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Impact of cooking and handling conditions on furanic compounds in breaded fish products

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ABSTRACT

This study evaluates the influence of cooking and handling conditions on the quantity of furanic compounds (furan, 2-furfural, furfuryl alcohol, 2-pentylfuran, 5-hydroxymethylfurfural) in breaded fish products. Oven-baking and reheating in the microwave lead to low furanic compounds formation in comparison with deep-frying. The use of olive oil for deep-frying promoted higher levels of furanic compounds than sunflower oil. The amounts of these compounds diminished as the temperature and time of deep-frying decreased as well as after a delay after deep-frying. Thus, the generation of furanic compounds can be minimized by adjusting the cooking method and conditions, such as using an electric oven, deep-frying in sunflower oil at 160 °C during 4 min, or waiting 10 min after cooking. However, these conditions that reduce furanic compounds levels also reduce the content of volatile compounds related to the aroma and flavour of fried foods. In this sense, new efforts should be done to reduce the formation of furanic compounds without being detrimental to the volatile profile.

1. Introduction

The development of aroma and flavour in cooked products is a complex process in which different compounds react to produce intermediary or volatile compounds. Frying induces oxidation and Maillard reactions, which are essential for the final aroma and flavour attributes of the food (Bastida and Sanchez-Muniz, 2001; Romero et al., 2000) and simultaneously responsible for the formation of undesirable compounds (Mottram, 1998; Nawar, 1998).

Furanic compounds are recognized as important contributors to the characteristic odour of fried products (Wagner and Grosch, 1998; Cerny and Grosch, 1992), particularly in coated products, due to the intense heat effect on carbohydrates and polyunsaturated fatty acids. These compounds have low thresholds and provide pleasant odour characteristic, such as cocoa, butter or fruity (Belitz and Grosch, 1997). However, furan is considered a possible human carcinogen (Group 2B) by the International Agency for Research on Cancer (IARC, 1995). Furan can be formed from various precursors naturally present in foods, namely, ascorbic acid, carbohydrates, amino acids, fatty acids, and carotenoids (Pérez-Locas and Yaylayan, 2004; Becalski and Seaman, 2005; Mark et al., 2006; Limacher et al., 2007, 2008; Fan et al., 2008). Most of the results concerning furan content in foods (coffee, infant formula, baby food, cereal, meat, fish, vegetal, dairy and fruit products) have been obtained from samples analysed as purchased, however, it is claimed that further evaluation of furan content in foods should be performed in the samples as they are consumed (EFSA, 2010). Thus, the effect of usual cooking conditions, namely time, temperature and handling information should be studied. Additionally, furan derivatives should be analysed since they are also present in thermally treated products, for example 2-furfural, furfuryl alcohol and 2-pentylfuran were found in smoked-cured bacon by Yu et al. (2008). Gili et al. (2010) found 2-ethylfuran, 2-butylfuran, 2-acetylfuran, 2-pentylfuran, 2-furfuraland furfuryl alcohol in paste fish. There are also studies revealing the toxicity of these furanic compounds in animals and humans (Sujatha, 2008; Arts et al., 2004; Goldsworthy et al., 2001; Wilson et al., 1992).

Concerning 5-hydroxymethylfurfural (HMF), it is less volatile than other furanic compounds and has been mainly analysed in cereal products, honey, fruit products and coffee (Capuano and Fogliano, 2011; Abraham et al., 2011). This furanic compound is an intermediate product in the Maillard reaction (Berg and Van Boekel, 1994; Morales et al., 1997) and is also formed from the

Abbreviations: MO, frozen breaded fish products deep-fried in sunflower oil and reheated in the microwave; OL, frozen breaded fish products deep-fried in olive oil; OV, frozen breaded fish products oven-baked; SF, frozen breaded fish products deep-fried in sunflower oil; STO, frozen breaded fish products deep-fried in sunflower oil and analysed straightaway; ST1, frozen breaded fish products deep-fried in sunflower oil and analysed with a delay of 10 min; ST2, frozen breaded fish products deep-fried in sunflower oil and analysed with a delay of 20 min.

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degradation of sugars at high temperatures (Kroh, 1994). HMF is usually used to evaluate the quality of processing and it also raises toxicological concerns (Capuano and Fogliano, 2011; Abraham et al., 2011).

