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Physico-chemical changes occurring in oil when atmospheric frying is combined with post-frying vacuum application

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ABSTRACT

The aim of this study was to investigate the effect of atmospheric frying followed by drainage under vacuum on the stability of oil, compared to similar frying with drainage at atmospheric pressure. Changes in the oil were assessed by the free fatty acid (FFA) content, *p*-anisidine value (AnV), colour, viscosity, fatty acid profile and concentration of tocols. The rate of FFA formation in the case of vacuum drainage was found to be about half that of atmospheric drainage. Oil deterioration by oxidation and polymerisation was also reduced by the use of vacuum drainage. The AnV of the oil after vacuum drainage was lower by about 12%, the total colour difference was improved by 14% and viscosity was slightly reduced after 5 days of frying, compared to the values for oil that had been drained at atmospheric pressure. There was a reduction in the loss of polyunsaturated fatty acids in the case of vacuum drainage after 5 days of frying but differences in retention of tocols were only evident in the first two days of frying.

1. Introduction

Frying is extensively employed in the domestic and industrial sectors due to its ability to create unique sensory characteristics in food (Ahmad Tarmizi & Ismail, 2008). Despite its operational simplicity, convenience and economic viability, frying oil can deteriorate by various complex physical and chemical reactions, including hydrolysis, thermal degradation, oxidation and polymerisation (Bensmira, Jiang, Nsabimana, & Jian, 2007; Karoui, Dhifi, Jemia, & Marzouk, 2011). Degradation of the oil not only affects the usability and frying life of the oil but, in extreme cases, may also contribute over time to health hazards, such as potential gastrointestinal disorders and even mutagenesis in the human body (Dana & Saguy, 2001).

A number of studies have been undertaken to improve the frying stability of oil by modifying the fatty acid composition, either by blending, hydrogenation or fractionation. Blending is preferred since the process is simple and cheap, and does not generate any unnatural fatty acids such as *trans* fatty acids, which are formed in hydrogenated oils (Naghshineh & Mirhosseini, 2010). However, there is evidence that fatty acid composition and the degree of unsaturation are not the sole predictors of oil stability. This might be partly due to the positioning of fatty acids in the triglycerides and partly to the unsaponifiable constituents, such as alcohols, hydrocarbons, fat-soluble vitamins and phytosterols (Dobarganes, Marquez-Ruiz, & Perez-Camino, 1993).

Fortifying the oil with antioxidants to preserve oil quality has been widely reported. Incorporation of synthetic antioxidants such as *tert*-butylhydroquinoine (TBHQ), butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA) has been shown to inhibit oil deterioration during storage and frying. However TBHQ is not allowed in Europe, and synthetic antioxidants in food are of concern to consumers because of animal tests that demonstrate health hazards, for example toxicity and carcinogenicity, at high levels of intake (Sharayei, Farhoosh, Poorazrang, & Haddad Khodaparast, 2011). Thus, there is considerable interest in the use of natural substances or extracts that have antioxidant properties, even though the costs can be quite high and the extracts will not have received the same degree of toxicological testing (Berger, 2005).

Several attempts have been made to develop frying systems that are able to control air exposure during frying and thus protect the oil from oxidative deterioration. Negishi, Nishida, Endo, and Fujimoto (2003) designed a deep-fat fryer with smaller oil surface area to height ratio, which was able to retard thermal deterioration by minimising oil contact with air. Flushing the frying oil with nitrogen or carbon dioxide whilst heating and frying has been reported as a method to lessen the concentration of oxygen (Aladedunye & Przybylski, 2009). A recent study by Aladedunye and Przybylski (2009) showed that vacuum frying was highly effective in protecting the oil from oxidative degradation: the use of lower oxygen concentration and lower frying temperature had a remarkable reductive effect on oil degradation.

In a recent study, we have investigated several protocols involving the application of vacuum, either towards the end of frying or after

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frying, and reported a protocol involving vacuum drainage that significantly lowered the oil content of potato chips (Ahmad Tarmizi & Niranjan, 2010). Furthermore, this protocol also provides an opportunity to reduce the product moisture content without the need to increase frying time. An additional potential advantage of this protocol is the retardation of deterioration of the oil. In this paper, we report the physicochemical changes occurring in oil when used for intermittent frying by a procedure which involves vacuum drainage and we compare the data obtained with oil quality when drainage occurs under conventional conditions.

2. Materials and methods

2.1. Materials

Refined, bleached and deodorised (RBD) palm olein was imported from Golden Jomalina Food Industries Sdn Bhd (Banting, Malaysia) and distributed by Britannia Food Ingredients Ltd (Humberside, UK). Potatoes of Maris Piper variety were purchased from a local store, kept in a refrigerator at 4 °C and conditioned at ambient temperature for at least 12 h prior to use. All chemicals and reagents were obtained from Fisher Scientific UK Ltd (Loughborough, UK) and Sigma–Aldrich Ltd (Dorset, UK), unless stated otherwise.

2.2. Frying protocol and oil sampling

The frying setup has been described in detail by Ahmad Tarmizi and Niranjan (2010). Potatoes of Maris Piper variety were initially washed, peeled and cut into slices of 2.5 mm thickness × 45 mm diameter to ensure the uniformity of heat transfer between the frying medium and the potato slices. The potato slices were then soaked in water to remove excess starch before blotting with tissue paper.

