Furan Formation

Subjects: Food Science & Technology
Contributor: Cristian Ramírez

Furan and its derivates are present in a wide range of thermally processed foods and are of significant concern in jarred baby and toddler foods. Furan formation is attributed to chemical reactions between a variety of precursors and a high processing temperature. Also, some kinetic models to represent its formation in different food materials have been studied and could predict the furan formation under simulated operating conditions.

furan formation thermally processed foods microstructure baby food variable retort temperature profile

1. Introduction

Thermal food sterilization of low-acid food products at a high constant retort temperature profiles (CRTPs) is a standard method that has been used to achieve long-term shelf stability of packaged foods [1]. The processing conditions are mainly based on the use of high temperatures (120–130 °C) for a long duration (usually over 60 min) to ensure a safe and shelf-stable low-acid product. At the same time, texture, taste, flavor, and nutritional value of the food are significantly affected by the extreme processing conditions (time and temperature) and cause a weakening of and damage to the food microstructure [2][3][4][5]. These changes promote the accessibility of nutrients [6][7][8] but also favor the chemical interaction between different nutrients that are now free and able to react, which form other compounds in the food and some compounds are toxic to human health; these compounds are called thermal process contaminants (TPC) [5][9][10][11].

There is strong evidence that TPC exerts adverse toxicological effects and present potential health risks to humans [12]; the most studied of these toxic compounds are furan, acrylamides and advanced glycation end-products (AGEs). Furan compounds represent a wide class of heterocyclic, low-molecular-weight molecules that are formed as products or intermediates in heat-induced reactions. Since 1995, furan and its derivates have received attention because of their classification as “possibly carcinogenic to humans” by the International Agency for Research on Cancer (IARC) [13]. The Food and Drug Administration (FDA) announced that furan was present in many thermally processed foods, such as fruit and vegetable juices, bakery products, canned and jarred foods (for example, soups, sauces, gravies, pasta, vegetables, fish), including jarred food for young children [9][14][15][16]. One of the main concerns is the commercial baby and toddler foods due to the high susceptibility of this consumer group to the amount of furan present in these foods that puts this group at risk because of the amount of food consumed per day relative to their body weight [17].

Thus, researchers have identified the problem that the commercial food sterilization process has been developed and optimized from a macroscopic point of view. It considers the food as a whole system where the objective function maximizes quality retention (e.g., color, vitamin, and texture) or minimizes processing time, keeping lethality (F 0) as a constraint. The exposure of the raw materials to high temperatures for long processing times produces important microstructural changes that increase the loss of nutrients such as nonreducing sugars, amino acids, ascorbic acid, polyunsaturated fatty acids (PUFAs), and carotenoids into the medium, favoring conditions that result in the formation of furans. Therefore, the sterilization of food based on food microstructure changes requires a process that can be controlled according to the changes occurring in the food microstructure. Then, a process performed under variable retort temperature profiles (VRTPs) conditions might be an interesting and better alternative compared to the classic CRTPs process. Variable retort temperature profiles mode is based on the optimal temperature control of the retort, allowing the generation of positive and negative temperature ramps [18][19][20][21][22][23][24][25]. The VRTP has been applied and studied as a tool to improve quality retention, but the paramount factor of the application is related to the reduction in processing time [18][19][21][22][23]. Thus far, no studies have reported that VRTPs and food microstructure evolution through the thermal process.

2. Food Microstructure and Its Contribution to Furan Formation during Thermal Processing

Thermal processing plays an important role in food texture and the bioaccessibility of nutrients due to changes at the microstructural level. It has been reported that the total nutrient content can be decreased due to chemical degradation during the thermal process and/or storage. At the same time, the bioaccessibility can increase, as a result of three aspects: (1) cell wall rupture of the vegetable tissues, (2) matrix-nutrient complex dissociation, and (3) molecular transformation in an active structure form [6][7][26][27].

