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The impact of partial oil substitution and trace metal ions on the evolution of peroxidation products in thermally stressed culinary oils

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ABSTRACT

Suppressing toxic aldehydic lipid oxidation product (LOP) generation in culinary oils is now considered vital, since the deleterious effects arising from their ingestion are implicated in a wide range of disease conditions. Partial substitution involves the replenishment of thermally-stressed culinary oils with corresponding unheated ones. This technique was tested by employing 10%, 25%, 50%, and 75% (v/v) partial substitutions of coconut, olive, rapeseed, and sunflower oils at 180℃ for a 300 min continuous thermo-oxidation duration. Oil samples were analysed by proton nuclear magnetic resonance (^{1}H NMR) spectroscopy. Trace metal levels, including oxidation–reduction (redox)-active metal ions credited with enhancing cooking oil oxidation were also analysed using inductively coupled plasma-optical emission spectroscopy (ICP-OES). As expected, the degree of oil unsaturation, and the % partial substitutions significantly influenced their susceptibility to thermo-oxidation. In view of the very low polyunsaturated fatty acid (PUFA) and monounsaturated fatty acid (MUFA) contents of coconut oil, both the class and concentrations of evolved LOPs were found to be least affected by this partial substitution process. Aldehydic LOPs were greatly suppressed in partially-substituted rapeseed oil. The % suppression activity of LOPs evaluated for the partially substituted oils were generally high making partial oil substitutions an effective chemical-free method in suppressing LOPs at both industrial and commercial levels. In general, the % partial oil substitutions were directly related to the dilution effect observed for LOPs quantified in the oils. Furthermore, trace metal ion concentrations measured in the culinary oils did not influence the evolution of LOPs in the oils.

1. Introduction

1.1. Background

Culinary oils with a higher degree of unsaturation have gained an increased popularity in their use in food preparation and cooking processes, and this is attributed to their potential valuable health benefits offered to humans (Catalá, 2009; Alberdi-Cedeño et al., 2017). Nonetheless, such products with a higher degree of unsaturation have been reported to be highly susceptible to thermo-oxidation, a process primarily giving rise to the generation of highly toxic conjugated lipid hydroperoxides (primary LOPs), which are then thermally fragmented to a series of lower-molecular-mass secondary LOPs, notably similarly toxic aldehydes, both saturated and unsaturated. The order of thermo-oxidation susceptibility is established to be polyunsaturated fatty acids (PUFAs) > monounsaturated fatty acids (MUFAs) > saturated fatty acids (SFAs) (Claxson et al., 1994; Poyato et al., 2014; Grootveld et al., 2018; Le Gresley et al., 2019a).

Traditionally, culinary oils are heated and/or repeatedly heated at 180℃ under standard frying conditions. The heating duration may be short or long. The implications of this have been previously extensively reviewed and reported (Martínez-Yusta et al., 2014; Le Gresley et al., 2019a). Another observation is that in many restaurants and fast-food outlets, including mainstream global ones where culinary oils are subjected to high-temperature frying practices at 180℃ are constantly being replenished with unheated, identical oils for many days. Frying is a food cooking and 'preservation' technique that substitutes water in foods for cooking oils. This reduces the volume of culinary oil in the

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[1] This paper is dedicated to Simon De MARS, a dear colleague who passed away suddenly in 2019. He was responsible for obtaining the ICP-OES data.

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Table 1
A comparison between product-label (w/w %) and ^{1}H NMR-investigation of (molar %) of FA groups and IVs of culinary oils.

Culinary oil	Product Label (% (w/w))								^{1}H NMR-Derived (molar %)							
	SFA	ω-3	MUFA O	L	Ln	PUFA L + Ln	UFA O + L + Ln	IV#	SFA	ω-3	MUFA O	L	Ln	PUFA L + Ln	UFA O + L + Ln	IV#
Coconut oil	90.22	–	–	–	–	–	–	–	96.10 ± 0.09	–	3.34 ± 0.06	0.57 ± 0.03	–	0.57 ± 0.03*	3.90 ± 0.09*	15.08 ± 0.18
Olive oil	15.02	–	76.38	–	–	8.60	84.98	–	16.21 ± 0.21	–	75.40 ± 0.29	7.48 ± 0.05	0.90 ± 0.05	8.38 ± 0.08	83.79 ± 0.21	78.38 ± 0.10
Rapeseed oil	7.96	–	63.03	–	–	29.01	92.04	–	8.62 ± 0.05	9.77 ± 0.17	62.35 ± 0.12	20.92 ± 0.27	8.12 ± 0.12	29.04 ± 0.15	91.38 ± 0.05	106.52 ± 0.21
Sunflower oil	10.87	–	28.26	–	–	60.87	89.13	–	12.76 ± 0.59	–	30.22 ± 0.48	57.02 ± 0.10	–	57.02 ± 0.10*	87.24 ± 0.59*	120.13 ± 0.18

*Absence of linolenic acid acyl group. #IV is measured in unit. Abbreviations: SFA, Saturated FA acyl groups; MUFA, Monounsaturated FA acyl groups; PUFA, Polyunsaturated FA acyl groups; UFA, Unsaturated FA acyl groups; ω-3, Omega-3 FA acyl groups; O, Oleic acid acyl groups; L, Linoleic acid acyl groups; Ln, Linolenic acid acyl groups; and IV, Iodine value. The values derived from ^{1}H NMR data are presented as mean ± SD molar % (FA) and mean ± SD unit (IV) of oil.

fryer as food increasingly absorbs the oil, and the water in food is evaporated into airborne environments. Many mainstream restaurant outlets cope with this oil shortage by adding unheated, 'new' oils to that already thermally stressed in the deep fryer. The constant replenishment of thermo-oxidised culinary oil is termed 'partial substitution' in this study.

Culinary oils are also susceptible to pro-oxidative catalysis by metal ions (Choe & Min, 2006). Some metal ions such as those of iron and copper are indeed present as contaminants in culinary oils and may facilitate the formation of LOPs. This may be by perpetuating the decomposition of lipid hydroperoxides, catalysing the oxidation of fatty acyl (FA) groups, and/or accelerating the chemical conversion of molecular oxygen (O_2) into singlet oxygen ($^1O_2$) and oxygen-derived free radical species – in all these cases, LOPs generation during thermal stressing episodes in enhanced (Lu et al., 2016).

