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Continuous injection of water and antioxidants possible roles on oil quality during frying

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A B S T R A C T

Frying is an important process in cooking a wide spectrum of food products in homes, restaurants and the food industry due to the unique sensory characteristics of fried foods combined with a relatively low-cost operation. Due to health and nutritional concerns however, novel approaches are being sought to reduce oil uptake and minimize deleterious oil degradation. This study investigated the potential of utilizing water injection and as a vehicle for continuous delivery of one or a combination of antioxidants at different pH values. Selected antioxidants were tested during simulated frying at 180 °C by monitoring commercial canola oil quality indices. Water injection increased free fatty acids (FFA) during frying, while simultaneously enhancing oil stability as indicated by conjugated diene value, radical-scavenging activity and *p*-anisidine value. It was demonstrated as an effective carrier for continuous incorporation of antioxidant, which maintained a low concentration of FFA during deep-fat frying. Selection of buffer and/or neutralizing chemical and antioxidant is of high importance. Catechin had both antioxidant and pro-oxidant activities, highlighting the need for system optimization. The protective role of water injection could be significant for foodservice and restaurants where the frying oil is maintained idle at high temperatures for relatively long periods.

1. Introduction

Deep-fat frying is an important, ubiquitous and highly versatile process that has been used since antiquity to cook a wide spectrum of food products and snacks. Some have even defined it as one of the most popular culinary delights enjoyed by consumers throughout the world (Aladedunye, Catel, & Przybylski, 2012). Its unique contribution to sensory characteristics, together with a relatively low cost of operation, have made fried foods the staple of the fast-food industry (Dana & Saguy, 2006; Saguy & Dana, 2003). However, the market trend toward the consumption of healthier foods has forced the frying industry to develop alternative technologies as well as make continuous and significant improvements to traditional frying, while maintaining characteristic flavor and texture (Crosa et al., 2014) and color (Fan, Zhang, Xiao, Sun, & Tao, 2005).

Different types of oils can be used to fry foods. Their physical and chemical properties influence the degree of oxidation and the hydrolysis reactions that occur during the process (Crosa et al., 2014; Dana & Saguy, 2006; Warner & Moser, 2009). Their stability depends on the composition of fatty acids and natural antioxidants, as well as frying temperature and other processing and product parameters such as air, food composition, turnover time and others (Warner & Moser, 2009).

One option for maintaining oil quality during frying is the additions of antioxidants. The effectiveness of natural (e.g., tocopherols or other phenolic compounds) and synthetic [e.g., tertiary butyl hydroquinone (TBHQ), butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT)] antioxidants during the frying process has been intensively studied (Aladedunye et al., 2012; Marmesat, Morales, Velasco, & Dobarganes, 2010). TBHQ is considered to be more effective than BHA or BHT in controlling oxidation reactions during frying (e.g., Crosa et al., 2014). Natural antioxidants have also been shown to be effective for protecting oil from deterioration, but they are rapidly degraded at conventional frying temperatures (170–190 °C) and under other processing conditions (Marmesat et al., 2010). Among the natural antioxidants reported to protect oils during frying are vitamin E (Allam & El-

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Sayed, 2004), alfa, gamma and delta tocopherol fractions (Marmesat et al., 2010; Warner & Moser, 2009), rosemary (Ozyurt, 2013), polyphenols (Salta, Mylona, Chiou, Boskou, & Andrikopoulos, 2007), ascorbic acid (Hwang et al., 2013) and the flavanol group of polyphenols known as catechins (Cheng et al., 2009). Fresh tea leaves are unusually rich in catechins, which may constitute up to 30% of the dry leaf weight (Graham, 1992). Due to its antioxidant activity, the primary application areas of green tea extract include meat, poultry, seafood, mayonnaise, salad dressings, soups, sauces, margarines, fat spreads, shortening, frying oils, bakery products, pizza toppings, cereals and snack foods, among many others (Namal Senanayake, 2013). Catechins may also act as a pro-oxidant (Huang & Frankel, 1997; Wanasundara & Shahidi, 1998). For instance, in a study with marine oils from seal blubber and menhaden, both antioxidant and pro-oxidant effects of green tea extracts were reported (Wanasundara & Shahidi, 1998). It has also been shown that some of the effects of catechins may be related to induction of oxidative stress. Such pro-oxidant effects appear to be responsible for the induction of apoptosis in tumor cells. These pro-oxidant effects may also induce endogenous antioxidant systems in normal tissues that offer protection against carcinogenic insult (Lambert & Elias, 2010).

It is worth noting that common synthetic and endogenous antioxidants (tocochromanols, BHT, BHA, and TBHQ), are easily degraded and evaporated during frying and polyphenolic constituents of antioxidative plant extracts are more thermally stable (Aladedunye, 2014).