As Aguilera [28] exposed, the food microstructure is a key aspect that should be considered in the food process design because a great part of nutrients are enclosed into the food matrix [6]. For example, Cilla et al. [27] published a review article that presented some cases in which thermal treatment modified the food microstructure to allow nutrient release, which can be considered as a benefit because of the bioaccessibility of sugars, lipids, amino acids, ascorbic acid, and carotenoids was increased due to cell wall rupture. Zhou et al. [29] studied the effect of thermal processing on the nutritional characteristics of an edible fungus. Their results showed that a cooking process using boiling water (100 °C) increased the total polyphenolic compound and free amino acid content and benefitted the in vitro bioaccessibility in terms of total soluble protein and total soluble sugar for control samples. Lemmens et al. [7] showed that thermal treatment (boiling water for 3 min or boiling water for 25 min) of carrots notably favors the amount of β-carotene that is bioaccessible due to a weakening of the cell wall, especially when the most extended thermal treatment. As was reported, bioaccessibility is related to releasing the compound fraction from the food matrix and thus is available for the gastrointestinal tract [6][27]. Nevertheless, it is clear that after a thermal process, the released active compounds from the food matrix are available not only for gastrointestinal tract absorption but also for other types of interactions.

Based on the aforementioned, it is possible to think that the thermal process produces a weakening of the structure, allowing the nutrient release into the medium (i.e., furan precursors), exposing all of the compounds to the heating medium, and thereby allowing chemical reactions between them and forming furan and its derivates. Based on an in-depth knowledge of the kinetics of microstructural damage, it is possible to imagine that thermal processing could be optimized for the food microstructure at the specific time at which nutrient loss begins, which is important for furan formation. In this sense, one aspect that should be considered is the use of frozen raw materials. Some important microstructural changes are accelerated during the thermal treatment when the raw material is in a frozen state. These changes can facilitate the migration of precursors into the medium at an early stage of the thermal processing and place the precursors in contact with one another for a longer time [6].

3. Furan Formation in Thermally Processed Baby Food

In terms of the kinetics of furan formation, Palmers et al. [11] showed that furan formation in spinach puree could be fitted to a zero-order model in the temperature range of 110 to 117 °C. Before this study, there was only one approach, namely, that of [30], who developed an experiment to evaluate the formation of furan from ascorbic acid during the heating process under reducing and oxidizing conditions. Between 100 °C and 140 °C, the furan data were fitted with a first-order model.

The other furan precursors are lipids and carotenoids. For lipids, the work developed by Owczarek-Fendor et al. [31], based on the study of the role of fat oxidation in the generation of furan during the thermal treatment of a model food based on a starchy-emulsion system, showed that oil that reached an unrealistically high level of oxidation could promote furan formation. They also found that the fatty acid composition of the oil can have a remarkable influence on furan formation. Additionally, products of lipid oxidation were shown to procure 2-MeF in presence of amino acids [32], and 4-hydroxy-2-butenal was reported as a key intermediate from polyunsaturated fatty acid (PUFA) degradation undergoing cyclization to dihydro-2-furanol, prior to further decomposition to afford furan by the loss of water [33]. Both monounsaturated linoleic and α-linolenic acids were described as being effective in the formation of furan under thermal conditions [34].

Lipid oxidation is most likely one of the most studied pathways for furan formation using model systems. The intermediate degradation product 4-hydroxy-2-butenal rapidly cyclizes to dihydro-2-furanol, which subsequently furnishes furan after the loss of H 2O. Mixtures of PUFAs reveal that linolenic acid is an efficient precursor of furan [35], particularly in the presence of transition metals that can accelerate lipid oxidation with the subsequent formation of conjugated dienes.

Limacher et al. [36] studied the formation of furan from sugars and specific amino acids (with a focus on Maillard-type reactions) in a model food system and pumpkin puree under thermal conditions simulating sterilization (121 °C for 25 min). Although the study was carried out in the presence of amino acids, the focus was aimed at evaluating sugars. At pH 7, the results showed that the furan level was in the range of 2–17 µmol/mol and that more furan is produced from pentoses than from hexoses. The presence of amino acids was also found to favor the formation of furan from glucose. However, at pH 4, the furan formation was significantly lower, with furan levels below 1.8