This study builds on the impact of continuous and discontinuous thermo-oxidation on the evolution of LOPs in culinary oils (Le Gresley et al., 2019a), the clinical potential consequences of LOPs in French fries (and by implication other fried food products) prepared in reheated culinary oils over a prolonged period, as reported in such samples sourced from two global chain fast-food restaurants (Le Gresley et al., 2021), as well as the use of a World Health Organization (WHO) approved polymer known as polydimethylsiloxane (PDMS) to suppress these cytotoxic and genotoxic LOPs in thermo-oxidised culinary oils (Ampem et al., 2021).

1.2. Rationale

The present study seeks to tackle the following questions:

i. During the exposure of culinary oils to laboratory-simulated high-temperature frying practices, how do partial substitutions of these products at different added levels influence the nature and levels of aldehydic LOPs subsequently generated?
ii. Is the difference between the concentrations of different LOPs systemic across partial substitutions of culinary oils, irrespective of the oils' degree of unsaturation?
iii. Is there a difference between the concentrations of different LOPs and catalytic redox-active metals quantified in the thermally stressed culinary oils?

Partial substitutions of pre-used culinary oils are commonly employed in many commercially based food or take-out restaurants to replenish portions lost during their prolonged exposure to high-temperature frying practices. Perhaps fortuitously, this process also renders the admixed oils arising therefrom more acceptable for use by consumers and in view of their enhanced food quality indices, which are reflected by the diminished polarities, free FA and potentially also LOP levels arising therefrom. Hence, such composite, partially replenished oils will primarily be expected to have a somewhat lower content of LOPs since levels of these toxins are usually very much lower in their unheated forms; however, for PUFA-rich oils such as sunflower, corn or soybean oils, the thermo-oxidatively reduced levels of PUFAs in the original frying oil will be replenished with further levels of these readily-peroxidizable FAs. However, investigations focused on monitoring the rate of formation of these LOPs, specifically a broad spectrum of chemically reactive aldehydes and their lipid hydroperoxide precursors, along with epoxy-fatty acids and additional LOPs, will provide valuable insights regarding the impact of such partial oil substitutions. Moreover, an addressment of the above drafted questions could aid in the prevention of emerging public health issues in humans associated with the dietary ingestion and/or inhalation of LOPs (Grootveld et al., 2014).

Therefore, in this study we have employed high-resolution ^{1}H NMR analysis to explore, for the first time, the effects of partially replenishing cooking oils (10–75% (v/v)) on the generation of a range of LOPs in these frying media when exposed to subsequent laboratory-simulated frying episodes. We have also evaluated the effects of these partial substitutions on the contents of trace metal ions in these oil admixtures. This report, therefore, profiles all partially substituted culinary oils based on their susceptibility to thermo-oxidation at 180°C. It also characterizes long-standing LOPs that evolve from UFAs present in some commercially available frying oils subjected to laboratory-simulated frying episodes with increasing added percentages of partial oil substitution according to standard frying practices. The report also compares the data obtained from partial substitution of oil with the findings by Le Gresley et al. (2019a) to evaluate how partial substitutions at a given time point could lead to a reduced amount of LOPs in culinary oils thermally stressed at 180°C.

2. Materials and methods

2.1. Culinary oil samples

Culinary oils of variable unsaturation degree were procured from a local retail outlet store in London, United Kingdom. Prior to analysis, all oil samples were stored in the dark, under the same ambient temperature conditions for not more than 72 h. Table 1 compares the product label's percentage compositions of some key acylglycerol FA chains (% (w/w)) and iodine values (IVs) of the procured culinary oils with those arising from their ^{1}H NMR profiles (molar %). Based on these compositions, coconut oil is classified as SFA-rich oil, olive, and rapeseed oils as MUFA-rich oils, and sunflower oil as PUFA-rich oil (Le Gresley et al., 2019a).

2.2. Partial substitutions of culinary oils

Partial substitutions of culinary oils were performed at four levels, specifically at 10, 25, 50 and 75% (v/v). These partial substitutions were calculated taking into consideration the total volume of culinary oil to be subjected to laboratory-simulated frying episodes at 180℃. By definition, 10% partial substitutions (v/v) are translated as withdrawing 2.0 mL out of total volume of 20.0 mL thermo-oxidised culinary oil and replenishing the remaining 18.0 mL, which was retained on the continuous thermo-oxidation regimen, with 2.0 mL of the corresponding unheated oil. The same principle was applied to the 25 (v/v), 50 (v/v) and 75% (v/v) partial substitutions of each culinary oil, i.e., by partially substituting 5.0, 10.0, and 15.0 mL of oil respectively. It should also be noted that during sampling for ^{1}H NMR analysis, the volume of oil was reduced by 0.3 mL per sampling time-point at 30 min time intervals. However, this was not factored in the calculation of the partial substitutions of the oils, since the % volumes of substituted oils were fixed throughout the thermo-oxidation process (oil withdrawal and replenishment time-points are represented by -x% and + x% arrows in Supplementary Information Fig. S.1, respectively). Partial substitutions of oil were performed hourly and throughout the 300 min continuous thermo-oxidation period using laboratory-simulated frying episodes (Supplementary Information Fig. S.1).

2.3. Thermal stressing of culinary oils

Briefly, 20.0 mL volumes of culinary oil were aliquoted into a clean, air-dried 100 mL capacity beaker. The lipid-air surface area of the oil in the beaker was calculated to be 61.26 cm^2 for all samples. Samples were then thermally stressed in open air continuously for a total duration of 300 min, at 180℃ on an electronic hot plate (230 V, 50 Hz, 750 W, Stuart heat-stir (UK), Model SB162). Partial substitutions of culinary oil designated to be 10% (v/v), 25% (v/v), and 50% (v/v) were performed at the 60, 120, 180, and 240 min time-points (Supplementary Information Fig. S.1). 1.00 mL Volumes of thermally stressed oil were sampled every 30 min until the 300 min time-point into a 12 mm Fisherbrand soda glass specimen tube, which was capped with its polystopper. This was cooled rapidly on ice and then prepared for ^{1}H NMR analysis. Each experiment was conducted with three replicate samples for each % partial substitution, and for each culinary oil investigated.

