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Formation and reduction of furan in a soy sauce model system

Min Yeop Kim, Jae-Young Her, Mina K. Kim, Kwang-Geun Lee *

Department of Food Science and Biotechnology, Dongguk University-Seoul, 30, Pildong-ro-1-gil, Jung-gu, Seoul 100-715, Republic of Korea

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ABSTRACT

The formation and reduction of furan using a soy sauce model system were investigated in the present study. The concentration of furan fermented up to 30 days increased by 211% after sterilization compared to without sterilization. Regarding fermentation temperature, furan level after 30 days' fermentation was the highest at 30 °C (86.21 ng/mL). The furan levels in the soy sauce fermentation at 20 °C and 40 °C were reduced by 45% and 88%, respectively compared to 30 °C fermentation. Five metal ions (iron sulfate, zinc sulfate, manganese sulfate, magnesium sulfate, and calcium sulfate), sodium sulfite, ascorbic acid, dibutyl hydroxyl toluene (BHT), and butylated hydroxyanisole (BHA) were added in a soy sauce model system. The addition of metal ions such as magnesium sulfate and calcium sulfate reduced the furan concentration significantly by 36–90% and 27–91%, respectively in comparison to furan level in the control sample ($p < 0.05$). Iron sulfate and ascorbic acid increased the furan level at 30 days' fermentation in the soy sauce model system by 278% and 87%, respectively. In the case of the BHT and BHA, furan formation generally was reduced in the soy sauce model system by 84%, 56%, respectively.

1. Introduction

Furan is a heterocyclic compound formed in various heat-treated commercial foodstuffs (Crews & Castle, 2007; Rufian-Henares, Delgado-Andrade, & Morales, 2009). Furan has a unique characteristic, which is its colorlessness, and it has high volatility due to its boiling point of 31 °C (Bolger, Tao, & Dinovi, 2009). In addition, the international Agency for Research on Cancer considers it to be a dangerous chemical and classify it as possibly carcinogenic to humans (Group 2B) (IARC, 1995). One of the most common causes of furan in canned and jarred foods, coffee, and baby foods could be thermal treatment processing (FDA, 2004; Nie et al., 2013). As furan is generated during the manufacturing process of various food groups, it is necessary to find methods of reducing furan concentration based on the formation mechanisms (Limacher, Kerler, Davidek, Schmalzried, & Blank, 2008).

Unlike most other materials, furan has multiple routes of formation involving different precursors and intermediates (Locas & Yaylayan, 2004; Yaylayan, 2006). Furan formation has been identified as having a variety of pathways and precursors, such as amino acids, carbohydrates, polyunsaturated fatty acids, ascorbic acids, and carotenoids (Anese, Manzocco, Calligaris, & Nicoli, 2013; Mariotti et al., 2012; Van Lancker et al., 2011). The Maillard reaction is a major pathway to form the furan formation (Contreras-Calderon, Guerra-Hernandez, & Garcia-Villanova, 2009; Limacher et al., 2008; Rufian-Henares et al., 2009). This reaction forms between the specific amino acids and carbonyl groups of reducing sugars. This reaction has a desirable effect on the flavor and quality of foods, but it also leads to furan formation during the thermal processing of foods in general through each step of this reaction (Van Boekel, 2006). When the furan levels of related foodstuffs (e.g., breads, soy sauces, savory snacks, and coffee) containing amino groups and sugars through the Maillard reaction are examined, it is shown that the levels of furan are higher than those of any other foods (Kim, Kim, & Lee, 2010; Kim, Lee, Kim, Park, & Lee, 2009; Zoller, Sager, & Reinhard, 2007).

