THE HYDROXYMETHYLFURFURAL AND FUROSINE CONTENT IN HOME- MADE AND COMMERCIALLY PROCESSED FOODS

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KEYWORDS	ABSTRACT
Hydroxymethylfurfural, Furosine, Cookies, Bread, French fries & Potato chips	In present study, we investigated the hydroxymethylfurfural and furosine content in different products prepared (home-made) and collected from market (commercially processed) include cookies, bread, fried potatoes. The detection of hydroxymethylfurfural and furosine was done through high pressure liquid chromatography. In this study, hydroxymethylfurfural content of different products was observed from 0.076 to 3.605 mg/kg. Moreover, the furosine content of the home-made and commercially processed foods was found in the range of 2.62-16.10 mg/kg. Present study indicated that highest level of hydroxymethylfurfural was detected in potato chips while, highest furosine level was found in the commercially produced cookies. The presence of the hydroxymethylfurfural and furosine in food products accentuates the safety issue and present findings established that processing conditions could be optimized to achieve desirable processing effects with enhanced consumer safety.

INTRODUCTION

In recent times, the advancement of processing has led to increase consumption of snacks worldwide including cookies, potato chips, French fries. On one hand, Maillard reaction is imperative in order to achieve the characteristic color and sensory attributes of food. On other hand, it causes formation of malignant products including hydroxymethylfurfural, acrylamide and other compounds of toxicological concern (Nguyen, Klerx, Peter & Boekel, 2016). Several publications have reported the development of a wide range of potentially toxic products in Maillard reaction (Rakete, Klaus & Glomb, 2014). In this connection, furosine and hydroxymethylfurfural (HMF) attracted greater scientific attention due to their wide occurrence in different food products and potential endpoints (Teixidó, Núñez, Santos & Galceran, 2011). The occurrence of HMF in food underscores the safety issues since, HMF and its derivatives are found to be carcinogenic and mutagenic (Nguyen, Klerx & Boekel, 2017).

Generally, HMF is the heterocyclic compound and usually recognized as the heat process contaminant. It is an intermediary compound, which is developed in the Maillard reaction through the breakdown of hexoses at elevated temperature and acidic environment (Lorenzo & Morales, 2010). In fact, it is developed in early stages, and present in various carbohydrates-rich foods (Teixidó et al., 2011). The occurrence of HMF usually take place in over-processed foods i.e., baked goods but, it may also be present in honey, fruit and vegetable products, baby foods (Capuano, Ferrigno, Acampa, Serpen & Fogliano, 2009; Capuano & Fogliano, 2011; Klerx, Capuano, Nguyen, Mogol, Kocada, Boekel & Gökmen, 2014; Gökmen, 2016; Nguyen et al., 2017; Viegas, Prucha, Gökmen & Ferreira, 2018). The presence of HMF is related to heat intensity, which is supplied to a food during processing (Petisca et al., 2014). Furthermore, HMF have tendency to be transformed in furan and acrylamide, which are possibly known as carcinogens as reported previously (Zou et al., 2015).

Furosine (N-3-2-furoylmethyl-L-lysine), an amino acid derivative that is formed during early phase of Maillard reaction by acidic degradation of Amadori compounds and could be measured during the protein hydrolysis (Troise, Fiore, Wiltafsky & Fogliano, 2015). It usually divulges the degree of damage that deteriorate protein quality as well as amino acids because of lysine blockage in early stages of Maillard reaction (Li, Liu, Meng & Wang, 2017; Andrade, Seiquer, Haro, Castellano & Navarro, 2010). It is commonly used for the cereal-based foods since, lysine is a limiting amino acid of this product therefore, and its occurrence specify the loss of protein biological value. The evaluation of the content and formation of furosine assists tailor the process conditions to protect the nutritional significance of foods (Henares & Andrade, 2009; Gökmen & Senyuva, 2006). The present project intended to ascertain these toxic compounds in diverse home-made and processed foods.

