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Effects of formulation and extrusion cooking conditions on furfural and hydroxymethylfurfural content

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ABSTRACT

The objective of this research was to investigate the effects of different ingredients (reducing sugars, leavening agents, citric acid), processing conditions (feed moisture content, exit die temperature), and extrusion cooking methods (with/without CO_2 injection) on furfural and 5-hydroxymethylfurfural (HMF) formation in corn-based extrudates. The decrease in furfural levels was 16% upon addition of sodium-bicarbonate, while the increase was 12% upon addition of ammonium-bicarbonate for extrudates produced at 150 °C and feed moisture content of 22%. The furfural concentration of extrudates produced at 150 °C and feed moisture content of 22% without leavening agents was 810 μg/100 g and increased to 11,901 μg/100 g upon citric acid addition (about a 15-fold increase). Furthermore, both low feed moisture and high exit die temperature had promoting effects on furfural and HMF contents. The CO_2 injection method did not have considerable effect on furfural and HMF levels of the extrudates; however, it positively affected the physical properties of extrudates.

1. Introduction

Extrusion cooking is a continuous high-temperature-short-time process, which cooks, forms and dries the product in one integrated operation. Functional and nutritional properties of food components might change during extrusion process. Mild extrusion conditions (high moisture content, low residence time, low temperature) favour higher retention of amino acids and vitamins, high protein and starch digestibility and increased soluble dietary fibre (Moscicki and van Zuilichem, 2011; Singh et al., 2007).

Addition of chemical leavening agents is a common practice in the extrusion cooking industry to improve expansion properties (Lai et al., 1989). The most commonly utilized sources of carbon dioxide (CO_2) are sodium and ammonium bicarbonates. Sodium bicarbonate is the most popular leavening agent due to various advantages (e.g., relatively low cost, non-toxic and almost no effect on the taste). Ammonium bicarbonate leaves no residual salt after reaction, and therefore does not affect dough rheology or end flavour if the moisture content is below 5% (Delcour and Hoseney, 2010).

An extrusion method utilizing injection of CO_2 gas into extruder barrel was introduced for the processing of expanded cereal products. Many researchers have reported the advantage of CO_2 injection method to protect nutrients in food materials from the effects of high temperature (Bilgi-Boyaci et al., 2012; Masatcioglu et al., 2013). Since, the extrusion process combines the application of high temperature and low moisture; it is expected to promote the development of Maillard reaction products (MRPs). Therefore, potential detrimental consequences of thermal processes must be carefully assessed. However, only a limited number of previous publications have been concerned with the effects of the CO_2 injection method on MRPs (Masatcioglu et al., 2014a).

The major concern due to heat treatment is the formation of harmful compounds that are not naturally present in foods, but that may build up during heating. These are called neo-formed contaminants (NFCs). Familiar examples of the NFCs are heterocyclic amines, nitrosamines and polycyclic aromatic hydrocarbons which are reported to have mutagenic, carcinogenic and cytotoxic effects (Cheng et al., 2006). Recently, two NFCs have received much interest as a consequence of their potential toxicological effects along with their wide occurrence in foods: acrylamide and HMF (Capuano and Fogliano, 2011).

Upon heating at high temperature, sugars decompose into furfural compounds by two possible pathways: (i) the Maillard

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reaction, where the Amadori product, formed by reaction of reducing sugars with amino group of amino acids or proteins, undergoes enolisation and then dehydration of the sugar moiety (Nursten, 2005; Olano and Martínez-Castro, 2004); and (ii) caramelization, where reducing sugars, go through 1–2 enolisation, dehydration and cyclization reactions (Kroh, 1994). Caramelization requires higher temperatures than the Maillard reaction to progress (Kroh, 1994). HMF is considered as the main decomposition product of hexoses, especially when the pH is low, while furfural is principally produced from pentoses (BeMiller and Huber, 2008; Nursten, 2005).

Sugars are generally used to develop flavour and colour and play an important role in controlling texture and mouthfeel in extruded snack products. Sucrose and fructose are commonly used in the production of extruded products, but there is few published information (Masatcioglu et al., 2014a,b) concerning the utilization of ribose in extrusion products or its comparison with common sugars such as glucose. Hence, ribose and glucose were the sugars of interest for this research. Furthermore, pentose and hexose sugars are known to have different effects on the rate of Maillard reaction in various conventional processes while such information is lacking with respect to extrusion cooking.

HMF at high concentrations is cytotoxic, irritating to eyes and mucous membranes. The major concern for HMF is related to its conversion to SMF (5-sulfoxymethylfurfural) which has genotoxic properties (Monien et al., 2009). European Food Safety Authority (EFSA) concluded based on the mutagenicity of SMF, that there is sufficient evidence to raise concern about its genotoxic potential (EFSA, 2005). Since HMF levels in various heat processed foods are quite high, even a limited conversion of HMF to SMF would expose humans to amounts of SMF that could have deteriorative health effects.