About 3 L of oil were placed in the fryer and heated to 180 °C for 30 min prior to frying. Two frying protocols were evaluated: (1) Frying time of 3 min and subsequent draining under vacuum (pressure = 1.33 kPa) for 6 min; (2) frying time of 4 min and subsequent draining under atmospheric pressure for 6 min. These combinations of frying and drainage times were selected to ensure that both protocols gave a product with a final moisture content of just under 2% (product weight basis), which is generally the final moisture content of commercially sold potato chips (crisps).

It is interesting to note that the frying time was relatively shorter (3 min) in the case of vacuum drainage because the water vapour is continuously released from the product even after discharge from the oil. Draining the product under vacuum for 6 min sufficiently reduced its moisture content to the targeted value. In the latter case, however, no moisture loss took place after the product is lifted from the oil, due to water vapour condensation. Hence, a longer frying time (4 min) is needed to produce product having similar moisture content to the former.

For each protocol, a batch of 10 potato slices (approximately 50 g) was processed every 30 min, over 8 h each day for five consecutive days, giving a total of 80 batches (16 batches × 5 days) of potato chips and 40 h of heating. In the case of vacuum drainage, the samples were drained under vacuum for only 6 min for each frying batch performed while the pressure between batches and between days remained at atmospheric pressure; these procedures were also applied for the atmospheric drainage experiments. Details of the frying procedure have been described earlier by Ahmad Tarmizi and Niranjan (2010).

At the end of each day, the oil was allowed to cool to 120 °C and sampled in two 125 mL dark amber bottles, flushed with argon and stored at −20 °C for subsequent physicochemical analyses. In addition, prior to use on the next day of operation, the oil in the fryer was filtered to remove debris and replenished with fresh oil to make up for the oil absorbed by the product. The oil was covered, stored at ambient temperature (20 °C) and left overnight.

2.3. Free fatty acid

Free fatty acid content (FFA) was assessed by a titration method defined in AOCS Official Method Ca 5a-40 (AOCS, 2009). About 20 g oil sample were dissolved in 50 ml isopropanol and 2 ml phenolphthalein indicator solution. The mixture was then titrated with 0.1 M sodium hydroxide until the first permanent faint pink colour appeared and persisted for at least 30 s. The FFA was expressed as the percentage of palmitic acid.

2.4. p-anisidine value

The *p*-anisidine value (AnV) was analysed following the AOCS Official Method Cd 18–90 (AOCS, 2009). About 0.5 g oil sample were initially homogenised with iso-octane, until a total volume of 25 ml was obtained. From the solution, 5 ml were taken and reacted with 1 ml of *p*-anisidine solution (mixture of *p*-anisidine and glacial acetic acid). Measurement of AnV was performed spectrophotometrically at a wavelength of 350 nm using a Cecil 1000 Series spectrophotometer (Cecil Instruments Ltd, Cambridge, UK).

2.5. Fatty acid composition

Fatty acid composition was quantified using an Agilent 6890 gas chromatograph (GC) (Agilent, Cheadle, UK). The fatty acid methyl ester mixture (FAME) was prepared as described by Christie (1993). The oil sample (0.02 ml) was first dissolved in 0.4 ml toluene containing 50 mg L^{-1} of butylated hydroxytoluene (BHT), followed by addition of 0.8 ml of 1.5% sulphuric acid in methanol mixture prior to incubation at 70 °C for 1 h. The solution was allowed to cool before addition of 2 ml neutralising agents (a mixture of 0.1 M potassium carbonate and 0.1 M potassium bicarbonate), followed by 2 ml *n*-hexane. The solution was then centrifuged and the upper layer (FAME) was collected and dried under nitrogen, re-suspended with 0.5 ml *n*-hexane, and decanted for GC analysis.

The GC was equipped with a flame ionisation detector (FID), electronic integrator and data processor. Helium was used as carrier gas with a pre-column split ratio of 50:1 and a head pressure of 257.5 kPa. A cyanopropyl fused silica capillary column (Chrompack CP Sil88, 50 m × 0.25 mm i.d.; Kinesis Solutions, St Neots, UK) was fitted to the GC. The FID and injector temperature were 240 °C. The column was initially heated to 100 °C and maintained at that value for 10 min before heating to 240 °C at a rate of 4 °C min^{-1}. The FAME components were identified and quantified by comparing the retention time and the peak areas with methyl ester standards (Supelco, Dorset, UK).

2.6. Tocols content

The content of tocols (tocopherols and tocotrienols) was analysed using an Agilent 1050 high performance liquid chromatograph (HPLC), equipped with UV detector and autosampler, as described in AOCS Official Method Ce 8–89 (AOCS, 2009). The oil sample (2 g) was dissolved in *n*-hexane to a total volume of 25 ml. From the solution, 20 μl were injected into the HPLC which was fitted with a 250 mm × 4.6 mm Spherisorb S5W column, packed with 5 μm microparticulate silica (Hichrom Ltd, Theale, UK). The wavelength of the UV detector was set at 292 nm. The mobile phase was 0.35% isopropanol in *n*-hexane at a flow rate of 0.9 mL min^{-1}. A run time of 30 min was necessary to determine the tocols content of each sample. Tocols were identified by