The influence of the various factors involved in a culinary process on the nutritive value of processed foods is of major concern (Guidurus et al., 2010). In house holding conditions the controllable variables are the cooking process, the oil variety and time/temperature of processing. Several studies about the modifications of fat and oil composition during heating and frying under very different conditions have been carried out (Dobarganes et al., 2000). However, papers on the changes in the foods are less abundant, and most of them focused on fat uptake and water loss mechanisms during frying (Debnath et al., 2003). Moreira et al. (1997) studied the effect of oil temperature (130, 160 and 190 °C) on the final oil content of tortilla chips. Miranda et al. (2010) evaluated how the cooking method (baking and deep frying in olive or sunflower oil) affects fatty acids profiles of frozen breaded foods.

Recent results obtained for furanic compounds in coated deep-fried fish have indicated that this type of product should be included in the group of food products with high furan content, such as coffee samples (Pérez-Palacios et al., 2012). Thus, this work aims to study the effect of cooking and handling conditions (deep-frying at different combinations of time and temperature; deep-frying in different oils and dry oven-baking; reheated in the microwave oven; time after cooking) on the content of furanic compound in a breaded fish product, in order to provide data on the reduction of these compounds. Moreover, the influence of the cooking conditions on the profile of volatile compounds was also investigated. Coated fish products are very consumed by kids and teenagers due to its high sensory acceptance, its assumed good health characteristics (i.e. high polyunsaturated fatty acid content) and its quick and easy preparation.

2. Materials and methods

2.1. Chemical and standards

D_4-furan (98%) was provided by ISOTEC (Ohio, USA). Furan (⩾99%), furfuryl alcohol (99%) were supplied by SIGMA ALDRICH (Steinheim, Germany). Furfural was purchased by MERCK (99%) (Darmstadt, Germany). 2-pentylfuran (98%) was provided by ALFAAESAR (Karlsrula, Germany). HMF (98%) was supplied by Sigma–Aldrich (Steinheim, Germany). Ethyl acetate, hexane, sodium formate, formic acid, and methanol were supplied by Merck (Darmstadt, Germany), and ultrapure water (0.055 μS/cm) was obtained by using a Serial Milli-Q system for Millipore (Supor DCF, Gelman Sciences, Chentelham, Australia). Frozen breaded fish products, sunflower and olive oils (extra virgin with 0.8% acidity) were obtained from a local stored.

2.2. Experimental design

Frozen breaded fish products were prepared by deep-frying in sunflower ($n = 6$) (SF) and olive oil ($n = 6$) (OL) using a domestic deep-fryer (KENWOOD DF-150; 1 l) at 180 °C during 4 min, and by baking using an electric oven (ELECTRIC Co MF22VD, 22 l), at 200 °C during 17 min (turning over after first nine min) (OV) ($n = 6$). These conditions are recommended by the manufacturer. Deep-frying and oven temperature was monitored using a cooking thermometer (Model 26003DeltaTRAK, USA). In addition, other batch of breaded fish products ($n = 6$) were deep-fried in sunflower oil (at 180 °C during 4 min), placed into the fridge (4 °C) during 16 h and reheated in a domestic microwave (HAIER M01700, 17 l) at 750 W during 40 s (MO).

Moreover, the breaded fish products were deep-fried in sunflower oil at nine different combinations ($n = 6$) of temperature (160, 180 and 200 °C) and time (2, 4 and 6 min).

In order to study the stability of the volatile compounds, three batches of breaded fish products were deep-fried in sunflower oil and analysed straightaway ($n = 6$) (ST0) and with a delay of 10 min ($n = 6$) (ST1) and 20 min ($n = 6$) (ST2) kept at ambient temperature (18–20 °C).

All samples were slightly drained after frying, placed on paper towel for removing external excess oil, and grinding by using a device named "masticator shears straight" (BUENO HERMANOS, S.A., La Rioja, Spain, ISO 9001-2000 Quality Certified Company) which simulates the chewing process. The oil was replaced every six frying sessions. All samples were processed individually.

2.3. Standard solutions

Stock solution of d_4-furan 2 mg ml^{-1} was prepared by injecting 20 μl of refrigerated d_4-furan with a syringe through the septum of a 10 ml headspace (HS) vial filled with 10 ml of methanol and sealed. The exact weight of methanol and d_4-furan was recorded, expressing the concentration in mg ml^{-1} and taking into account the density of methanol. Working solutions 1 mg ml^{-1} were prepared daily by adding 500 μl of stock solution to a 2 ml vial containing 500 μl of water using the same procedure.

