermal processing is an important treatment for food preservation, especially in the manufacture of shelf stable foods. Heat, at levels sufficient to destroy microorganisms, is applied to foods packed into sealed or airtight containers. Thermal process calculations are needed to achieve safe levels of microbial inactivation (lethality) and should be carefully carried out to ensure public health safety.

Bigelow developed the first procedure in early 20th century to evaluate thermal processes (Bigelow *et al.*, 1920). This makes direct use of the time-temperature history at the coldest point to obtain the lethality value of a process. The severity of a thermal process is calculated as an integrated F-value or P-value (Ball and Olsen, 1957), using thermal inactivation kinetic data on the likely pathogenic or spoilage organisms present. The time-temperature history at the coldest point of food is used to build a lethality plot (lethal rate versus time) in which the area under the curve corresponds to the accumulated lethality of the process. The Bigelow's procedure earned the name 'general method' because it applies to any product/process situation.

As an analogy, the Bigelow's procedure can be used to evaluate the thermal process safety risks, for instance the formation of acrylamide in biscuits during baking. The analogical comparison of thermal inactivation of microorganisms (microbial safety) and thermal formation of processing contaminants (chemical safety) is schematically illustrated in Figure 4. Since acrylamide and several other thermal process contaminants concentrate at the surface,

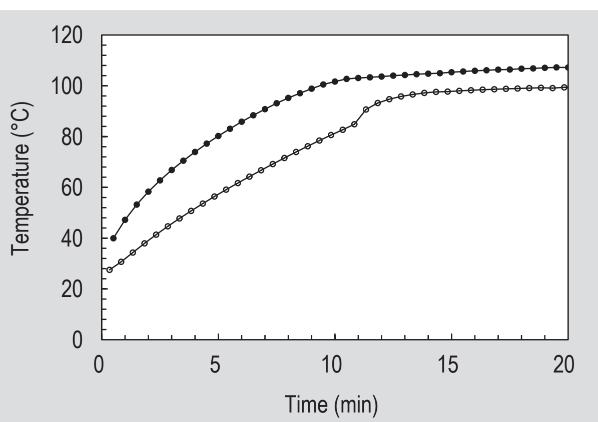

Figure 2. A typical time-temperature history of the edge (black circles) and centre (white circles) of a cookie during baking at 180 °C (Açar and Gökmen, 2009).

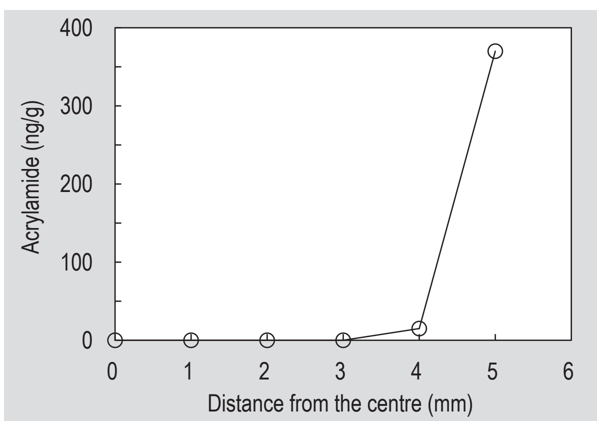

Figure 3. Concentration of acrylamide on the surface and nearby region of a cookie (Açar and Gökmen, 2009).

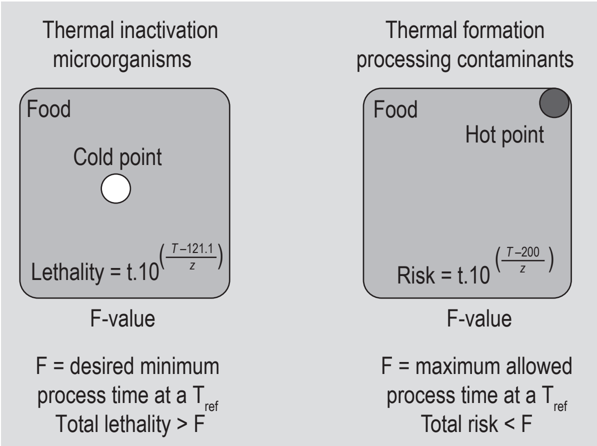

Figure 4. Analogy between thermal process calculations for thermal inactivation of dangerous microorganisms (process microbial safety) and formation of thermal processing contaminants (process chemical safety).

the process safety calculation should be based on the time-temperature history recorded at the product's surface, namely the hottest point. In order to perform a process safety calculation, it is prerequisite to determine the kinetic constants (D-value, z-value) for target compound(s) based on a valid chemical mechanism.