In Asian countries such as Korea, China, Japan, Indonesia, and Thailand, many foods involve the Maillard reaction (Feng et al., 2013; Kim & Lee, 2008; Zhang & Tao, 2009). In particular, *kanjang* (Korean soy sauce) is one of the traditional Korean foods in which furan is made via the Maillard reaction. According to statistical research about consumption of soy sauce in Korea, it occupied 30% of the sauces market during 2010 (soy sauce: $200 million, total market: $780 million). In particular, annual domestic consumption of soy sauce has been more than 200,000 kL since 2000. Soy sauces are widely used as seasoning for cooking in Korea, as indicated in this statistic. When viewed in comparison with previous studies that analyzed furan levels in various foods, the furan levels of naturally brewed and fermented soy sauce showed a range of 44.32–178 ng/mL (Feng, Cui, Zhao, Gao, Zhao, & Sun, 2013; Kim et al., 2010; Wu, Wang, & Yuan, 2014; Zhang, & Tao,

* Corresponding author. Tel.: +82 2 2260 3370; fax: +82 2 2285 3370.
E-mail address: kwglee@dongguk.edu (K.-G. Lee).

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2009; Zoller, Sager, & Reinhard, 2007), which is significantly higher than in most other foods. Based on this result, it might be anticipated that many people in Korea will be exposed frequently to furan in soy sauce.

Various furan-mitigation strategies in foods have been explained, including, physical removal, ionizing radiation, thermal input reduction, and fermentation (Anese & Suman, 2013; Anese et al., 2013). Among them, one of the best methods has been to use food additives to reduce furan concentration. According to the FAO/WHO, food additives are non-nutritive substances added intentionally to food (and generally in small quantities) to improve its appearance, aroma, texture, or storage properties. The aim of the study is to understand the formation of furan in soy sauce generated by sterilization and fermentation temperature. In addition, the effect of various food additives on the formation of furan in soy sauce model system.

2. Materials and methods

2.1. Chemical reagents and materials

Furan and d4-furan with purity higher than 99% were purchased from Sigma–Aldrich Corporation (St. Louis, MO, USA). Water and methanol (HPLC grade), for use in the analysis of furan concentration, were bought from J. T. Baker (Phillipsburg, NJ, USA). For the food additives, iron sulfate n-hydrate (Fe^{2+}, 60–80% purity) was obtained from Kanto Chemical Co, Inc. (Japan). Zinc sulfate (Zn^{2+}, 99% purity) and magnesium sulfate (Mg^{2+}, 99% purity) were purchased from Junsei Chemical Co., Ltd. (Japan). Calcium sulfate dehydrate (Ca^{2+}, 97% purity) and manganese (II) sulfate monohydrate (Mn^{2+}, 98% purity) were purchased from Daejung reagents Chemicals (Seoul, Korea). Sodium sulfite (Na^{+}, 98% purity), L-ascorbic acid (vitamin C, 99%, purity), dibutyl hydroxyl toluene (BHT, 99% purity), and butylated hydroxyanisole (BHA, 98.5% purity) were obtained from Sigma–Aldrich Corporation (St. Louis, Mo, USA). For the manufacturing of soy sauce, the main ingredients (soybeans, sun-dried salt, and roasted wheat) were purchased from a local market in Seoul, Korea. A powder of *Aspergillus oryzae* was obtained from the Suwon Fermentation Food Research Institute (Hwaseong-si, Gyeonggi-do Province, Korea).

