Food Control 96 (2019) 445–455

Contents lists available at ScienceDirect

Food Control

journal homepage: www.elsevier.com/locate/foodcont

Impartial assessment of oil degradation through partitioning of polar compounds in vegetable oils under simulated frying practice of fast food restaurants

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ARTICLE INFO

Keywords:
Total polar compounds
Thermal resistance
Fractions of polar compounds
Intermittent frying

ABSTRACT

Measurement of total polar compounds (TPC) is recognised as one of the objective indicators to gauge oil resistance against high temperature. Dependency to TPC measurement alone in arbitrating the quality and safety of oils can be misleading especially for those oils that are rich with significant amount of natural diacylglycerols (DAG). In fact, the results generated could be at the higher side when the analysis protocol involves excessive drying. Method modification has been established to isolate and quantify the individual polar compound fractions without the involvement of drying stage to protect the integrity of samples and therefore produce credible results. Performance of the established method is validated with the DAG quantified from the acylglycerols analysis. A series of vegetable oils, *i.e.* palm olein (POo), soybean oil (SBO), canola oil (CAN) and sunflower oil (SFO), were subjected to 9 days of intermittent frying, 8 h day^{-1} and 144 frying cycles. The transient of TPC across frying time was coincided with polymerised triacylglycerols (PTAG) following the linear model with coefficient of determination (R^2) greater than 91% while DAG and oxidised triacylglycerols (OxTAG) showed good regression with the quadratic model ($R^2 > 0.97$). Oils with equal amount of polyunsaturated fatty acids (PUFA) were found to have similar rate of combined PTAG and OxTAG. Whilst liquid oils have similar OxTAG contents with POo, they were much distressed with polymeric reaction given that their PTAG levels were 1.6–2.4 folds higher than POo. Blending liquid oils with POo has been proven to moderate the level of PTAG when similar frying conditions were applied.

1. Introduction

In recent years, frying industry capitalises significant share of the global oils and fats produced for food applications, evidenced by the increment of more than two-and-the-half folds in the oils and fats consumption in 2016 as compared to early 1990s (Mielke, 2017). As the demand of fried food continues to grow, the quality and safety aspects of frying oil are of concern. It is well established that frying involves heating the oil as high as 190 °C to yield fried food with unique organoleptic characteristics (Aydınkaptan & Barutçu Mazı, 2017). Despite frying is considered as economical, convenience and versatile cooking method, allowing the oil to excessive heating in the presence of oxygen (air) and moisture leached out from food leads to myriad of chemical reactions comprising of mainly hydrolysis, oxidation and polymerisation (Dobarganes & Màrquez-Ruiz, 2013). The complexity of these reactions very much relies on the composition of oil used for frying (Olivero-David et al., 2014), food structure and matrices (Karoui, Dhifi, Jemia, & Marzouk, 2011), frying procedures (Aladedunye & Przybylski, 2009a), and process conditions (*i.e.* frying time, temperature and pressure) (Aladedunye & Przybylski, 2009b). Since fried food absorbs considerable amount of oil, quality loss with regard to frying oil would not only exerts undesired effects on its sensory attributes (Gertz & Behmer, 2014) but also elicits unwanted breakdown derivatives that can adversely affect consumer health (Zribi et al., 2014). Many literature reported that majority of edible oils have their own experience on the prevalence of process-induced contaminants (Kushairi, Singh, & Ong-Abdullah, 2017) particularly when the oils are subjected to high temperature.

Measurement of total polar compounds (TPC) provides critical information on the amount of newly developed compounds that have higher polarity than that of triacylglycerols (TAG) (Rehab & El Anany, 2012). Without doubt, TPC analysis is rather tedious and time consuming albeit it provides more robust measurement of oil deterioration due to its higher accuracy and reproducibility in generating results. In

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https://doi.org/10.1016/j.foodcont.2018.10.010
Received 15 April 2018; Received in revised form 2 October 2018; Accepted 7 October 2018
Available online 08 October 2018
0956-7135/

principal, polar compounds are referred to a group of non-volatile constituents that are primarily deposited from oxidative and polymeric reactions (Casarotti & Jorge, 2014). Many European countries including Portugal, Germany, France, The Netherlands and Switzerland can only tolerate with the maximum TPC allowance within 24 and 27% given that severely deteriorated oil is unfit for human consumption (Li, Li, Cai & Liu, 2016). In China, the onset of 27% as the legal limit for TPC is following the hygiene standard of oil used for frying (Wang, Sun, & Pang, 2004). Significant level of TPC in used oil due to oxidation and polymerisation has been reported to be potentially toxic and the adverse effect can be more apparent when the polar artefacts can be easily absorbed by human body (Petersen, Jahreis, Busch-Stockfisch, & Fritsche, 2013). Animal studies even revealed that oxidised and polymerised oil is responsible for higher incidence of gastrointestinal irritants and skin diseases such as eczema and seborrhea (Cohn, 2002; Saguy & Dana, 2003). In the worst case scenario, high polarity oil could detriment vital organs (*i.e.* liver and kidney), interfere the development of fetus growth and promotes chromosomal aberrations and mutagenesis (Lin, Lin, Wu, Tao, Chang & Chao, 2017; Liu, Mu, Shan, Fan, & Wang, 2010). As considerable amount of frying oil is taken up by the fried food, the oil quality and safety should not to be taken lightly so that oil deterioration is minimal (Ahmad Tarmizi, Ismail, & Kuntom, 2016).