As a precaution, withdrawal of thermo-oxidized oil was always carried out first, after which an equivalent volume of fresh oil was immediately added to supplement for the withdrawn thermally- stressed oil. Moreover, in view of its solid-state at ambient temperature, 100% organic virgin coconut oil was primarily melted at 180℃ within a timeframe of $<$ 20 s to facilitate the partial substitutions exchange. Preliminary ^{1}H NMR measurements made on coconut oil liquidized in this manner showed no changes in its molecular composition, i.e., no loss of PUFAs and MUFAs, and no generation of LOPs. For comparative, quantitative ^{1}H NMR evaluations, it was ensured that the same size and type of 100 mL beakers were used for all the oil thermo-oxidation experiments. All procured oil containers were tightly sealed after discharging the amount required for thermo-oxidation, and then placed back into their original storage space.

2.4. ^{1}H NMR measurements

Changes in the composition of control (unheated) sampled thermally stressed oils were monitored by ^{1}H NMR analysis conducted on a Bruker Avance III 600 MHz (TXI) spectrometer (Kingston University facility, London, UK) operating at a frequency of 600.13 MHz. The acquisition parameters for the 600 MHz spectrometer were same as those reported by Le Gresley et al. (2019a). The sampling protocol and preparations were adopted from Claxson et al. (1994); Le Gresley et al. (2019a). Chemical shift, coupling patterns and coupling constants determined in this study were found to be consistent with all literature values available (Martínez-Yusta et al., 2014; Le Gresley et al., 2019a; Le Gresley et al., 2021; Ampem et al., 2021).

2.5. Analysis of ^{1}H NMR spectra

The central focus of the ^{1}H NMR analysis was on the molar percentages of key FA acyl groups, IVs and LOPs. The formulae for generating the molar percentages of each FA class were proposed by Martínez-Yusta et al. (2014). Computations of IV were in accordance with the equation established by Guillén and Ruiz (2003).

The signal resonances of LOPs identified in the ^{1}H NMR spectra of the analysed culinary oils were consistent with those reported in Grootveld et al. (1998), Grootveld et al. (2001), Martínez-Yusta et al. (2014), Le Gresley et al. (2019a), Moumtaz et al. (2019), Percival et al. (2020a), Le Gresley et al. (2021), Ampem et al. (2021). All aldehydic LOPs were quantified by expression of their resonance intensities relative to that of the integral value of the internal standard, TBB, and correction for the number of protons giving rise to them, i.e., 1 for aldehyde-C**H**O function, and 3 for TBB's aromatic proton signals.

2.6. Analysis of trace metal ions

Unheated coconut, olive, rapeseed, and sunflower oils were first investigated to ascertain their trace metal levels. These oils were then heated continuously at 180℃ for 300 min with no oil substitution (Le Gresley et al., 2019a). Thermally stressed oils were sampled at hourly intervals until the 300 min. These were analysed for their trace metal ion concentrations. Microwave digestion of the studied culinary oils was conducted in a Microwave Accelerated Reaction System (MARS) digester (North Carolina, USA), Model MARS 240/50, in accordance with the protocol originally described by Nunes et al. (2011) and modified Le Gresley et al. (2021).

Trace metals analysed were aluminium (Al), arsenic (As), barium (Ba), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), nickel (Ni), lead (Pb), titanium (Ti), thallium (Tl), vanadium (V) and zinc (Zn). Amongst these Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Ti, V and Zn are transition metals whereas Al, Pb, and Tl are not. Also, As, Cu, Fe and Pb are categorized as legislated metals (IOC, 2009), which underscores the requirement for regulating their levels.

Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) or Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) ULTIMA-2C Horiba JY ISA (France) were employed to investigate the roles that trace metal ions may play in catalysing the thermo-oxidation of UFA groups in culinary oil, particularly the redox-active species of Fe, Cu, Mn, Cr, Mo, V and Co, etc. The operating conditions of the ICP-OES instrument were the same as those described by Le Gresley et al., (2021). A multi-element standard solution was used to prepare the calibration standard solutions for the above analytes (Beltrán et al., 2015). Calibration curves prepared for Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Ti, Tl, and Zn were within the 0–50,000 μg.kg^{-1} range. Those of Ba and Mo were within the 0–10,000 μg.kg^{-1} range, and the calibration curve for V was within the 0–100,000 μg.kg^{-1} range. All analyses were conducted in duplicate. Metal ion concentration datasets obtained from ICP-OES analyses were expressed as mean ± SD values μg metal ion kg^{-1} oil (Le Gresley et al., 2021).

3. Results and discussion

This section considers the absolute variation in FAs and IVs, as well as LOPs, as a function of partial substitutions for the thermo-oxidized oils. It also considered the relative reduction in LOPs for partially substituted culinary oils when compared with oils thermally stressed without partial substitutions over selected thermo-oxidation duration to indicate that, depending on the rate of a given oxidation product formation, relative reduction facilitated by partial substitutions varies