Certain chemical reactions like acrylamide formation in baked or fried foods are characterised by a notable peak product concentration at relatively high temperatures. The dynamics of such reactions has been traditionally studied by following a set of several intermediate reactions. The simplest form is a reaction of the general type A→B→C, in which a peak concentration of the compound B can be observed depending on the formation and degradation reaction rates (Peleg, 2009; Van Boekel, 2009). It is a fact that formation and degradation of acrylamide occurs in the same time during heating at elevated temperatures (Claeys *et al.*, 2005; De Vleeschouwer *et al.*, 2006; Gökmen and Şenyuva 2006; Hedegaard *et al.*, 2007). Empirical models based on single-response modelling approach can be very useful for predicting chemical changes during processing, when details of the complex chemistry or mechanism is of less importance or unknown (De Vleeschouwer *et al.*, 2009a). In contrast to empirical models, mechanistic models are based on more detailed reaction mechanisms and require multiresponse modelling. This approach has been previously applied to acrylamide formation in different model and food systems under different conditions (De Vleeschouwer *et al.*, 2008, 2009b; Knol *et al.*, 2005; Parker *et al.*, 2012; Van der Fels-Klerx *et al.*, 2014). For a baking process of sweet biscuits, reactions leading to acrylamide and hydroxymethylfurfural and their eliminations can be considered as shown in Figure 5.

The decimal formation time (D-value) can be calculated from the thermal formation kinetic data for a range of temperatures. The kinetic data should be obtained using an appropriate experimental food model in which time lag to reach the working temperature within the food is limited. To achieve this, the crust model that is based on the use of same formulation in thinner form (1 mm) is useful for baking experiments (Açar and Gökmen, 2009). For thermal process safety calculation from the viewpoint of acrylamide formation risk, a new term, thermal formation time (τ) could be defined as the time required for the acrylamide concentration to reach a risk threshold value at a given temperature. The F value is the thermal formation time at a reference temperature. If established by the legal authorities, the maximum allowed concentration of a target thermal process contaminant such as acrylamide could be considered as the risk threshold value. In microbial inactivation, a reference temperature of 121.1 °C is widely used (Awuah *et al.*, 2007). It is a fact that baking process may cover a range of temperature from 170-180 up to 230-240 °C. Here, the reference temperature of 200 °C