However, measurement of TPC alone in gauging frying oil deterioration seems unfair to oils that contain significant amount of natural diacylglycerols (DAG) albeit no heating is applied. As DAG is one of the components of polar compounds, these oils are often perceived as abused oils. Misleading perception can be more prominent when oil testers used to rapidly measure TPC gave inaccurate results. Chen, Chiu, Cheng, Hsu, and Kuo (2013) observed that some of the results generated from the oil testers (*i.e.* Testo 270 and FOM 310) were incomparable to the standard method; the TPC of fresh oils tested can reach nearly 6 times more than the standard method. Another study discovered that Fri-check gave anomaly and incomparable results from those obtained using the official method (de Almeida, Curvelo, Costa, Viana, & de Lima, 2018). Hence, identification of individual fractions of polar compounds would provide more holistic perspective on the overall polar compounds in frying oil. Quantification of oxidised and polymerised artefacts is more meaningful to distinguish the rate of oil degradation throughout the frying process. With regard to polymerised triacylglycerols (PTAG), the legislative threshold value differs from one country to another, ranging from 10 to 16%. Belgium and Czech Republic endorse stringent discard point of 10% (Sharayei & Farhoosh, 2016) while The Netherlands and South Africa have higher legislative limit of PTAG (16%) of used oil (Inturrisi, 2013).

This paper reports the modification of analysis protocol for the isolation and quantification of polar compound fractions in eleven types of vegetable oils (*i.e.* four unitary oils, six binary oil blends and one tertiary oil blend) without affecting the original state of oils sampled throughout 9 days of intermittent frying. The outcome from the study would give better understanding on how each polar compound component behaves and correlates with the degree of fatty acid alteration during the frying process.

2. Materials and methods

2.1. Raw materials

Refined, bleached and deodorised (RBD) palm olein (POo), soybean oil (SBO), canola oil (CAN) and sunflower oil (SFO) were supplied by MOI Foods Ingredients Sdn Bhd (Pulau Indah, Malaysia). A total of eleven oils were initially prepared consisting of: (1) POo, SBO, CAN and SFO; (2) binary blends of POo with SBO, CAN and SFO, respectively of two ratios, *i.e.* 90:10 and 50:50; and (3) a tertiary blend containing POo, SBO and CAN with a ratio of 40:50:10. Pre-fried French fries were obtained from Ramly Food Processing Sdn Bhd (Kuala Lumpur, Malaysia).

2.2. Frying protocols and oil sampling

Intermittent frying was performed using 23-L capacity stainless steel electrical open fryer split with two pots (2 × 11.5 L of oil) (Frymaster Corporation, Shreveport, USA). The oils was transferred into the pots and heated at 180 °C for 30 min before commencing the frying sessions. For each pot, about 250 g of pre-fried French fries was fried for 3.5 min with the frying interval of 30 min across 8 h day^{-1} for 9 days; each experiment involved a total number of 144 frying cycles over 72 h of heating. At the end of frying day, 500 mL of used oil was withdrawn and sampled in a dark amber bottle, purged with nitrogen and kept at −20 °C for subsequent analyses. The fryer covers were placed on the pots and left overnight. Necessary amount of fresh oils were replenished into the pots on the next day of frying operation to maintain the oil level at 11.5 L.

2.3. Analysis of total polar compounds

The measurement of total polar compounds (TPC) was carried out gravimetrically using silica column chromatography following IUPAC 2.507 with minor modifications (Dobarganes, Velasco, & Dieffenbacher, 2003). The oil aliquot (1 g) was first dissolved in 20 ml of petroleum ether (PE) and diethyl ether (DE) mixture with the ratio of 87:13; the solvents were of analytical grade and obtained from Systerm (Shah Alam, Malaysia). The solution was then pipetted into a 45-cm glass chromatography column that was previously packed with 25 g of Silica Gel 60 No. 7734 (Merck, Darmstadt, Germany), suspended in the PE-DE mixture and layered with 4 g of sea sand. The non-polar fraction was eluted for 60–70 min using 150 mL of PE-DE mixture. Similar procedure was also applied to extract the polar fraction except that the solvent used for second elution was PE instead of PE-DE mixture.

Solvent was removed from the solutions of polar and non-polar fractions using a rotary evaporator (Büchi Labortechnik AG, Flawil, Switzerland) at a temperature, vacuum level and rotation speed of 60 °C, 380 mbar and 130 rpm, respectively for 15 min to avoid any losses due to foaming. Nitrogen was further introduced to the sample for another 15 min to ensure the solvent remnant was completely removed and hence obtained constant weight. Establishment of this procedure enables to safeguard the integrity of samples without the need of drying at high temperature (103 °C). It is noticed from the common practice that the samples are dried at 103 °C from 1 h until overnight in order to entirely remove traces of solvent, and achieve constant weight. Allowing the samples to expose at high drying temperature could elicit further deterioration, and consequently, the results obtained are not solely reflecting oil degradation due to frying.

The TPC was determined from the polar fractions residual based on the following equations:

$$TPC\,(\%) = \frac{m_0}{m_1} \times 100$$

where: m_0 is the mass (g) of polar compound fractions; and m_1 is the mass (g) of the sample.

2.4. Partitioning of polar compound fractions

In order to exploit in greater detail the components in polar compounds, the following fractions were individually quantified, *i.e.* polymerised triacylglycerols (PTAG), oxidised triacylglycerols (OxTAG), diacylglycerols (DAG), monoacylglycerols (MAG) and free fatty acids (FFA). The analytical measurement was employed using a High Performance Liquid Chromatography with Evaporative Light Scattering Detector (HPLC-ELSD) (Agilent 1260 Infinity, Santa Clara, USA) in accordance to IUPAC 2.507 with modifications (Dobarganes et al., 2003). The use of ELSD provides advantage of producing good separation and distribution of polar compound fractions especially when the laboratory ventilation system is inconsistent.