2.2. Preparation for manufacturing koji and soy sauce

Fig. 1 shows the procedure for manufacturing *koji* and soy sauce in accordance with standard manufacturing protocol (Feng et al., 2013; Kim & Lee, 2008; MFDS-b, 2014). The process used was slightly modified from the standard protocol. Raw soybeans (460 g) were soaked in 552 mL water (120% of the soybean weight), in a 1 L glass for a day at room temperature. The sample bottle was then put into an autoclave and steamed at 121 °C for 40 min. After steam processing, the soaked soybeans were ground by mortar and pestle. Roasted wheat (100 g) was added, and the mixture was inoculated with 4 g of *A. oryzae*. The mixture was stirred once every day to ensure the propagation of *A. oryzae* in the fermentation at 20 °C and 40 °C. In previous studies carried out in the various laboratories, the optimized temperature for the fermentation of soy sauce is between 20 and 40 °C. In the case of at 30 °C, the mixture was stirred every 3 days. After 3 days, 40 g of *koji*, 280 g of diluted water, and 72 g of salt were mixed in the bottle according to the mixing ratio of soy sauce processing [*koji*: water: salt = 1: 7: 1.8]. The mixture was incubated at 30 °C, and sampling for the analysis of furan was carried out every 5 days for 30 days. In sampling, filtration was processed to separate the liquid soy sauce. The mixture was sterilized at 80 °C for 10 min on a hot plate (180 × 180 mm plate-type: MSH-20D, DAIHAN-brand, Korea) after each sampling. Sterilized soy sauce was cooled down for at least 1 h in a refrigerator. Soy sauce obtained through this manufacturing method was used for furan analysis in this study.

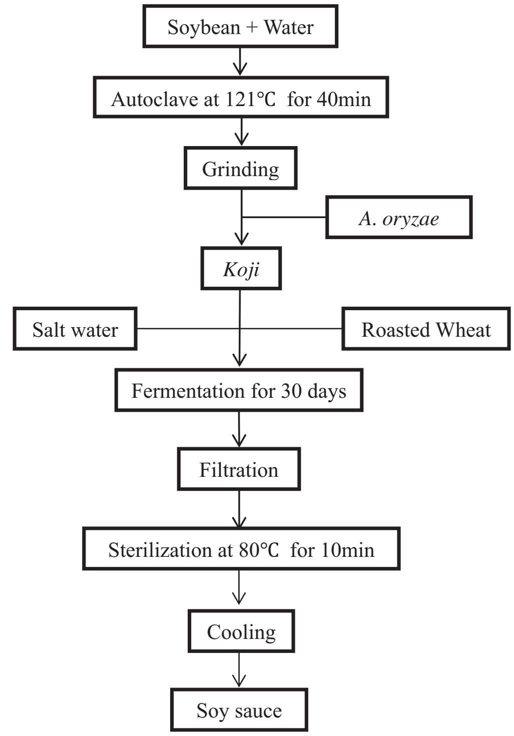

Fig. 1. Procedure for manufacturing soy sauce in the laboratory.

2.3. Sample preparation for the analysis of furan in the soy sauce model system

HPLC-grade water (5 mL) and 5 mL of soy sauce were added to a 20-mL headspace vial (Agilent Santa Clara, CA, USA). Then, 0.05 M, 0.1 M, and 0.2 M of various food additives were added to the vials before the sterilization of soy sauce every 5 days. Vials were sealed completely with silicone-PTFE septa and aluminum seals and heated at 80 °C for 10 min on hot plates. After sterilization, vials containing in soy sauce and various food additives were cooled in a refrigerator for at least 1 h. To examine the amount of furan under the different fermentation temperatures, the incubation temperature was set at 20, 30, or 40 °C. Three temperatures were set by using particular temperature as specified incubator (IL-11 incubator model, JEIO TECH, Co., Ltd., Korea).

2.4. Furan analysis

2.4.1. Preparation of stock and working solutions, and validation of the analysis of furan

Stock solutions of furan and d4-furan were prepared individually in 20-mL headspace vials by adding 1 µl aliquot of native (d-4) furan via a gastight syringe in cold methanol weekly. Working solutions were prepared every day with 100 µl of refrigerated stock solutions and 10 mL of HPLC-grade water. All vials of stock and working solutions were sealed with silicone-PTFE septa, aluminum seals and stored at −18 and 4 °C, respectively, until analysis. The following validation parameters were used: linearity, correlation coefficient (r^2), repeatability, recovery percent, limit of detection (LOD), and limit of quantification (LOQ). For the analysis of furan levels in the soy sauce model system, 10 µl of internal standard working solution of d-4 furan were injected through the