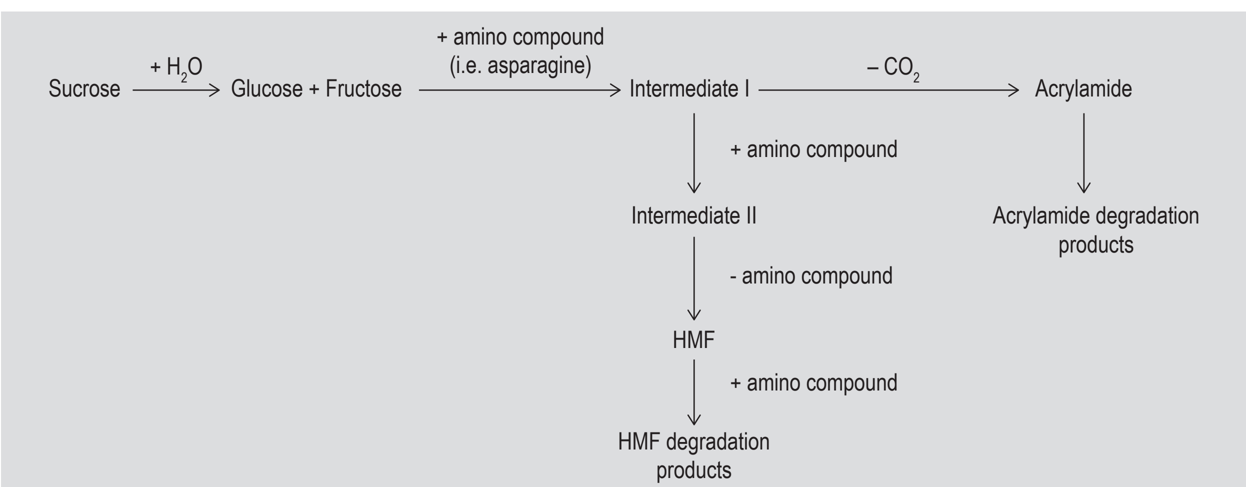

Figure 5. A simplified reaction scheme for acrylamide and 5-hydroxymethylfurfural (HMF) formations in biscuits during baking.

is considered as midpoint of this range. From a kinetic point of view, it is also highly relevant for the formation of acrylamide and several other process contaminants in biscuits during baking. However, the approach to be described in the following section should take into account the temperature dependence of the kinetic constants for a target process contaminant in the whole temperature range mentioned above.

In a previous study by Açar and Gökmen (2010), the F-value was calculated to be 0.20 at a reference baking temperature of 200 °C for a provisional acrylamide risk threshold value of 200 ng/g in cookies prepared using the recipe described in the American Association of Cereal Chemists method 10.54 (AACC, 2000).

The relation between thermal formation time (τ) and F value can be expressed as:

$$\frac{\log(\tau) - \log(F)}{(T - T_{ref})} = -\frac{1}{z} \tag{1}$$

Here, the z-value reflects temperature dependence of the reaction. It can be calculated from the slope of thermal formation curve (log D versus T). In a previous study, the z-value was found as 30 °C for acrylamide formation in cookies (Açar and Gökmen, 2010). It should be noted here that reactions with small z values are highly temperature dependent.

For the reference temperature of 200 °C, the equation becomes as follows:

$$F = \tau \times 10^{\left(\frac{T-200}{z}\right)} \tag{2}$$

Here, the F-value represents a desired level of thermal process effect. For microbial inactivation, the total lethality (L) achieved by the process should be higher than the F-value. In the thermal process safety calculation approach, the term lethality replaces with the risk value (R-value) that can be expressed as:

$$R = t \times 10^{\left(\frac{T-200}{z}\right)} \tag{3}$$

Where t is time at a given temperature (T). From a time-temperature history data, partial risk values are calculated for each time-temperature combinations, and the plot of R-value versus time is built. The total risk created by the process is the area under the curve of this plot, and can be calculated as follows:

$$\text{Total risk} = \int_{t_2}^{t_1} 10^{\left(\frac{T-200}{z}\right)} dt = \int_{t_2}^{t_1} R dt \tag{4}$$

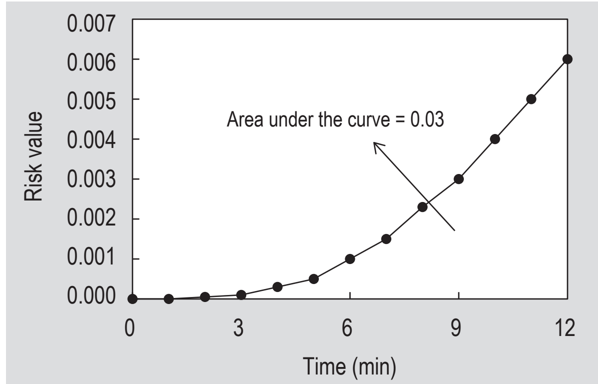

Figure 6. Increase of the risk value for acrylamide formation in cookies baked at 200 °C for 12 min.

Figure 6 illustrates the increase of risk value for acrylamide formation in cookies during baking at 200 °C. The total risk at the end of baking process was calculated to be 0.024, which is less than the F-value of 0.2 (Açar, 2010). This meant that the baking cookies at 200 °C for 12 min did not form acrylamide at amounts higher than the risk threshold value of 200 ng/g. Experimental analysis of these cookies indicate an acrylamide concentration of 150 ng/g confirming the validity of above mentioned process safety calculation approach.