MATERIALS AND METHODS

Collection and Samples

Samples of bread, cookies and potato chips were collected from supermarket, Faisalabad-Pakistan. Most of samples tested in present study for sampling were commercial brands. In addition, bread and cookies were prepared for experiment according to the procedures given by American association of cereal chemists (2000). Fries were prepared by adopting the method of Mestdagh, Meulenaer, Poucke, Cromphout & Peteghem (2005). Frying was achieved using an uncovered stainless steel pan fryer with the dimensions *i.e.*, 5 cm depth and 30 cm dia. During frying, oil temperature was examined using a digital thermometer attached with a steel probe. For frying, commercially available oil was heated at 175°C and then potatoes were dipped and fried for 6-8 minutes. When frying was over then, potatoes were kept on a dry grill for 5 minutes in order to drain the excess oil.

Color Values

Color measurements of home-made and processed foods were measured by a Color meter (Color Test II, Nehaus Neotech) as described by McLaren and Rigg (2005). Before testing samples, calibration of color meter was done by standards (151CTn for light and 54CTn for dark). Afterwards, samples were positioned under photocell of color meter and values were recorded. Then, samples were analyzed in triplicates and values were compared with standards. *Chemical Characteristics:* The chemical characteristics of the home-made and processed foods was determined by adopting procedures mentioned in AACC (2000).

Total Phenolic Content (TPC)

The TPC values of home-made and processed foods were determined by Folin-Ciocalteu reagent (FCR) according to method described by Pasha, Riaz, Saeed & Randhawa (2015). In a test tube, 125 µL sample was taken and 500 µL deionized water was added in test tube following addition of 125 µL of FCR. Then, it was allowed to stand for 6 min. Afterwards, 1.25 mL of 7% Na_2CO_3 was added and final volume was made up to 3 ml using 1 mL of distilled H_2O. Now, the samples were allowed to stand for 90 minutes in order to complete reaction. Absorbance of samples were taken by UV-vis spectrophotometer at 760 nm. TPC values of samples were calculated by running gallic acid as a standard and likewise, its absorbance was taken at 760 nm.

Hydroxymethylfurfural Content

Hydroxymethylfurfural content of different food products was detected according to the method of the Henares, Villanova & Hernandez, (2001) using the High Pressure Liquid Chromatography (HPLC; Shimadzu, Kyoto, Japan). *Furosine Content:* Furosine levels of different food products were reckoned following methods of Andrade, Henares & Andrade (2009).

STATISTICAL ANALYSIS

Data acquisition was carried out in triplicates and analyzed through Analysis of Variance (ANOVA). The average values ± standard deviation of triplicate measurements were calculated. Means were separated by Duncan's test at 5% probability level (Steel, Torrie & Dickey, 1997) by statistical software SPSS version (version 13, 2004).

RESULTS AND DISCUSSION

The chemical characteristics (Table 1) of the home-made and processed foods have shown moisture content (1.37-36.82), ash content (0.75-1.70), fat content (5.14-28.23), fiber content (0.17-3.08) and protein content (6.14-9.63%). In this study, ash and fat content of potato chips and French fries is obviously higher as compared to their counterparts. The difference is more prominent between the bread and French fries. In deep-frying, usually exchange of water and oil occur which is accompanied by the low moisture and high fat content. A most plausible explanation may be a reduction in water level of fried potatoes, which increases the relative ash and protein level (Andrade et al., 2009). Present findings are in conformity with other study who observed moisture (35.94-38.57%), ash (1.63-1.67%) and protein (8.08-8.52%) in five different brands of bread marketed in Pakistan. However, present results are discordant to the study conducted by Andrade et al. (2009) who established that fried potatoes contain moisture (54.0-56.7%), lipid (8.2-9.3) and protein content (3.9-5.4%).

