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Original Article

Effects of calcium supplements on the quality and acrylamide content of puffed shrimp chips

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ABSTRACT

The quality and acrylamide content of deep-fried and microwave-puffed shrimp chips fortified with 0.1%, 0.5%, or 1.0% calcium salts (calcium lactate, calcium carbonate, calcium citrate, or calcium acetate) were investigated. Microwave-puffed shrimp chips contained higher amounts of acrylamide (130.43 ppb) than did deep-fried shrimp chips. The greatest mitigation of acrylamide formation in overfried chips was obtained with 0.1% calcium lactate. All browning indexes of fortified shrimp chips, whether deep-fried or microwave-puffed, were reduced. L^* values of microwave-puffed shrimp chips were higher than those of deep-fried shrimp chips, whereas a^* and b^* values and browning indexes were lower. Color differences (ΔE) between deep-fried puffed shrimp chips fortified with calcium salts and a control sample were higher than 5, and the sensory scores of shrimp chips were significantly decreased by the addition of calcium lactate.

1. Introduction

Puffed shrimp chips, commonly known as *krupuk*, are a common snack in most Asian countries, including Taiwan, Indonesia, and Thailand. Raw shrimp chips are traditionally manufactured by mixing shrimp, starch, and water to form a paste, which is steamed, cooled down, cut into chips, and sun-dried. Raw shrimp chips are quite hard and are smaller and darker than puffed shrimp chips. Raw shrimp chips have been traditionally puffed by deep-frying; however, microwave-puffed products are currently available in the market for health-conscious consumers.

Calcium is an essential nutrient that is recognized for its ability to prevent osteoporosis. The presence of polyvalent calcium ions in foodstuffs reduces acrylamide formation during heating [1]. Therefore, fortifying shrimp chips with calcium salts might theoretically reduce the formation of acrylamide during deep-frying or microwave puffing. Investigating the quality of puffed shrimp chips and the acrylamide

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content produced during microwave puffing could help the food industry design more effective methods for reducing the formation of acrylamide and for improving the nutritional value of shrimp chips.

Acrylamide is a potentially carcinogenic, neurotoxic compound that is present in heat-processed starchy food products [2]. It can also be generated by oils and nitrogen-containing compounds, or when oils in food ingredients are heated to temperatures above 100°C. However, acrylamide has not been detected in unheated or boiled foods [3]. The fatty acid oxidation product acrolein ($CH_2{=}CH{-}CHO$) reacts with ammonia to form $CH_2{=}CH{-}CHOH(NH_2)$, which can convert into acrylamide either by reacting with asparagine or by oxidizing to form an *N*-glycoside, which converts into acrylamide via oxidation [4]. The actual mechanism of acrylamide formation from the reaction of a carbonyl-containing compound and asparagine in fried midoleic sunflower oil at a temperature of 205°C has been described [5]. Tareke et al [6] reported that food heated at elevated temperatures is the main source of acrylamide. Becalski et al [7] proposed that acrylamide may be generated by the rearrangement of nitrogen-containing components present in cooked foodstuffs. Acrylamide is formed from food components during heating as a result of the Maillard reaction between reducing sugars and amino acids [8,9]. Levels of acrylamide in fried and baked starchy foods range between 150 and 4000 μg/kg [3]; therefore, finding an effective way to reduce the formation of acrylamide in fried snack foods is an urgent issue in the food processing industry.

In general, heat-processed commercial protein-rich foods, such as fish, meat, and poultry, contain lower amounts of acrylamide than do carbohydrate-rich foods, such as French fries, potato chips, tortilla chips, cereals, and baked goods [3]. The formation of a Schiff base is considered to be the first reaction step. The reaction is initiated by the addition of nucleophilic asparagine to the partially positive carbonyl carbon of the dicarbonyl compound, followed by the loss of a proton from nitrogen and the addition of a proton to oxygen [9].

Several strategies for reducing the formation of acrylamide in heated foods have been proposed in recent years, including the following: adding divalent cations such as calcium salts [10,11]; replacing reducing sugars with nonreducing sugars such as sucrose [12–14]; diluting asparagine levels by adding glycine [15]; adding asparaginase to reduce free asparagine [16,17]; and substituting ammonium salts with baking powder [18].