A standard calibration solution containing 8.69, 0.52, 10.84 and 0.07 mg ml^{-1} for furan, furfural, furfuryl alcohol and 2-pentylfuran, respectively, was prepared by the addition of 100, 5, 100 and 5 μl of furan, 2-furfural, furfuryl alcohol and 2-pentylfuran, respectively, into a 15 ml HS vial containing 15 ml of methanol. The exact weight of methanol and each added furanic compound was recorded.

Stock solution of HMF in methanol 1.2 mg ml^{-1} was prepared. A standard working solution 0.056 mg ml^{-1} was made by injecting 50 μl of the stock solution into a vial containing 1 ml of the 40 mM sodium formate (pH = 3)/methanol (1:1) mixture. The exact weight of methanol and HMF was recorded, expressing the concentration in microgram per microlitre. Consecutive dilutions of the standard calibration solution in methanol were made.

2.4. Volatile analysis

The procedure used for the quantification of furanic compounds was described by Pérez-Palacios et al. (2012). Straightaway after grinding, 2 g of sample were transferred to a 50 ml headspace (HS) vial, containing 5 ml of water and 3 g of NaCl. 100 μl of d_4-furan working solution was added, and the vial immediately sealed at once and kept at −4 °C during 10 min. Afterwards, the vial was placed into an ultrasonic cleaner (FUNGILAB, Portugal) during 15 min. To extract furanic compounds a carboxen–polydimethylsiloxane (CAR–PDMS) solid phase microextraction (SPME) fibre (75 μm thickness, Supelco Co., Bellefonte, PA, USA) was used. Prior to analysis, the SPME fibre was preconditioned at 300 °C for 60 min in the chromatograph injection port. The fibre was inserted into the sample vial through the septum and exposed to the HS for 40 min at 37 ± 1 °C under constant agitation (600 rpm). Thereafter, the SPME fibre was inserted and desorbed for 10 min at 280 °C, in the split-less mode, with 1 ml min^{-1} flow.

Chromatographic analysis was performed using an Agilent 6890 gas chromatograph (GC) (Agilent, Avondale, PA, USA) coupled to a mass selective (MS) detector (Agilent 5973). Volatiles were separated on a 5% phenyl–methyl silicone (HP-5) bonded phase fused-silica capillary column (Hewlett–Packard, Palo Alto, CA, USA; 60 m × 320 μm i.d., film thickness 1 μm), operating at 80 kPa column head pressure, resulting in a flow of 1 ml min^{-1} at 40 °C. The oven temperature programme was isothermal for 5 min at 40 °C, raised to 135 °C at a rate of 3 °C min^{-1} and then raised to 220 °C at 20 °C min^{-1}. The transfer line to the mass spectrometer was

Table 1
Content of furanic compounds (μg/g sample) in breaded fish products deep-fried in sunflower (SF) and olive (OL) oils, oven-baked (OV) and reheated in the microwave after deep-frying in sunflower oil (MO)*.

	SF	OL	OV	MO	p
Furan	5.51 ± 0.37^{a}	4.02 ± 0.61^{b}	4.36 ± 0.75^{ab}	ND	<0.001
2-Furfural	0.23 ± 0.01^{b}	0.57 ± 0.01^{a}	ND	0.06 ± 0.02^{c}	<0.001
Furfuryl alcohol	10.54 ± 0.20^{b}	18.87 ± 1.25^{a}	4.67 ± 0.19^{d}	7.13 ± 0.23^{c}	<0.001
2-Pentylfuran	1.50 ± 0.32^{b}	2.23 ± 0.13^{a}	0.25 ± 0.09^{c}	1.09 ± 0.05^{b}	<0.001
HMF	1.78 ± 0.08^{b}	4.47 ± 0.98^{a}	0.64 ± 0.09^{bc}	ND	<0.001
TOTAL	19.46 ± 0.88^{b}	30.36 ± 2.68^{a}	9.99 ± 1.08^{c}	8.15 ± 0.29^{c}	<0.001

On the same row, means with different letters differ significantly ($p < 0.05$).
ND: non detected.
* The results are expressed as means values ± standard deviation.