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Impact of nitrogen flushing and oil choice on the progression of lipid oxidation in unwashed fried sliced potato crisps

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ABSTRACT

Unwashed, sliced, batch-fried potato crisps have a unique texture and are growing in popularity in the UK/EU premium snack food market. In this study, the storage stability of unwashed sliced (high surface starch) potatoes (crisps) fried in regular sunflower oil (SO) or in high oleic sunflower oil (HOSO) was compared over accelerated shelf life testing (45 °C, 6 weeks); with and without nitrogen gas flushing. Primary oxidation products (lipid hydroperoxides) were measured with a ferrous oxidation-xylenol orange (FOX) assay and volatile secondary oxidation products (hexanal) were quantified by using solid phase microextraction gas chromatography mass spectrometry (HS-SPME-GC/MS). Results revealed that crisps fried in SO were the least stable. Flushing the stored crisps with nitrogen gas proved to be effective in slowing down the oxidation rate after frying with sunflower oil, significantly stabilizing the crisps. However, crisps fried in HOSO were the most stable, with the lowest rate of development of oxidation markers, and this has previously not been shown for crisps with a high free starch content.

1. Introduction

Rancidity of edible oils and fatty foods due to lipid oxidation is a serious problem within the deep-frying industry (Gómez-Alonso et al., 2004; Matthäus, 2007; Sanches Silva, López Hernández, & Paseiro Losada, 2004; Sanches-Silva et al., 2004). Autoxidation, defined as the spontaneous reaction of atmospheric oxygen with lipids (St Angelo, 1996), is the most common process leading to oxidative deterioration and, as a consequence, to rancidity. Lipid hydroperoxides are the primary products of autoxidation and decomposition of the hydroperoxides leads to the formation of aldehydes, ketones, alcohols, hydrocarbons, volatile organic acids, and epoxy compound production; collectively these compounds are known as secondary oxidation products. The presence of these compounds accounts for the perception of off flavours, rancidity and loss of nutritional value in the food, which can eventually lead to rejection by the customer. Autoxidation of oil has been identified as the main cause of crisps quality deterioration (Choe & Min, 2007) and the reaction rate of autoxidation has been shown to strongly correlate with the shelf-life of the product (Frankel, 1980).

Since the lipid oxidation process occurs at a relatively slow rate at room temperature, it is convenient to use accelerated methods to estimate the oxidative stability and hence the products' shelf life. Accelerated shelf life tests (ASLT) allow for an evaluation of shelf life in a relatively short time and can be used to accurately predict shelf life for individual products or to compare the storage stabilities of different products, e.g. crisps fried in different oils. It is not straightforward to find the best conditions for ASLT; these conditions depend on the purpose of the study and on the time and facilities available. Many different physical and chemical parameters, such as temperature, metal catalysis, rise in oxygen partial pressure and shaking/forced mixing accelerate oxidation and, as a consequence the development of rancidity. However, since oxidation rates have been shown to increase exponentially with absolute temperature, due to the stability and simplicity of application to control ASLT, this parameter is the most commonly used (Gómez-Alonso et al., 2004; Ragnarsson & Labuza, 1977).

After production, crisps are stored at room temperature, and the initial quality of the product has to be maintained throughout the shelf life of the product. The desire to expand sales in overseas markets and for a more flexible supply chain, has led UK crisps manufacturers to look at methods to extend the shelf life of their products and to withstand temperature fluctuations during transport. Both regular sunflower oil (SO) and high oleic oil sunflower oil (HOSO) provide good frying performances; it has been demonstrated, however, that HOSO is more resistant to oxidative degradation than SO (Niemelä, Wester, & Lahtinen, 1996; Sébédio

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et al., 1996). HOSO has a frying and storage stability comparable to that of more saturated vegetable oils, such as palm olein (Lahtinen, Wester, & Niemela, 1996; Martin-Polvillo et al., 1996).

Additionally, in recent years, there has been an increase in the use of modified atmosphere packaging (MAP), to further extend shelf life. The three main gases used in MAP are O_2, CO_2 and N_2 and the choice of gas is relative to the food product being packed. Used singly or in combination, these gases are used to balance safe shelf life extension with the optimal organoleptic properties of the food (Bhat, Alias, & Paliyath, 2012). Inert gases have been used in commercial applications for products such as coffee and snack foods, however, the literature on their application and benefits is limited. The most commonly used gas is nitrogen (N_2).

Potato slices fried by batch processes in kettle fryers have distinctive texture and flavours which are usually recognized by consumers as being distinctly different from those of typical commercially produced continuous processed potato chips. When manufacturing kettle-style fried potato slices, some of the characteristic flavours and texture are believed to be associated with the elevated levels of surface lipids entrapped in the free starch coating, which increases its instability to lipid oxidation. If washed, there is less free surface starch and many of the cooked notes that are associated with fried potato crisps are present at lower levels (Gould, 1999); furthermore crisps with a low surface free starch can be produced with a lower lipid content. Little is known on the shelf life stability of these kettle-style chips (Desai et al., 2014; Johnson, 1990).