3. Process optimisation taking into account the risks and benefits induced thermal treatment

From a thermal process optimisation point of view, it is necessary to find the relationship time and temperature for risks and benefits induced by the process. Greenwood *et al.* (1944) have first published a technique, which they used to study the destruction of thiamin in cured pork luncheon meat compared with microbial destruction. Figure 7 illustrates the relationship between time and temperature for the destruction of microbial spores (line F) and for the cooking of a food product to a specified degree (line C). From this, it can be seen that the only acceptable combinations of time and temperature fall within the area 'cooked sterile', all other combinations of time and temperature being unacceptable. Similar evaluation can be applied to baked, fried and roasted foods taking into account the formation of thermal process contaminants (line R) and development of acceptable sensory properties (line S). In this case, the appropriate combinations of time and temperature would fall within the area 'non-risky acceptable'.

4. Conclusions

It is a fact that local time-temperature data is a strong determinant on the formation and elimination of thermal processing contaminants in foods during processing. This data can be recorded by appropriate engineering tools or

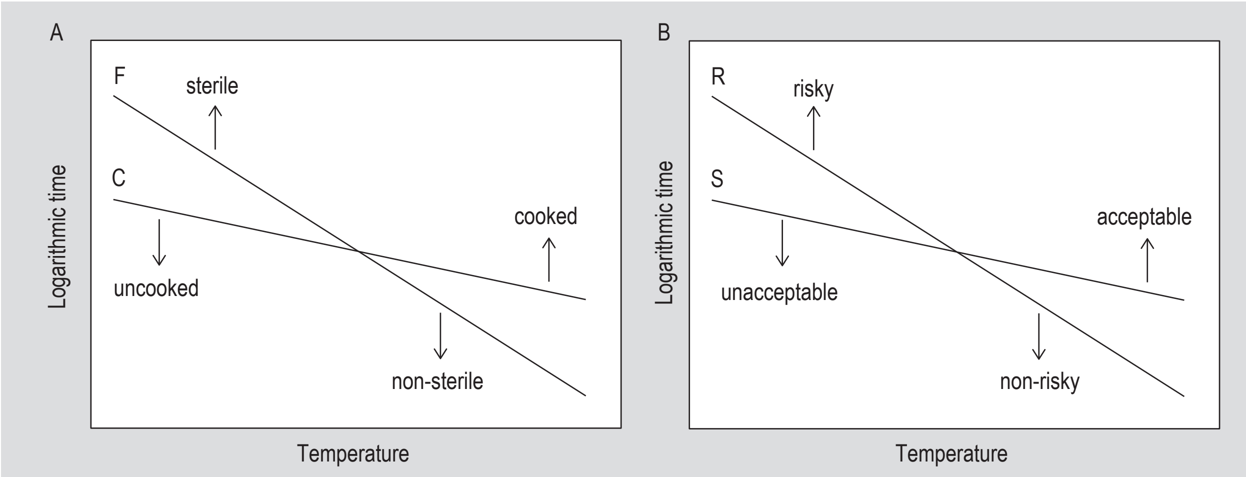

Figure 7. Diagram of t-T relationship for (A) microbial destruction (F) and cooking (C); and (B) formation of process contaminant (R) and sensory (S).

can be predicted by means of realistic process models based on simultaneous heat and mass transfer occurring in baked, fried and roasted foods. Using the time-temperature history, local rates of formation and elimination can be estimated for any thermal process contaminant. As described and exemplified above for acrylamide formation in baked goods, this requires a kinetic data obtained using valid models and conditions like the crust model for bakery products. Bakery products are too diverse in terms of their recipe and processing conditions. Hence, it should be kept in mind that the kinetic constants (F- and z-values) used to calculate total process risk are product-specific like biscuit with a fixed recipe. For this reason, any significant alteration in the product's recipe such as changes in the type and amount of sugars or leavening agents will affect the kinetics of acrylamide formation, so the F- and z-values. It should be noted here that this is also true for the thermal inactivation kinetics of spoilage bacteria in foods with different pH values.

References

Açar, Ö.Ç., 2010. Investigation of the formation of thermal process contaminants in biscuit like products during baking. PhD thesis, Institute of Science, Hacettepe University, Ankara, Turkey, 138 pp.

Açar, Ö.Ç. and Gökmen, V., 2009. Investigation of acrylamide formation on bakery products using a crust-like model. Molecular Nutrition and Food Research 53: 1521-1525.