μmol/mol. Comparing the results obtained between the model food with those of the pumpkin puree, only 21% of the total furan formed in pumpkin puree was generated by the sugar-amino acid reaction route, which implies that the remaining 79% was generated from precursors other than sugar. Thermal decomposition of amino acids leads to reactive glycolaldehyde and acetaldehyde as transient intermediates, resulting in furan [37]. In model systems, the levels of 2-MeF obtained by thermal decomposition of pure glucose, fructose, or arabinose were significantly lower than those of furan; however, the levels of 2-MeF were shown to increase to levels that were higher than those of furan with heat treatments of the same sugars in the presence of alanine and serine. Amino acids subjected to oxidation may also procure reactive carbon-2 units such as glycolaldehyde and acetaldehyde. Carbohydrates reacting with amino acids in a classical thermally driven Maillard process furnish 3,4-dihydroxybutenal that subsequently cyclizes to the furanoic backbone [38]. However, amino acids alone (for example, alanine, serine) or glucose alone was shown to represent only a minor source of furan.

4. Kinetic Model Applied to Describe Furan Formation in Food Materials

Given the toxicological properties of furan, actions should be taken to minimize exposure to an acceptable level. Accordingly, knowing the kinetics of furan formation in thermally processed foods is an interesting and powerful tool to adjust process parameters so that furan concentration in the final product can be control or reduce. However, to date, there is very little information on this subject. Below we proceed to describe some models proposed in the literature:

Palmers et al. [11] worked with furan formation in sterilization of spinach puree and described by an empirical a zero-order model. The authors compared the amounts of furan formed in classic sterilization using three temperatures (110, 117 and 124 °C) versus high-pressure high temperature (HPHT) process. The rate of formation was modeled according to the rate law: (1) $r = \frac{dF}{dt} = k^n$ where r is the rate of furan formation, F the furan concentration at time t, k is the reaction rate constant at the selected pressure and temperature levels, and n the order of the equation (0 for this case). The reaction rate constants at each processing temperature were 0.035, 0.071 and 0.142 ng furan/g of pureé/min at 110, 117 and 124 °C, respectively.

The importance of counting with reliable models that describe the furan formation according to temperature is related to the possibility of simulation of the sterilization process to predict the furan content. As we can estimate the quality retention of nutrients based on D-value and z-value calculated for nutrients, in the same way, using E_a and k_{ref} is possible to simulate the evolution of furan inside the can or jar. With this information, it is possible to optimize the VRTP able to minimize the furan formation.

The kinetic modeling of furan generation should be considered a powerful tool to control its final occurrence in foods, since kinetic parameters can help predict the influence of processing conditions over its concentration. In this sense, knowing the kinetics of furan formation in foods could be considered a useful tool for designing thermal processes that control the level of furan content in the final product, so the process can be more efficient in reducing furan formation.

References

1. Holdsworth, S.D.; Simpson, R. Thermal Processing of Packaged Foods, 3rd ed.; Springer: Berlin/Heidelberg, Germany, 2016; ISBN 9783319249025.
2. Joardder, M.U.H.; Kumar, C.; Karim, M.A. Food structure: Its formation and relationships with other properties. Crit. Rev. Food Sci. Nutr. 2015, 57, 1190–1205.
3. Karim, M.A.; Rahman, M.M.; Pham, N.D.; Fawzia, S. 3-Food Microstructure as affected by processing and its effect on quality and stability. In Woodhead Publishing Series in Food Science, Technology and Nutrition; Woodhead Publishing: Sawston, UK, 2018; pp. 43–57. ISBN 978-0-08-100764-8.
4. Ko, W.-C.; Liu, W.-C.; Tsang, Y.-T.; Hsieh, C.-W. Kinetics of winter mushrooms (Flammulina velutipes) microstructure and quality changes during thermal processing. J. Food Eng. 2007, 81, 587–598.
5. Mariotti, M.S.; Granby, K.; Rozowski, J.; Pedreschi, F. Furan: A critical heat induced dietary contaminant. Food Funct. 2013, 4, 1001–1015.
6. Parada, J.; Aguilera, J. Food Microstructure Affects the Bioavailability of Several Nutrients. J. Food Sci. 2007, 72, R21–R32.
7. Lemmens, L.; Van Buggenhout, S.; Van Loey, A.M.; Hendrickx, M.E. Particle Size Reduction Leading to Cell Wall Rupture Is More Important for the β-Carotene Bioaccessibility of Raw Compared to Thermally Processed Carrots. J. Agric. Food Chem. 2010, 58, 12769–12776.
8. Ma, Z.; Boye, J.I.; Simpson, B.K.; Prasher, S.O.; Monpetit, D.; Malcolmson, L. Thermal processing effects on the functional properties and microstructure of lentil, chickpea, and pea flours. Food Res. Int. 2011, 44, 2534–2544.
9. Crews, C.; Castle, L. A review of the occurrence, formation and analysis of furan in heat-processed foods. Trends Food Sci. Technol. 2007, 18, 365–372.
10. Paciulli, M.; Ganino, T.; Carini, E.; Pellegrini, N.; Pugliese, A.; Chiavaro, E. Effect of different cooking methods on structure and quality of industrially frozen carrots. J. Food Sci. Technol. 2016, 53, 2443–2451.
11. Palmers, S.; Grauwet, T.; Celus, M.; Kebede, B.T.; Hendrickx, M.E.; Van Loey, A. Furan formation as a function of pressure, temperature and time conditions in spinach purée. LWT 2015, 64, 565–570.