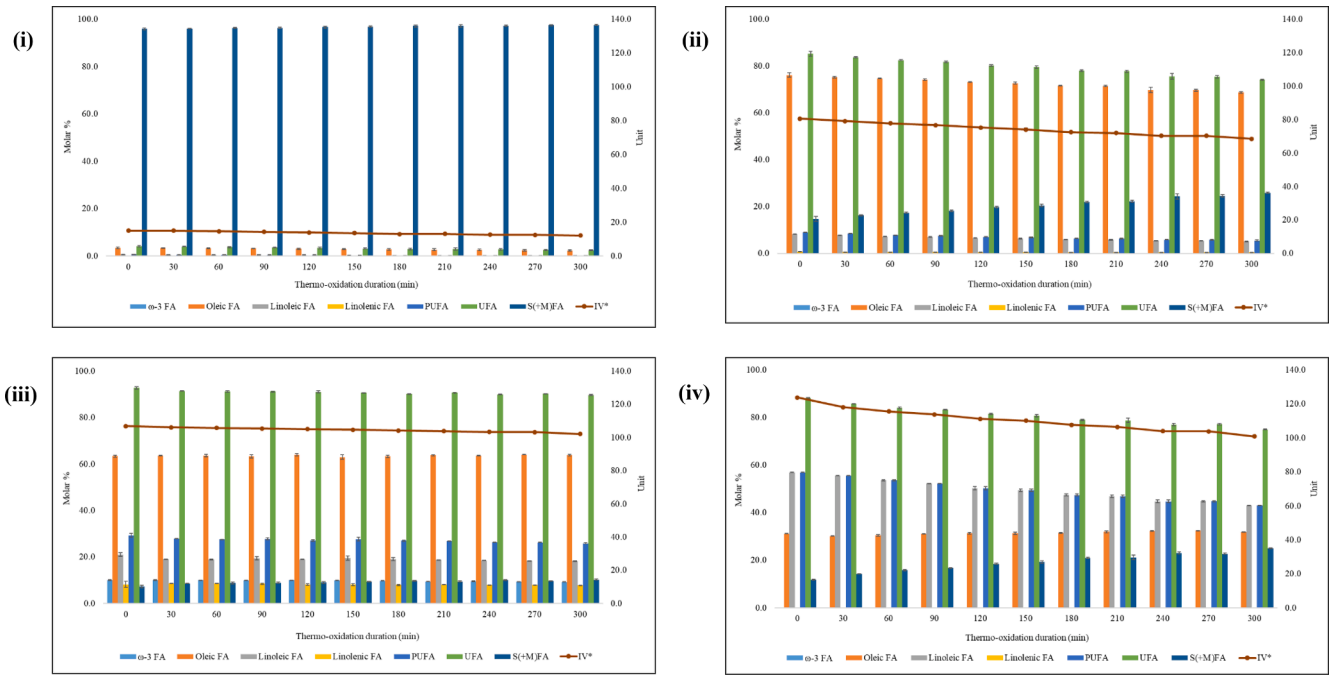

Fig. 1. Chemical modifications in acyl groups and IV of thermally stressed coconut oil (i), olive oil (ii), rapeseed oil (iii), and sunflower oil (iv) subjected to a 10% partial substitutions. IV* is measured in unit. The values are presented as mean ± SD molar % (FA) and mean ± SD unit (IV) of oil.

depending on the oxidation product, potentially enabling a target partial substitution for a given oxidation product to be established for optimum relative reduction. In addition, the characterization of partially substituted culinary oils based on their ^{1}H NMR spectra is provided in 'SI.2. Results and discussion' in the Supplementary Information.

3.1. Thermo-oxidation of culinary oils

3.1.1. Chemical modifications to FA groups and IVs

Thermo-oxidation of culinary oils at 180°C resulted in the breakdown of UFAs and the build-up of increasing proportions of saturated and modified/degraded fatty acyl S(+M)FA groups. Thermally stressed oils partially substituted with previously unheated oils led to a greater dilution effect, and therefore a significant decrease in the levels of thermally oxidised UFAs. However, on exposure to atmospheric oxygen, this has the potential of generating greater amounts and types of toxic LOPs throughout prolonged thermo-oxidation periods, since partial substitutions provides a replenishment of the unsaturation status of these frying media, i.e., the main source of LOP evolution therein.

At the 120 min thermal stressing time-point, partially substituted for coconut oil, the substitution of 50% of this pre-heated medium with that of the corresponding unheated oil resulted in a major reduction of the thermo-oxidation of oleic and linoleic acyl chains (and UFAs and PUFAs in general). As expected, this simultaneously decreased the formation of S(+M)FA groups in 50% partially substituted coconut oil admixtures (Supplementary Information Fig. S.6 (i)). There were no significant changes in the molar % of acyl groups for 50% partial substitution (Supplementary Information Fig. S.7 (i)) when compared with those observed for 10% (Fig. 1 (i)) and 25% (Supplementary Information Fig. S.6 (i)) for partial substitutions of coconut oil. Overall, for this oil smaller changes in the acyl groups of coconut oil were observed, and this is attributed to the very low content of UFAs present.

Both MUFA- (olive oil and rapeseed oil) and PUFA-rich oils (sunflower oil) produced a similar trend where the extent of changes in acyl group compositions, the effects of a 25% partial substitution being intermediate to those observed at 10 and 50% partial substitutions, as expected. For example, a partial substitution of only 10% (v/v) resulted in a greater thermo-oxidation of linoleic and linolenic acyl groups (Fig. 1). Simultaneously, substituting 50% of the thermo-oxidised oil with the unheated version suppressed changes in acyl groups of olive, rapeseed, and sunflower oils (Supplementary Information Fig. S.7). Amongst the key FA acyl groups, the oleoylglycerol levels of rapeseed and sunflower oils remained stable throughout the whole thermo-oxidation process, regardless of the partial substitution extent. The percentage composition of oleic acyl groups was predominantly 63% and 31% in thermally stressed rapeseed oil and sunflower oil, respectively. The IVs of all oils studied followed a similar trend to that of the UFA groups of the oils. Regardless of the percentage partial substitution made, changes in acyl groups and IVs of the oils were in the order sunflower oil > olive oil > rapeseed oil > coconut oil, as we might expect. In addition, the chemical modifications in the acyl groups and IVs of partially substituted culinary oils were less profound than that presented by Le Gresley et al. (2019a) for continuous thermo-oxidised culinary oils without partially substitutions (Supplementary Information Fig. S.8).

According to Choe & Min (2007), the oxidation of a non-radical UFA chain begins with the abstraction of ^{1}H by a radical. The site of radical formation in SFA chains varies from that UFA chains. During thermo-oxidation, alkyl radicals form at the α position of the carboxyl group of SFA chains. The carboxyl group tends to be electronegative – pulling any shared electron pair towards itself. These alkyl radicals react with other alkyl radicals, alkoxy radicals, and peroxy radicals to form dimers and polymers (Choe & Min, 2007). The peroxy radicals can also directly abstracts hydrogen form oleic FAs and linoleic FAs to produce hydroperoxide, which is an oxidation product. Hydroperoxides formed are decomposed to alkoxy radicals and hydroxy radicals by homolysis of the peroxide bond to produce oxy- and hydroxy radicals (Choe & Min, 2007). At the cessation of these series of radical formation in the oils, alkoxy radicals reacts with other alkoxy radicals or are decomposed to form nonradical products (Choe & Min, 2007).