Jung et al [19] demonstrated that acrylamide formation in corn chips (baked and fried) and French fries was reduced when an acidulant was added to lower pH values. Amrein et al [14] suggested that free asparagine levels are a limiting factor in acrylamide formation.

To better understand the interactions that occur when fortified shrimp chips are deep-fried, we supplemented the standard chips recipe with calcium lactate, calcium carbonate, calcium citrate, or calcium acetate in order to determine the roles of calcium salts and reducing sugars in the formation of acrylamide. The quality of traditional puffed shrimp chips versus shrimp chips fortified with calcium salts was evaluated in order to develop better strategies for reducing the acrylamide content of snack products.

2. Materials and methods

2.1. Raw materials and chemicals

Cassava starch was obtained from Ding Yuh Foods (Taichung, Taiwan). Frozen white shrimp, sucrose, sodium chloride, and soybean oil were purchased from the local Ren Ai Traditional Market (Keelung, Taiwan).

3,5-Dinitrosalicylic acid, D-glucose, sulfuric acid, potassium sodium tartrate, $^{13}C_3$-labeled acrylamide, and sodium hydroxide were purchased from Sigma Aldrich (St. Louis, MO, USA). All calcium salts (including calcium lactate, calcium acetate, calcium carbonate, and calcium citrate) were purchased from Ninhon Shiyaku Industries, Ltd. (Taipei, Taiwan). All of the chemical reagents used were of analytical grade. The standard chemical compound 99.9% acrylamide was purchased from J.T. Baker (Phillipsburg, NJ, USA). Oasis HLB (6 mL, 200 mg) and Oasis MCX (3 mL, 60 mg) solid-phase extraction cartridges were obtained from Waters (Milford, MA, USA).

2.2. Preparation of raw shrimp chips and physicochemical properties of shrimp chips

The formula for raw shrimp chips is 200 g of white shrimp, 5.0 g of sodium chloride, 5.0 g of sucrose, 100 mL of distilled water, and 200 g of cassava starch. The base ingredients were blended with a 12-speed blender (Oster 6642; Oster, Canton, OH, USA). The resulting paste was supplemented with calcium salts (calcium lactate, calcium citrate, calcium acetate, or calcium carbonate) on a paste weight basis of 0.1%, 0.5%, or 1.0%. The shrimp paste was rolled out to a thickness of 20 mm, steamed for 1.5 hours, cooled down, refrigerated at 7°C for 8 hours, sliced into 3-mm chips, and dried at 80°C for 4 hours. The raw shrimp chips were either deep-fried in 500 mL of soybean oil at 180°C for 20–75 seconds in an electrical fryer (KR-4K009; Korlea Corporation, Kaohsiung, Taiwan) or puffed in a microwave oven (NN-GD587; Panasonic, Shanghai, China) for 40–80 seconds at 900 W.

The effects of calcium salts on the pH of raw shrimp chips were measured using the slightly modified Sung method [20]. The approximate chemical composition of puffed shrimp chips was determined according to the method of the Association of Official Analytical Chemists [21]. The moisture content of raw shrimp chips was measured according to Association of Official Analytical Chemists method 984.25, using oven drying at 105°C for 24 hours. The lipid content of the sample was determined using an ether extraction method [21]. The ash content of puffed shrimp chips was measured according to procedure 46-12 of the American Association of Cereal Chemists [22]. Water activity in puffed shrimp chips was determined using a Novasina Thermoconstanter RTD 33 TH-1 avumeter (Novasina Co. Ltd., Pfaffikon, Switzerland). The puffing ratio was calculated by measuring shrimp chips before and after puffing, using a sucrose granule displacement method. The puffing ratio was calculated as:

$$(V_2/W_2) \times 100\%/(V_1/W_1)$$

where W_1 = weight of raw shrimp chips; V_1 = volume of raw shrimp chips; W_2 = weight of puffed shrimp chips; and V_2 = volume of puffed shrimp chips.