To the best of the authors' knowledge there are no studies comparing the relative effectiveness of HOSO to nitrogen flushing on the storage stability of un-prewashed batch fried crisps. In this study, the relative storage stability of potato slices batch fried industrially in regular SO, in HOSO and in SO subjected to nitrogen gas flushing was compared over an accelerated shelf life storage trial. The primary oxidative degradation products (peroxide value, PV) were measured using a ferrous oxidation-xylenol orange (FOX) assay, while volatile secondary decomposition products (hexanal) were studied by means of solid phase micro-extraction gas chromatography mass spectrometry. This study is unique due to the high free starch on the surface of the sliced fried potato crisps and the combination of approaches evaluated.

2. Materials and methods

2.1. Potato crisps

Freshly-fried potato crisps were obtained from a commercial batch frying line (Pipers Crisps LTD, United Kingdom), before they were salted and flavoured. The unwashed (high surface starch) potato slices were produced using a batch frying setting. Potatoes were washed prior to slicing in ambient tap water.

2.2. Oil and packaging

Crisps were fried in 100% sunflower oil (SO) or 100% high oleic sunflower oil (HOSO) (Kerfoot, Northallerton, United Kingdom). One batch of SO crisps was flushed with nitrogen gas before sealing the packets, with a residual oxygen content of below 2%. The packaging material used was 25 μm OPP Matt Clear/35 μm Met OPP Laminate Film (Roberts Mart, Leeds, United Kingdom).

2.3. Reagents and standards

Chloroform, methanol (HPLC grade), dichloromethane (HPLC grade), ethanol (Reagent grade), isopropanol and phenolphthalein were purchased from Fisher Scientific, Loughborough, UK. Xylenol orange tetrasodium salt (ACS reagent grade), cumene hydroperoxide (80%, technical grade), ammonium iron (II) sulphate hexahydrate (ACS reagent grade, 99%), pentanal, heptanal, octanal and nonanal and ethyl butyrate were supplied by Sigma–Aldrich-, Dorset, UK.

2.4. Test frying

200 g batches of potato slices were fried in two test fryers (Tefal Easy Pro 2100 W, Ecully Cedex, France) containing 1.8 L SO or HOSO at 175 °C for 300 s, to compare the frying stability of the two oils.

2.5. Total polar materials and free fatty acids

Total polar materials (TPM) was measured using a Testo 270 Cooking Oil Tester (Testo, Alton, UK) and free fatty acid (FFA) was quantified by manual titration according to AOCS official method code (AOCS, 1989) with slight modifications: 28.2 g oil taken from a fryer was weighed in a conical flask, 50 mL of propan-2-ol was added, followed by two drops of indicator (phenolphthalein). The solution was mixed and titrated with 0.1 M potassium hydroxide until a stable pink colour was reached. The percentage of FFA in the sample was calculated as follows: FFA% = potassium hydroxide used (mL) × 0.1. Standard error of the methods was <5%.

2.6. Accelerated shelf life (ASLT)

Sealed bags of crisps fried in SO, either gas flushed or non-gas flushed, and of crisps fried in HOSO, and were stored at 45 °C. Additional samples were stored at 25 °C and 35 °C for more accurate shelf life predictions (data not shown). Bags were collected at fixed intervals and stored individually in air tight containers at −20 °C prior to analysis.

2.7. HS-SPME experimental procedure

2.7.1. Sample preparation

Crisps were ground using a commercial grinder (De Longhi KG49, Havant, UK) at maximum speed for 40 s. Approximately 0.3 g of sample was mixed with 5 mL ultrapure water in 20 mL amber headspace vials (Supelco, Bellefonte, PA, USA) and 100 μL of 1 mmol ethyl butyrate (internal standard) was added. The vials were hermetically capped with PTFE-faced silicone septa (Supelco, Bellefonte, PA, USA). Then, samples were mixed for 30 s in a vortex mixer (Grant, PV1, Shepreth, UK) to form a slurry.

2.7.2. Headspace SPME (HS-SPME)

Analysis was performed with ISQ Single Quadrupole Mass Spectrometer, paired with TRACE 1300 GC, equipped with a ZB-WAX column (30 m × 0.25 mm i.d. × 0.25 μm film thickness), and a TriPlus RSH autosampler (Thermo-Fisher Scientific, Waltham, MA, USA). Following homogenisation, the vials were heated at 70 °C for 5 min to reach equilibrium. A fused silica fibre coated with a 50/30 μm layer of divinylbenzene–carboxen–polydimethylsiloxane (DVD–CAR–PDMS; Supelco) was used to sample analytes from the headspace. Prior to first use, fibres were pre-conditioned, (4 h at 270 °C). After equilibrium, the fibre was exposed to the headspace for a total extraction time of 20 min at 70 °C. After extraction, the fibre was immediately thermally desorbed at 250 °C (5 min).

The oven temperature was as follows: 40 °C for 1 min, then to 120 °C at 20 °C/min, held for 8 min, then to 260 °C at 20 °C/min and finally held for 2 min (Sanches-Silva et al., 2004). MS was operated in electron impact (EI) ionisation mode at 70 eV and data acquisition was achieved at a scan rate of 0.20 s^{-1} over an m/z