Rapeseed oil partially substituted at a level of 75% (v/v) produced relatively smaller changes in its FA contents. Indeed, ω-3, oleic and linolenic acyl groups were largely unaffected, and therefore remained at the unheated oil 10%, 63%, and 8% levels, respectively (Supplementary Information Fig. S.9). In contrast, there was an approximately 2% loss of linoleic, PUFA, and UFA contents, as well as IV evidence between the

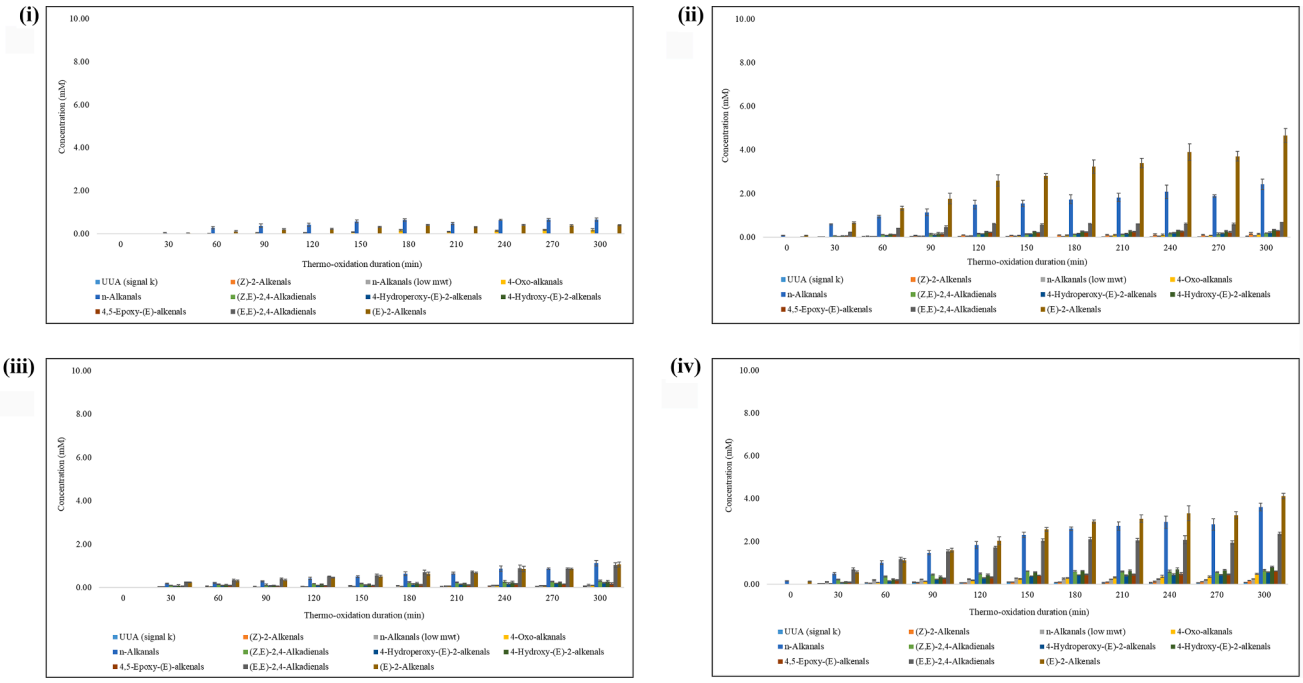

Fig. 2. Evolution of LOPS in thermally stressed coconut oil (i), olive oil (ii), rapeseed oil (iii), and sunflower oil (iv) subjected to 10% partial substitutions. Abbreviation: UUA, unidentified unsaturated aldehyde. All values are presented as mean ± SD mM (mmol LOP per 1.0 L oil).

unheated products and that thermally-stressed for a 300 min period for the 75% (v/v) partially substituted rapeseed oil (Supplementary Information Fig. S.9).

3.1.2. *Evolution of LOPs*

Unheated coconut and rapeseed oils were found to contain no ^{1}H NMR detectable LOPs. In contrast, (*E*)-2-alkenals (0.09 ± 0.01 mM), (*E*, *E*)-2,4-alkadienals (0.02 ± 0.00 mM), and *n*-alkanals (0.09 ± 0.00 mM) were quantified in unheated olive oil. Similarly, (*E*)-2-alkenals (0.15 ± 00 mM) and *n*-alkanals (0.15 ± 0.01 mM) were also determined in unheated sunflower oil, observations consistent with the report by Le Gresley et al. (2019a). Of course, the detection of these toxic secondary LOPs in these unheated oils presents health hazards to consumers, even if they are not using these products for culinary frying episodes. The

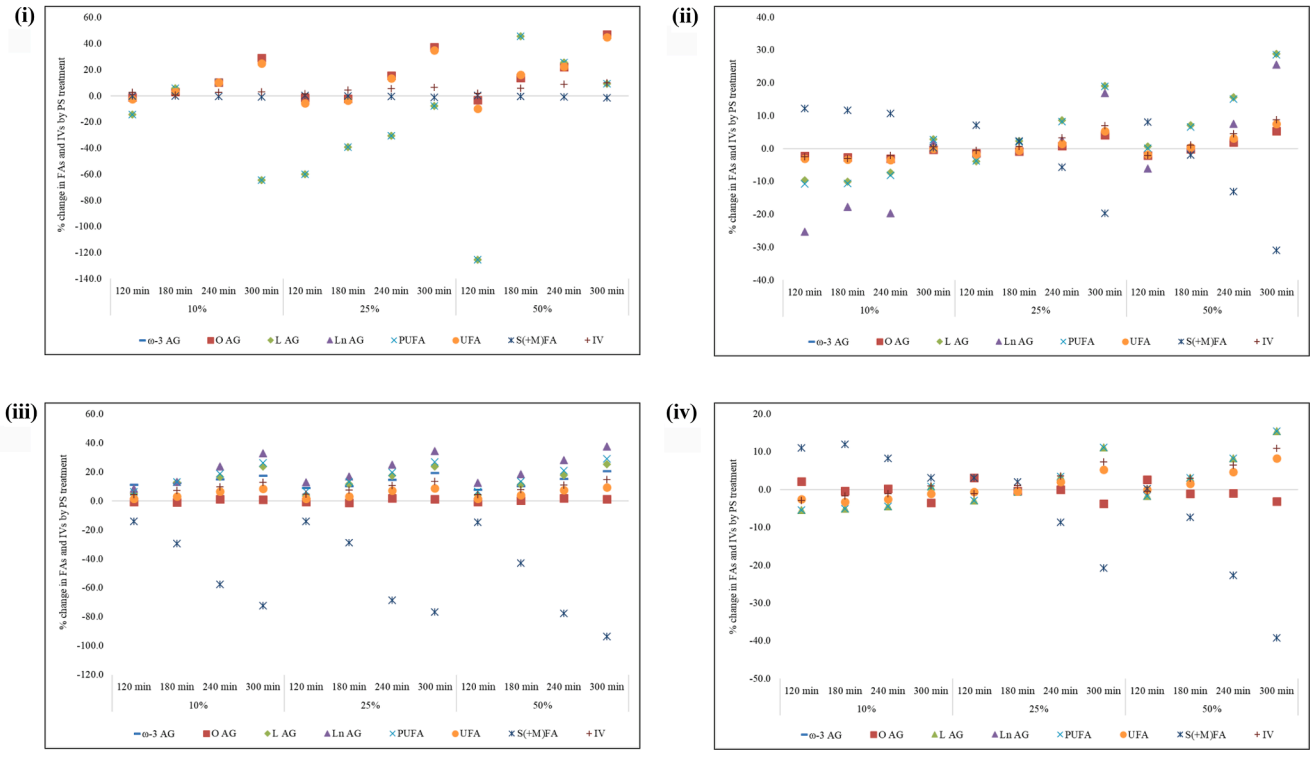

Fig. 3. The percentage change in FAs and IVs by partially substituted coconut oil (i), olive oil (ii), rapeseed oil (iii), and sunflower oil (iv) after comparisons with LOPs concentrations provided by Le Gresley et al. (2019a) for continuous, thermo-oxidised culinary oils of the same types without oil substitutions.