Açar, Ö.Ç., and Gökmen, V., 2010. A new approach to evaluate the risk arising from acrylamide formation in cookies during baking: total risk calculation. Journal of Food Engineering 100: 642-648.

American Association of Cereal Chemists (AACC), 2000. Approved Methods of the American Association of Cereal Chemists (10th Ed.). AACC, St. Paul, MN, USA.

Awuah, G.B., Ramaswamy, H.S. and Economides, A., 2007. Thermal processing and quality: principles and overview. Chemical Engineering and Processing 46: 584-602.

Ball, C.O. and Olsen, F.C.W., 1957. Sterilization in food technology. McGraw-Hill Book Co., New York, NY, USA, 654 pp.

Becalski, A., Lau, B.P.Y., Lewis, D. and Seaman, S., 2003. Acrylamide in foods: occurrence, sources and modeling. Journal of Agricultural and Food Chemistry 51: 802-808.

Bigelow, W.D., Bohart, G.S., Richardson, A.C. and Ball, C.O., 1920. Heat penetration in processing canned foods. National Canners Association Bulletin 161.

Capuano, E. and Fogliano, V., 2011. Acrylamide and 5-hydroxymethylfurfural (HMF): a review on metabolism, toxicity, occurrence in food and mitigation strategies. LWT-Food Science and Technology 44: 793-810.

Claeys, W.L., De Vleeschouwer, K. and Hendrickx, M.E., 2005. Quantifying the formation of carcinogens during food processing: acrylamide. Trends in Food Science and Technology 16: 181-193.

Crews, C., Brereton, P. and Davies, A., 2001. The effects of domestic cooking on the levels of 3-monochloropropanediol in foods. Food Additives and Contaminants 19: 271-280.

De Vleeschouwer, K., Van der Plancken, I., Van Loey, A. and Hendrickx, M., 2006. Impact of pH on the kinetics of acrylamide formation/elimination reactions in model systems. Journal of Agricultural and Food Chemistry 54: 7847-7855.

De Vleeschouwer, K., Van der Plancken, I., Van Loey, A. and Hendrickx, M., 2008. Investigation of the influence of different moisture levels on acrylamide formation/elimination reactions using multiresponse analysis. Journal of Agricultural and Food Chemistry 56: 6460-6470.

De Vleeschouwer, K., Van der Plancken, I., Van Loey, A. and Hendrickx, M., 2009b. Role of precursors on the kinetics of acrylamide formation and elimination under low-moisture conditions using a multiresponse approach. Part II: competitive reactions. Food Chemistry 114: 535-546.

De Vleeschouwer, K., Van der Plancken, I., Van Loey, A. and Hendrickx, M.E., 2009a. Modelling acrylamide changes in foods: from single-response empirical to multiresponse mechanistic approaches. Trends in Food Science and Technology 20: 155-167.

European Food Safety Authority (EFSA), 2011. Scientific opinion on the re-evaluation of caramel colours (E 150 a,b,c,d) as food additives. EFSA Journal 9: 103.

Gökmen, V., Palazoğlu, T.K. and Şenyuva, H.Z., 2006. Relation between the acrylamide formation and time-temperature history of surface and core regions of French fries. Journal of Food Engineering 77: 972-976.

Gökmen, V. and Şenyuva, H.Z., 2006. A simplified approach for the kinetic characterization of acrylamide formation in fructose-asparagine model system. Food Additives and Contaminants 23: 348-354.

Gökmen, V., Serpen, A., Çetinkaya Açar, Ö. and Morales, F.J., 2008. Significance of furosine as heat-induced marker in cookies. Journal of Cereal Science 48: 843-847.

Greenwood, D.A., Kraybill, H.R., Feaster, J.F. and Jackson, J.M., 1944. Vitamin retention in processed meats. Industrial and Engineering Chemistry 36: 922.

Hedegaard, R.V., Frandsen, H., Granby, K., Apostolopoulou, A. and Skibsted, L.H., 2007. Model studies on acrylamide generation from glucose/asparagine in aqueous glycerol. Journal of Agricultural and Food Chemistry 55: 486-492.