12. Mogol, B.A.; Gökmen, V. Thermal process contaminants: Acrylamide, chloropropanols and furan. Curr. Opin. Food Sci. 2016, 7, 86–92.
13. Rychlý, R.; Nývlt, J. Measuring and Calculating Heat of Crystallisation. Cryst. Res. Technol. 1974, 9, 799–810.
14. FDA Exploratory Data on Furan in Food: Individual Food Products. Available online: https://www.fda.gov/food/chemicals/exploratory-data-furan-food (accessed on 17 March 2021).
15. EFSA Scientific Committee Statement on the applicability of the Margin of Exposure approach for the safety assessment of impurities which are both genotoxic and carcinogenic in substances added to food/feed. EFSA J. 2012, 10, 2578.
16. Knutsen, H.K.; Alexander, J.; Barregård, L.; Bignami, M.; Brüschweiler, B.; Ceccatelli, S.; Cottrill, B.; Dinovi, M.; Edler, L.; Grasl-Kraupp, B.; et al. Risks for public health related to the presence of furan and methylfurans in food. EFSA J. 2017, 15, e05005.
17. Arisseto, A.P.; Vicente, E.; Toledo, M.D.F. Determination of furan levels in commercial samples of baby food from Brazil and preliminary risk assessment. Food Addit. Contam. Part A 2010, 27, 1051–1059.
18. Chen, C.; Ramaswamy, H. Modeling and Optimization of Constant Retort Temperature (CRT) Thermal Processing Using Coupled Neural Networks and Genetic Algorithms. J. Food Process. Eng. 2002, 25, 351–379.
19. Almonacid-Merino, S.F.; Simpson, R.; Torres, J.A. Time-Variable Retort Temperature Profiles for Cylindrical Cans: Batch Process Time, Energy Consumption and Quality Retention Model. J. Food Process. Eng. 1993, 16, 271–287.
20. Simpson, R.; Abakarov, A.; Teixeira, A. Variable retort temperature optimization using adaptive random search techniques. Food Control. 2008, 19, 1023–1032.
21. Ansorena, M.; Salvadori, V. Optimization of thermal processing of canned mussels. Food Sci. Technol. Int. 2011, 17, 449–458.
22. Simpson, R.; Ramirez, C.; Jiménez, D.; Almonacid, S.; Nuñez, H.; Angulo, A. Simultaneous multi-product sterilization: Revisited, explored, and optimized. J. Food Eng. 2019, 241, 149–158.
23. Simpson, R.; Jiménez, D.; Almonacid, S.; Nuñez, H.; Pinto, M.; Ramírez, C.; Vega-Castro, O.; Fuentes, L.; Angulo, A. Assessment and outlook of variable retort temperature profiles for the thermal processing of packaged foods: Plant productivity, product quality, and energy consumption. J. Food Eng. 2020, 275, 109839.
24. Durance, T.D. Improving canned food quality with variable retort temperature processes. Trends Food Sci. Technol. 1997, 8, 113–118.