types and amounts of LOPs in unheated culinary oils may arise from their exposure to various forms of oxidative stress, including subjection to light energy and/or prolonged storage periods at relatively high temperatures (Grootveld et al., 2014).

Although virgin coconut oil has a smoke point of 177℃ and would therefore be expected to degrade noticeably at 180℃, its higher saturation level accounted for its thermo-resistance, and this ultimately led to suppress the formation of greater amounts and types of LOPs. Amongst the aldehydic LOPs generated in all thermally stressed culinary oils, *n*-alkanals and α,β-UAs were predominantly those with the highest contents. (*E*)-2-alkenals and (*E*,*E*)-2,4-alkadienals were demonstrably the most concentrated α,β-UAs quantified in partially substituted thermo-oxidised olive, rapeseed, and sunflower oils. In coconut oil, however, the order of magnitude of aldehydic LOPs produced were *n*-alkanals > (*E*)-2-alkenals > 4-oxo-alkanals, with *n*-alkanals less than or equivalent to approximately 0.7 mM (Fig. 3 (i), Supplementary Information Fig S.10 (i), Fig. S.11 (i)). Partial substitutions did not influence the types of LOPs identified in thermally stressed coconut oil.

Partial substitutions of thermally stressed culinary oils influenced the evolution and distribution of some α,β-UAs. Indeed, (*Z*)-2-alkenals were undetectable in 50% partially substituted rapeseed oil (Supplementary Information Fig S.11 (iii)). However, the generation of this aldehyde was first observed in the ^{1}H NMR spectrum at time-points of 210 and 60 min for 10% (Fig. 1 (iii)) and 25% (Supplementary Information Fig. S.10 (iii)) partial substitutions of rapeseed oil, respectively. The unidentified unsaturated aldehyde (signal k) was not detectable at supplemented levels of 10 (Fig. 1 (iii)) and 50% (Supplementary Information Fig. S.11 (iii)) in partially substituted rapeseed oil. However, it was first detected and quantified at the 60 min time-point of 25% partially substituted rapeseed oil (Supplementary Information Fig. S.10 (iii)). Unidentified unsaturated aldehyde (signal k) was also undetected in 25% partially substituted olive oil (Supplementary Information Fig. S.10 (iii)), and its evolution was first quantified at the 60 min time-point of only 10% (Fig. 2 (ii)) and 50% (Supplementary Information Fig. S.11 (ii)) partially substituted olive oil.

As expected, 10% partially substituted culinary oils produced the highest concentrations of aldehydic LOPs in olive oil (Fig. 2 (ii)) when compared with oils with 25% and 75% partial substitutions. An exception was unidentified unsaturated aldehyde which was predominantly higher in samples of the oils which underwent 50% partial substitution (Supplementary Information Fig. S.11 (ii)). In comparison to 10% (Fig. 2 (ii)) and 50% (Supplementary Information Fig. S.11 (ii)) partially substituted olive oil, the 25% partial substitutions of olive oil was characterized to have a lower concentration of (*Z*,*E*)-2,4-alkadienals (Supplementary Information Fig. S.10 (ii)). Furthermore, lower concentrations of (*E*,*E*)-2,4-alkadienals, 4,5-epoxy-(*E*)-alkenals, 4-hydoxy-(*E*)-alkenals, 4-hydoperoxy-(*E*)-alkenals, and (*Z*)-2-alkenals were quantified in 25% partially substituted olive oil between the 30 and 120 min thermo-oxidation durations (Supplementary Information Fig. S.10 (ii)).

Between the 30 and 180 min thermo-oxidation time-points, the concentrations of 4-hydoxy-(*E*)-alkenals and 4-hydoperoxy-(*E*)-alkenals were lower in 25% partially substituted rapeseed oil (Supplementary Information Fig. S.10 (iii)) than in the 10% (Fig. 2 (iii)) and 50% (Supplementary Information Fig. S.11 (iii)) partial substitutions of rapeseed oil. Similar observations were observed for (*Z*,*E*)-2,4-alkadienals, except that at 180 min thermo-oxidation time-point, the concentration of (*Z*,*E*)-2,4-alkadienals in 25% partially substituted rapeseed oil (Supplementary Information Fig. S.10 (iii)) was higher than that quantified at 50% (Supplementary Information Fig. S.11 (iii)) partial substitutions of rapeseed oil. The incongruous data observed for some of the LOPs requires further research to understand how the rate of evolution of LOPs is affected by partial oil substitutions.

In partially-substituted, thermally-stressed sunflower oils, the concentrations of (*E*,*E*)-2,4-alkadienals, (*Z*,*E*)-2,4-alkadienals and low-molecular-mass *n*-alkanals were found to be highest in 25% partial substitutions at the 240–300 min thermo-oxidation duration (Supplementary Information Fig. S.10 (iv)). Similarly, the unidentified unsaturated aldehyde (signal k) was determined to be highest in 25% partial substitutions at 270–300 min thermo-oxidation time-points (Supplementary Information Fig. S.10 (iv)). However, the concentrations of (*E*)-2-alkenals, 4,5-epoxy-(*E*)-alkenals, 4-hydoxy-(*E*)-alkenals, 4-hydoperoxy-(*E*)-alkenals, *n*-alkanals, 4-oxo-alkanals, and (*Z*)-2-alkenals were favourably highest in 10% partial substitutions (Fig. 2 (iv)), and lowest at a PS level of 50% (Supplementary Information Fig. S.11 (iv)).