Table 1 Chemical Characteristics of Home-Made and Commercially Processed Foods

Samples	Description	Moisture	Ash	Fat	Fiber	Protein
Bread	Home-Made	36.82±1.66	1.59±0.06	5.47±0.24	0.17±0.08	8.75±0.39
	Commercial Process	36.41±1.64	1.65±0.07	5.14±0.23	0.18±0.09	9.63±0.43
Cookies	Home-Made	4.40±0.19	0.76±0.03	26.17±1.17	0.22±0.01	6.14±0.27
	Commercial Process	4.48±0.20	0.75±0.02	27.47±1.24	0.23±0.02	8.31±0.37
Fried Potatoes	French Fries	31.93±1.43	1.70±0.07	28.23±1.27	3.08±0.15	6.83±0.31
	Potato Chips	1.37±0.12	1.63±0.08	27.60±1.25	2.45±0.12	7.93±0.35

Results are presented as the mean of three separate measurements ± standard deviation.

The table 2 showed that color values for different food products were statistically different ($p<0.01$) and ranged from 62.00 to 154.33CTn. Color of food product depends upon type of cooking and nature of food constituents. Greater the value of color, lighter would be the color of the final product. For the relative assessment, the lighter color was found in potato chips (i.e., 154.33CTn) and French fries (113.33CTn). Total phenolic content of different food products significantly ($P< 0.05$) varied from 0.405 to 0.881 µg GAE/g. In an earlier study, Anese, Manzocco, Nicoli & Lerici (1999) have established that antioxidant activity of food products was retained or even improved through formation of Maillard reaction products though, content of natural antioxidant was considerably declined as consequence of heat treatments.

Table 2 Color & Total Phenolic Content of Home-Made & Commercially Processed Foods

Samples	Description	Color	TPC (µg GAE/g)
Bread	Home-made	72.33±3.25	0.73±0.032
	Commercially processed	69.00±2.76	0.67±0.026
Cookies	Home-made	62.00±2.48	0.41±0.016
	Commercially processed	75.00±3.37	0.45±0.018
Fried potatoes	French fries	113.33±4.53	0.71±0.028
	Potato chips	154.33±6.17	0.88±0.035

Results are presented as the mean of three separate measurements ± standard deviation.

Hydroxymethylfurfural Content

HMF content of different products was detected to be varying between 0.076 and 3.605 mg/Kg (Table 3). Highest HMF content delved in potato chips (3.605 mg/Kg) however, the lowest was found in home-made bread as 0.076 mg/Kg. HMF content in potato chips is mainly higher because of their large surface area as well as great exposure with frying oil. Also, potato chips usually acquire elevated temperature that supports development of HMF. The variations in HMF levels in products studied might due to varied formulation and processing conditions. The formation of HMF in food is mainly influenced by sugar type, pH and water activity (Capuano et al., 2009). Published data has reported higher concentrations of HMF in the breakfast cereals as 3.67-193.34 mg/kg, 12.6-46.2 mg/kg (Teixidó et al., 2011) and 0.40-85.10 mg/kg (Mankowska et al., 2017). In another study, Miao et al. (2014) referred that generation of HMF was strongly associated with water activity as well as HMF exhibited a significant relationship with production acrylamide in reconstituted potato chips. Some determined levels of acrylamide and HMF in extruded and non-extruded products and exhibited that extrusion process lead to the production of these analysts.