Water released from the food during frying enhances heat transfer, and can simultaneously cause oil deterioration while preventing oxidation (Saguy & Dana, 2003). The hydrolysis of triglycerides in frying oil is a key reaction that is affected by the presence of water in the fried product. During frying, water evaporates rapidly and is released into the oil. Under these conditions, triglycerides are hydrolyzed to diglycerides, monoglycerides, free fatty acids (FFA) and glycerol (Pokorny, 1998). This water turns into steam and is a major cause for the ‘steaming out’ of some antioxidants.

The protective role of water injection on oil quality during frying has been reported for corn and soy oil (Dana, Blumenthal, & Saguy, 2003). Water injection has a dual effect—it increases FFA while simultaneously maintaining the values of several quality indices [i.e., malondialdehyde, *p*-anisidine value (*p*-Av), conjugated dienes (CD) value]. Consequently, water injection has been suggested as a means of extending oil life during frying applications (Dana et al., 2003).

It is important to note that given the complexity of the frying process, the dependence of the antioxidative effect on the degree of oil unsaturation and on the content and chemical composition of other minor oil compounds and foods must be considered (Marmesat et al., 2010). Attention should also be paid to the rapid loss of antioxidants and their exhaustion below recommended effective levels. Special consideration should be given to maintaining a minimum level of antioxidants to protect fried products destined for storage. It was showed that attention has to be focused on the amount of active antioxidant remaining after frying and protecting the fried foods during storage. This amount depends on the type and level of the antioxidant in the frying medium at the time of each frying operation (Augustin & Berry, 1984).

The overall objective of this study was to explore the possibility of maintaining high oil quality by injecting water as a carrier and vehicle for continuous delivery of one or a combination of antioxidants and/or other ingredients, thereby providing their uninterrupted replenishment to overcome the natural deterioration of antioxidants and their depletion by steaming out.

2. Materials and methods

Commercial canola oil was purchased from a local market. *Iso*-octane (2,2,4-trimethylpentane) and *n*-hexane (HPLC-grade) were purchased from J.T. Baker (Deventer, Holland). Gallic acid, propyl gallate, (±)-catechin hydrate, 2,2-diphenyl-1-picrylhydrazyl (DPPH), sodium citrate trisodium salt, *p*-anisidine, *m*-cresol purple and phosphate buffered saline (PBS) were from Sigma–Aldrich (St. Louis, MO). TBHQ was from Fluka (Sigma–Aldrich). Ethyl acetate, ethanol (100%) and acetic acid glacial were from BioLab Ltd. (Jerusalem, Israel).

2.1. Frying procedure

Frying was simulated with continuous injection of water (Dana et al., 2003). To achieve maximum control over the frying process, no food was fried, and therefore oil quality could be attributed to the injected water and the constituents it carried. This also circumvented other expected interactions with foods undergoing frying. Oil (1.8 L) was placed in a 2.0 L beaker and heated to typical frying temperatures (180 ± 5 °C; measured with a thermometer inserted in the oil) on a hot plate with a magnetic stirrer. Distilled water with the added chemicals was continuously injected at a constant flow rate of 6 mL/h for 24 h, controlled by a peristaltic pump (Cole–Parmer, Vernon Hills, IL). At time zero and at 4-h intervals, oil samples (30–40 mL) were withdrawn from the beaker for analysis. The various compositions used in the experiments are given in Table 1.

To facilitate dissolution, catechin hydrate was dissolved in 1 mL ethanol (100%) and 5 mL of either double-distilled water or PBS. TBHQ (Run #8) was added as a powder to the oil every 4 h.

2.2. FFA content

FFA content was determined using an improved modified procedure (Ke & Woyewoda, 1978), because the oil color was brownish and the standard AOCS method Cd 3d-63 (American Oil Chemists' Society, 1993) was unsatisfactory for determining the titration end-point using phenolphthalein. The revised method was as follows: oil samples (1 g) were withdrawn periodically from the frying beaker and mixed with chloroform (50 mL), methanol (25 mL) and isopropanol (50 mL). Five drops of *m*-cresol purple as an indicator (0.5 g/100 mL) were added, and the solution was titrated with aqueous 0.05 mol equi/L NaOH to a light gray-purple end-point. Blank titration solution was prepared daily. The FFA concentration was derived from:

$$\mathrm{FFA}(\mathrm{g}/100\ \mathrm{g\ as\ oleic\ acid}) = 100 \cdot \mathrm{V} \cdot \mathrm{N} \cdot 282/\mathrm{w} \qquad (1)$$

where V – volume of NaOH titrant (mL), N – normality of NaOH (mol equi/L), 282 molecular weight of oleic acid (g/mol) and w – oil weight (g).

2.3. CD values

CD values were determined following the previously outlined IUPAC analytical method (Privett & Blank, 1962). An oil sample (1 g) was dissolved in hexane and absorption of the CDs (stable hydroperoxides) was measured at 234 nm against HPLC-grade hexane as the blank. An extinction coefficient of 29,000 $(\mathrm{mol/L})^{-1}\mathrm{cm}^{-1}$ was used to calculate the concentration of CD values (mmol/L).

2.4. p-AV

An adaptation of AOCS method Cd 18–90 (American Oil