The formation of LOPs is autocatalytic, self-propagating, and depends on the primary formation and subsequent fragmentation of lipid hydroperoxides (Wann et al., 2021). However, the evolutions of LOPs in partially substituted culinary oils were of lesser concentrations than that presented by Le Gresley et al. (2019a) for continuous thermo-oxidised culinary oils without partially substitutions (Supplementary Information Fig. S.12). Substituting thermo-oxidised culinary oil with unheated oil of the same type therefore played a crucial role in suppressing the evolution of LOPs in the oils. This is discussed in detail in section 3.1.3. It is also worth noting that the chemical identity of unidentified unsaturated aldehyde (signal k) will be researched further in the next project that is presently being undertaking.

Aldehydic LOPs have been identified and characterized in several oil types, and these include culinary oils of varying degree of unsaturation (Claxson et al., 1994; Haywood et al., 1995; Grootveld et al., 2001; Guillén & Uriarte, 2009; Goicoechea & Guillén, 2010; Grootveld et al., 2014; Castejón et al., 2017; Le Gresley et al., 2019a; Ampem et al., 2021), margarines (Ibargoitia et al., 2014), cod liver oils (Percival et al., 2020b), monounsaturated-rich algae oil (Moumtaz et al., 2019), extracts of French fries (Silwood & Grootveld, 1999; Grootveld et al., 2014; Grootveld et al., 2018; Le Gresley et al., 2019a; Le Gresley et al., 2021), as well as crude and processed pyrolysis oil (Le Gresley *et al.*, 2019b).

When initially tested at 180℃, 75% (v/v) partial substitutions of rapeseed oil resulted in consistent considerably lower concentrations of LOPs (i.e., <0.5 mM) (Supplementary Information Fig. S.13). The highest concentrations of LOPs of partially-substituted rapeseed oil peaked at the 240 min time-point. These concentrations were 0.47, 0.43, and 0.42 mM for (*E*,*E*)-2,4-alkadienals, *n*-alkanals, and (*E*)-2,-alkenals respectively (Supplementary Information Fig. S.13). These levels of LOPs were, however, somewhat lower than the concentrations of the most prevalent LOPs – *n*-alkanals – quantified as 0.66 mM, 0.67 mM, and 0.69 mM in thermally stressed coconut oil partially substituted at 10 (Fig. 2 (i)), 25% (Supplementary Information Fig. S.10 (i)), and 50% (Supplementary Information Fig. S.11 (i)) PS levels, respectively. In retrospect, starting with a fresh unheated culinary may not be significantly different from substituting 75% of the thermo-oxidized culinary oil. The application of 75% (v/v) partial substitutions of rapeseed oil was, therefore, not extended to study how they will impact upon coconut, olive, and sunflower oils.

3.1.3. *Impact of continuous thermo-oxidation with partial oil substitutions*

The comparison between the same types of culinary oils subjected under continuous thermo-oxidations with partial oil substitutions in this report and continuous thermo-oxidations without partial substitutions as reported by Le Gresley et al. (2019a) were necessary since the four culinary oils studied were of the same brand and batch in both studies. Comparisons were therefore made at 120, 180, 240, and 300 min sampling time-points. Since it was the first-time that culinary oils were partially substituted, the 60 min sampling time did not give rise to any profound changes in the compositions of the oils and was therefore, excluded from this comparison study. The inclusion of 300 min thermo-oxidation sampling duration was necessary to infer the overall impact of partial substitution on the oils' compositions of FAs and aldehydic LOPs. The % change in FAs and IVs, as well as % suppression activity of LOPs by partially substituted culinary oils were evaluated using equation S1, S2, and S3, respectively, presented in the Supplementary Information.

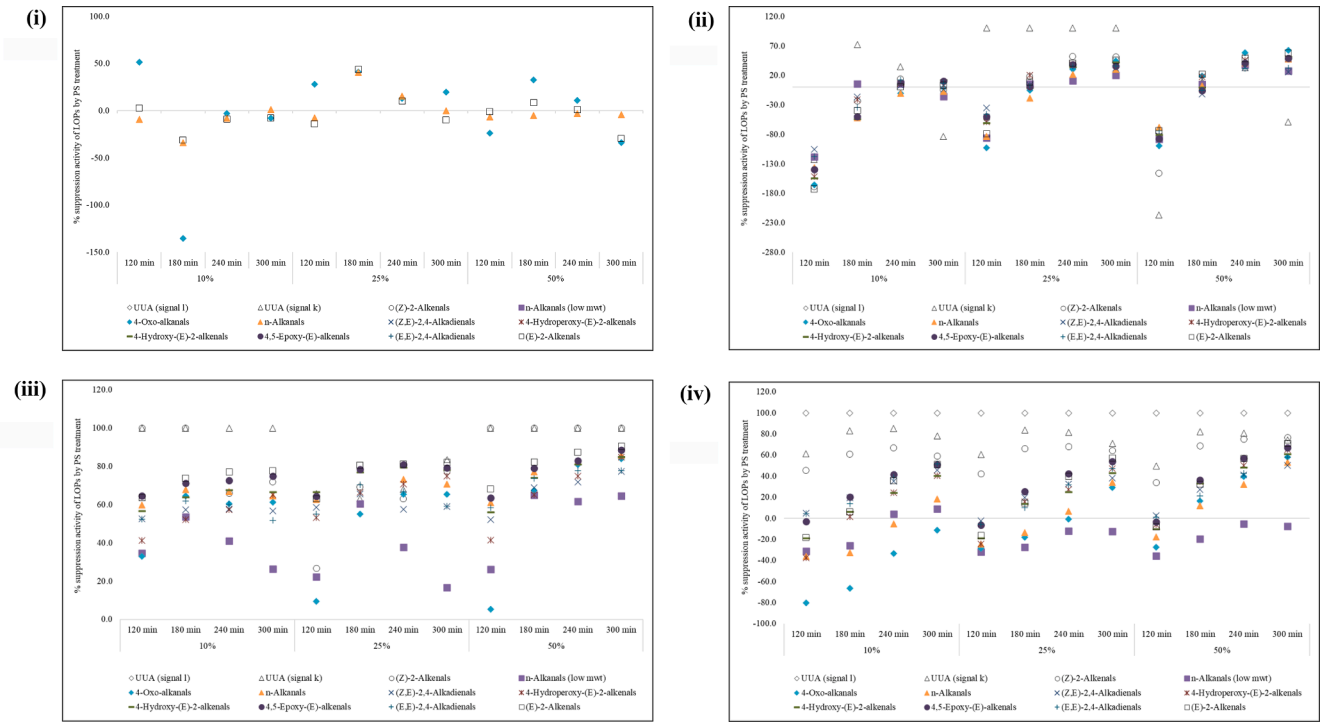

Fig. 4. The percentage suppression activity of LOPs by partially substituted coconut oil (i), olive oil (ii), rapeseed oil (iii), and sunflower oil (iv) after comparisons with LOPs concentrations provided by Le Gresley et al. (2019a) for continuous, thermo-oxidised culinary oils of the same types without oil substitutions. Abbreviation: UUA, unidentified unsaturated aldehyde.