Hodge, J.E., 1953. Dehydrated foods – chemistry of browning reactions in model systems. Journal of Agricultural and Food Chemistry 1: 928-943.

International Agency for Research on Cancer (IARC), 1994. Acrylamide. IARC monographs on the evaluation of the carcinogenic risk of chemicals to humans, volume 60. IARC, Lyon, France, pp. 389-433.

Knol, J.J., Van Loon, W.A.M., Linssen, J.P.H., Ruck, A.L., Van Boekel, M.J.S. and Voragen, A.G.J., 2005. Toward a kinetic model for acrylamide formation in a glucose-asparagine reaction system. Journal of Agricultural and Food Chemistry 53: 6133-6139.

Maga, J.A., 1979. Furans in foods. CRC Critical Reviews in Food Science and Nutrition 11: 355-400.

Matthäus, B., Haase, N.U. and Vosmann, K., 2004, Factors affecting the concentration of acrylamide during deep-fat frying of potatoes. European Journal of Lipid Science and Technology 106: 793-801.

Mottram, D.S., Wedzicha, B.I. and Dodson, A.T., 2002. Acrylamide is formed in the Maillard reaction. Nature 419: 448-449.

Parker, J.K., Balagiannis, D.P., Higley, J., Smith, G., Wedzicha, B.L. and Mottram, D.S., 2012. Kinetic model for the formation of acrylamide during the finish-frying of commercial French fries. Journal of Agricultural and Food Chemistry 60: 9321-9331.

Pedreschi, F., Moyano, P., Kaack, K. and Granby, K., 2005. Color changes and acrylamide formation in fried potato slices. Food Research International 38: 1-9.

Peleg, M., Corradini, M.G. and Normand, M.D., 2009. Isothermal and non-isothermal kinetic models of chemical processes in foods governed by competing mechanisms. Journal of Agricultural and Food Chemistry 57: 7377-7386.

Rydberg, P., Eriksson, S., Tareke, E., Karlsson, P., Ehrenberg, L. and Törnqvist, M., 2003. Investigations of factors that influence the acrylamide content of heated foodstuffs. Journal of Agricultural and Food Chemistry 51: 7012-7018.

Skog, K.I., Johansson, M.A.E. and Jagerstad, M.I., 1998. Carcinogenic heterocyclic amines in model systems and cooked foods: a review on formation, occurrence and intake. Food and Chemical Toxicology 36: 879-896.

Stadler, R.H., Blank, I., Varga, N., Robert, F., Hau, J., Guy, P.A., Robert, M.C. and Riediker, S., 2002. Acrylamide from Maillard reaction products. Nature 419: 449-450.

Tareke, E., Rydberg, P., Karlsson, S., Eriksson, M. and Törnqvist, M., 2002. Analysis of acrylamide, a carcinogen formed in heated foodstuffs. Journal of Agricultural and Food Chemistry 50: 4998-5006.

Tucker, G.S., 2008. Development and application of time-temperature integrators to thermal food processing. PhD thesis, School of Chemical Engineering, University of Birmingham, Birmingham, UK, 257 pp.

Van Boekel, M.A.J.S., 1996. Effect of heating on Maillard reactions in milk. Food Chemistry 62: 403-414.

Van Boekel, M.A.J.S., 2009. Kinetic modeling of reactions in foods. CRC Press, Taylor and Francis, Boca Raton, FL, USA, 767 pp.

Van der Fels-Klerx, H.J., Capuano, E., Nguyen, H.T., Mogol, B.A., Kocadağlı, T., Taş, N.G., Hamzalıoğlu, B.A., Van Boekel, M.A.J.S. and Gökmen, V., 2014. Acrylamide and 5-hydroxymethylfurfural formation during baking of biscuits: NaCl and temperature-time profile effects and kinetics. Food Research International 57: 210-217.

Wellner, A., Huettl, C. and Henle, T., 2011. Formation of Maillard reaction products during heat treatment of carrots. Journal of Agricultural and Food Chemistry 59: 7992-7998.

Yaylayan, V.A., Wnorowski, A. and Locas, C.P., 2003. Why asparagine needs carbohydrates to generate acrylamide. Journal of Agricultural and Food Chemistry 51: 1753-1757.