25. Avila-Gaxiola, E.; Delgado-Vargas, F.; Zazueta-Niebla, J.; López-Angulo, G.; Vega-García, M.; Caro-Corrales, J. Variable Retort Temperature Profiles for Canned Papaya Puree. J. Food Process. Eng. 2015, 39, 11–18.

26. Cilla, A.; Alegria, A.; De Ancos, B.; Sanchez-Moreno, C.; Cano, M.P.; Plaza, L.; Clemente, G.; Lagarda, M.J.; Barberá, R. Bioaccessibility of Tocopherols, Carotenoids, and Ascorbic Acid from Milk- and Soy-Based Fruit Beverages: Influence of Food Matrix and Processing. J. Agric. Food Chem. 2012, 60, 7282–7290.

27. Cilla, A.; Bosch, L.; Barberá, R.; Alegría, A. Effect of processing on the bioaccessibility of bioactive compounds–A review focusing on carotenoids, minerals, ascorbic acid, tocopherols and polyphenols. J. Food Compos. Anal. 2018, 68, 3–15.

28. Aguilera, J.M. Why food microstructure? J. Food Eng. 2005, 67, 3–11.

29. Zhou, L.-Y.; Li, W.; Pan, W.-J.; Sajid, H.; Wang, Y.; Guo, W.-Q.; Cai, Z.-N.; Wang, D.; Yang, W.-W.; Chen, Y. Effects of thermal processing on nutritional characteristics and non-volatile flavor components from Tricholoma lobayense. Emir. J. Food Agric. 2017, 29, 1.

30. Mogol, B.A.; Gökmen, V. Kinetics of Furan Formation from Ascorbic Acid during Heating under Reducing and Oxidizing Conditions. J. Agric. Food Chem. 2013, 61, 10191–10196.

31. Owczarek-Fendor, A.; De Meulenaer, B.; Scholl, G.; Adams, A.; Van Lancker, F.; Yogendrarajah, P.; Uytterhoeven, V.; Eppe, G.; De Pauw, E.; Scippo, M.-L.; et al. Importance of Fat Oxidation in Starch-Based Emulsions in the Generation of the Process Contaminant Furan. J. Agric. Food Chem. 2010, 58, 9579–9586.

32. Adams, A.; Bouckaert, C.; Van Lancker, F.; De Meulenaer, B.; De Kimpe, N. Amino Acid Catalysis of 2-Alkylfuran Formation from Lipid Oxidation-Derived α,β-Unsaturated Aldehydes. J. Agric. Food Chem. 2011, 59, 11058–11062.

33. Märk, J.; Pollien, P.; Lindinger, C.; Blank, I.; Märk, T. Quantitation of Furan and Methylfuran Formed in Different Precursor Systems by Proton Transfer Reaction Mass Spectrometry. J. Agric. Food Chem. 2006, 54, 2786–2793.

34. Becalski, A.; Forsyth, D.; Casey, V.; Lau, B.P.-Y.; Pepper, K.; Seaman, S. Development and validation of a headspace method for determination of furan in food. Food Addit. Contam. 2005, 22, 535–540.

35. Shen, M.; Liu, Q.; Jiang, Y.; Nie, S.; Zhang, Y.; Xie, J.; Wang, S.; Zhu, F.; Xie, M. Influences of Operating Parameters on the Formation of Furan During Heating Based on Models of Polyunsaturated Fatty Acids. J. Food Sci. 2015, 80, T1432–T1437.

36. Limacher, A.; Kerler, J.; Davidek, T.; Schmalzried, F.; Blank, I. Formation of Furan and Methylfuran by Maillard-Type Reactions in Model Systems and Food. J. Agric. Food Chem. 2008, 56, 3639–3647.

37. Locas, C.P.; Yaylayan, V.A. Origin and Mechanistic Pathways of Formation of the Parent FuranA Food Toxicant. J. Agric. Food Chem. 2004, 52, 6830–6836.
38. Van Lancker, F.; Adams, A.; Owczarek-Fendor, A.; De Meulenaer, B.; De Kimpe, N. Mechanistic Insights into Furan Formation in Maillard Model Systems. J. Agric. Food Chem. 2011, 59, 229–235.