In an earlier study, Jiménez et al. (2000) inferred that HMF content of selected baked items ranged between 4.1 and 151.2 mg/kg. Andrade et al. (2009) examined HMF content in the range of 3.10-182.50 mg/kg for digestive and semi-sweet biscuits consumed in Spain. They further reasoned that replacement of reducing sugar with saccharide alcohols like maltitol or lactitol may considerably reduce HMF formation during baking. Moreover, Andrade et al. (2009) investigated that HMF in fried potatoes varied between 0.20 and 1.06 mg/kg and noticeably augmented with sternness of thermal treatment. Gökmen & Senyuva (2006) found HMF in bread and biscuits varying from 0.2 to 57.2 mg/kg. As a matter of fact, HMF usually do not occur in fresh or raw foods nonetheless, the creation of HMF is directly linked with heat intensity applied to product. It could be employed to control heat treatment applied to food products including breakfast cereals, pasta and baked products as reported earlier (Henares & Andrade, 2009). The wide range of HMF content in the biscuits marketed in France ranged between 0.5 and 78.6 mg/kg and from 4.1 to 151.2 mg/kg for the selected bakery products (Jiménez et al., 2000; Ameur et al., 2006).

Table 3 HMF and Furosine Content of Home-Made and Commercially Processed Foods

Samples	Description	HMF (mg/kg)	Furosine (mg/kg)
Bread	Home-made	0.076±0.004	3.89±0.17
	Commercially processed	0.342±0.015	6.46±0.29
Cookies	Home-made	0.626±0.028	2.62±0.18
	Commercially processed	0.116±0.006	16.1±0.72
Fried potatoes	French fries	0.878±0.039	3.80±0.34
	Potato chips	3.605±0.162	3.28±0.15

Results are presented as the mean of three separate measurements ± standard deviation.

Furosine Content

In present study, furosine content in various food products was varied from 2.62 to 16.10 mg/Kg (Table 3). Maximum furosine (16.10 mg/Kg) was observed in the commercially processed cookies followed by 6.46 mg/Kg in bread. It can be reasoned here that highest furosine of commercially processed cookies may possibly due to their high protein level as compared to other counterparts. Greater the level of protein in a food, higher will be the furosine content. The level of furosine in foods is controlled by type of heating method and storage time. For instance, furosine was found to be decreased during prolonged storage and after overheating because of formation of other compounds like Nε-(carboxymethyl) lysine (CML) (Andrade et al., 2005). Mendoza et al. (2004) described the furosine values in Ready-To-Eat (RTE) cereals varying from 87 to 1203 mg/100 g protein. In another study, Bastos et al. (2011) observed furosine values to be varying between 50 and 119 mg/100 g protein for breakfast cereals in Portugal market.

Previously, Jiménez et al. (2001) established that no furosine was detected in the unbaked dough. But, during heating, the furosine content was increased to 299 mg/100 g protein (at 7 minutes) and subsequently, declined to 2.9 mg/100 g protein. Delgado-Andrade et al. (2010) reported 159 mg/kg furosine content in fried potatoes. As compared to furosine, HMF formation require harsher processing conditions and foods with high protein level will contain low HMF content. Li et al. (2017) determined furosine content of fresh and processed ginsengs and found that heating and addition of honey significantly enhanced furosine level from 3.35 to 42.28 g/kg protein. Recently, some investigated the HMF and furosine content in Spanish breakfast cereals in relation to various factors including fiber, protein, sugar content, grain type, honey and manufacturing process. They reported the average HMF and furosine contents as 21.7 mg/kg and 182 mg/kg, respectively. They also established that sugar content, presence of honey, and manufacturing process influenced HMF content of HMF however, fiber and protein were found to be directly correlated to furosine level.

CONCLUSION

Present study draws the attention concerning the presence of HMF and furosine in different products and reinforces to avoid the consumption of unsafe products. Present observations divulge highest concentrations of HMF in potato chips (3.605 mg/Kg) while, highest furosine in in commercially processed cookies (16.10 mg/Kg). Present study put forward that comparatively low level of HMF was determined in home-made bread than commercially produced bread. Likewise, lowest furosine was found in home-made cookies as compared to other counterparts. In this manner, present study strengthens the recommendations to limit the consumption of highly processed food products, which undergo Maillard reaction quite often. Since, HMF formation is associated with high temperature therefore, it could be inferred that by optimizing the processing conditions, processed foods can be developed with improved consumer safety.

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