Some of the mitigation strategies (e.g. Ca^{2+}, glycine and consumable acids additions) for acrylamide reduction in bakery products have been reported along with their simultaneous effect on HMF levels (Gökmen and Şenyuva, 2007; Gökmen et al., 2007). Gökmen et al. (2007) stated that lowering the pH, by adding citric acid to the dough containing glucose, resulted in a 67% reduction in acrylamide content of cookies while HMF levels significantly increased. Thus, alternative mitigation strategies are still needed due to potential risks of the suggested methods. A previous study by our group indicated that CO_2 injection during extrusion had a significant decreasing effect on acrylamide level (Masatcioglu et al., 2014a). However, we have not encountered any study related to the influence of CO_2 injection on intermediate stage MRPs (e.g. furfural and HMF).

The aim of this research was to investigate the effects of reducing sugars (D-glucose and D-ribose), extrusion cooking conditions (exit die temperature and feed moisture content), chemical leavening agents (sodium bicarbonate and ammonium bicarbonate), and citric acid on furfural and HMF formation in corn-based extrudates. Moreover, the influence of CO_2 injection as an alternative technology on furfural and HMF formation was also investigated.

2. Materials and methods

2.1. Materials

White corn flour was obtained from ADM Milling Company (Jackson, TN, USA), soy protein isolate (SPI) and glucose were provided by ADM Specialty Food Ingredients Co. (Decatur, IL, USA) and ribose was supplied by NutraBio Co. (Middlesex, NJ, USA). Food-grade anhydrous citric acid and L-asparagine were obtained from ADM (Southport, NC, USA) and Ajinomoto North America, Inc. (Fort Lee, NJ, USA), respectively. Sodium- and ammonium-bicarbonate were purchased from Church & Dwight Co., Inc. (Ewing, NJ, USA).

2.2. Chemicals

Furfural (Merck, Darmstadt, Germany) and HMF (Sigma–Aldrich, Diesenhofen, Germany) were used as the standards. Analytical grade formic acid, potassium hexacyanoferrate, and zinc sulphate were obtained from Sigma–Aldrich (Steinheim, Germany). Absolute ethanol, sodium acetate and acetic acid (all AnalaR grade) were obtained from Merck (Darmstadt, Germany). HPLC grade methanol (Merck, Darmstadt, Germany) was used to prepare the mobile phase. For furfural and HMF determination, Carrez-I solution (15% potassium ferrocyanide, w/v) and Carrez-II solution (30% zinc acetate, w/v) were used to prepare a clarified solution. All solutions were prepared with deionised water (Millipore, Bedford, MA, USA).

2.3. Methods

2.3.1. Sample preparation

Seven formulations were prepared with different ingredients (reducing sugars, chemical leavening agents, citric acid; Table 1). The mixtures were prepared in several steps to achieve a uniform level of mixing/blending without concentrated pockets of components of formulations. Initial mixing of ingredients (D-ribose, D-glucose, L-asparagine, SPI, sodium- and ammonium bicarbonates and citric acid) with corn flour up to 1 kg was performed in a KitchenAid mixer (K5SS, St. Joseph, MI, USA) at low speed for 30 min and then the mixture was transferred to a Hobart mixer (Hobart A-200, OH, USA) for diluting the ingredients with corn flour and further blending (up to 25 kg) and mixed at low speed for 30 min.

2.3.2. Extrusion process

2.3.2.1. Conventional extrusion method without CO_2 injection. A laboratory-scale co-rotating twin-screw extruder (MPF19, APV Baker Ltd, Staffordshire, England), with a 25:1 screw length to diameter ratio (L/D) and with five temperature zones, was used to produce corn extrudates at different process variables. The screw speed, feed rate, and die hole diameter were kept constant at 200 rpm, 2.5 kg/h, and 2.0 mm, respectively. The screw configuration is given below:

5*D* Twin lead feed screws
8 × 30° Forward kneading paddles
8*D* Twin lead feed screws
8 × 60° Forward kneading paddles
4 × 30° Reverse kneading paddles
2*D* Single lead feed screws
2*D* Twin lead feed screws
4 × 30° Reverse kneading paddles
4 × 30° Forward kneading paddles
1*D* Single lead feed screw
Screw diameter = 19.0 mm (1*D*)
One kneading paddle = 1/4 *D*

Extrusion was carried out with an exit die temperature of 110 or 150 °C and with a feed moisture content of 22, 24 or 26%. Extrusion temperature profile was set depending on the temperature of the exit die. Extrusion temperature profiles were 60/90/110/110/110 °C and 60/90/110/150/150 °C (increasing temperature toward die) when the temperature of the exit die was adjusted to 110 or 150 °C, respectively. When the extrusion system reached steady state, as indicated by constant torque, pressure and temperature, samples