3.1.3.1. Percentage (%) change in FAs and IVs by partial oil substitutions. In general, the higher or more positive the % change in FAs and IVs by partial oil substitutions, the less susceptible the oil to thermo-oxidation (Fig. 3). This was also proportionally applicable to the % suppression activity of LOPs by partial oil substitutions shown in Fig. 4. Simultaneously, the lower or more negative the % change in S(+M)FAs impacted by partial oil substitutions, the higher the resistance of the oil to thermo-oxidation. Notwithstanding, the % change in FAs and IVs (Fig. 3), and the % suppression activity of LOPs (Fig. 4) by partial substitutions are evaluated relative to the thermo-oxidation durations chosen for comparisons. This would therefore imply that partial substitution is a potential candidate and could therefore be implemented in suppressing LOPs evolution in thermo-oxidised oils at both industrial and commercial levels.

When comparing changes in molar % of FAs and units of IVs of the culinary oils, partial substitutions of the culinary oils resulted in the increased the thermo-resistance of the FAs to thermo-oxidation (Fig. 3). This was evident in the increasing % change recorded for the FAs and IVs of the culinary oils, as thermo-oxidation duration progressed at constant temperature of 180°C (Fig. 3). This also reflected in the continuous reduction in the % change in S(+M)FA groups in the partially substituted thermo-oxidised oils (Fig. 3). The same trend was reported for the 75% (v/v) partially substituted rapeseed oil (Supplementary Information Fig. S.14 (i)).

3.1.3.2. Percentage (%) suppression activity of LOPs by partial oil substitutions. The % suppression activity of the individual aldehydic LOPs varied substantially among the oils (Fig. 4). For instance, (*E*)-2-alkenals, *n*-alkanals, and 4-oxo-alkanals were suppressed by a maximum of 43.97% (25% PS), 40.55% (25% PS), and 51.58% (10% PS), respectively in partially substituted coconut oil (Fig. 4 (i)). Notwithstanding, the % suppression activity of some of the LOPs in olive, rapeseed, and sunflower oils were as high as 100% (Fig. 4). Partial substitutions did not greatly affect the LOPs evolution in coconut oil. This was independent of the % partial substitutions of coconut oil. To some extent, this however, provided more UFAs that served as fuel for the thermo-oxidation reactions in coconut oil, hence the negative % suppression activity of LOPs (Fig. 4 (i)).

Between MUFA-rich olive and rapeseed oils, the % suppression activity of partial substitutions was evidently higher in rapeseed oil. Partial substitutions produced a suppression potential on all LOPs in rapeseed oil (Fig. 4 (iii)). In contrast, the evolution of some of the aldehydic LOPs were rather enhanced by partial substitutions of olive oil (Fig. 4 (ii)). Furthermore, in partially substituted olive oil, only unsaturated unidentified aldehyde (signal k) was suppressed by 100% at 25% PS level (Fig. 4 (ii)). Notwithstanding, both unsaturated unidentified aldehyde (signal k) and (*Z*)-2-alkenals were suppressed by 100% at 10% and 50% PS levels (Fig. 4 (iii)).

Unsaturated unidentified aldehyde (signal l), which was ^{1}H NMR undetectable in coconut, olive, and rapeseed oils, was suppressed by 100% in PUFA-rich sunflower oil (Fig. 4 (iv)). Partial substitutions did fuel the evolutions of some of the aldehydic LOPs in sunflower oil. However, like the trend observed for olive oil (Fig. 4 (ii)), the % suppression activity of LOPs by partial substitutions increased with the thermo-oxidation duration in sunflower oil (Fig. 4 (iv)). In retrospect, the % suppression activity of aldehydic LOPs in partially substituted olive, rapeseed, and sunflower oils was in increasing order of 50% PS > 25% PS > 10% PS (Fig. 4 (i), (iii), (iv)).

Being highly susceptible to thermo-oxidation (Le Gresley et al., 2019a), sunflower oil offers a glimpse of how other PUFA-rich culinary oils could succumb to the thermo-oxidation of FAs when partially substituted. This is also true as MUFA-rich olive and rapeseed oils, as well as SFA-rich coconut oil could be useful to project into the activities of other MUFA- and SFA-rich oils, respectively, of similar chemical compositions.

From the % suppression activity of FAs and IVs, and LOPs calculated for the culinary oils, it may be argued that certain LOPs evolve faster than others during partial oil substitutions. An example is the comparison of the >4× suppression factor for some LOPs quantified in 25–50% partially substituted rapeseed oil, and a <4× % suppression factor for

Table 2
Trace metal contents of continuously thermo-oxidized culinary oils.

Thermo-oxidation duration	Chemical elements											
	Al	Ba	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Ti	V	Zn
Coconut oil												
Unheated	34927.76 ± 6845.79	1356.08 ± 104.18	16.27 ± 1.30	24.72 ± 1.55	37.98 ± 3.58	894.49 ± 248.06	62.52 ± 9.02	< LOQ	151.63 ± 22.61	195.92 ± 5.99	9.02 ± 2.27	187.14 ± 13.67
60 min	34332.43 ± 5379.50	1788.68 ± 57.67	11.18 ± 0.86	26.91 ± 1.71	61.67 ± 7.75	931.17 ± 181.64	66.39 ± 13.08	< LOQ	156.48 ± 26.12	95.31 ± 5.08	9.29 ± 2.26	698.34 ± 205.42
120 min	37708.27 ± 4264.01	2294.11 ± 548.37	20.86 ± 3.36	25.94 ± 5.07	59.33 ± 9.20	1544.11 ± 279.52	75.94 ± 13.79	< LOQ	126.86 ± 39.23	29.53 ± 4.62	12.86 ± 3.84	575.10 ± 100.47
180 min	31334.54 ± 2692.54	1997.50 ± 649.44	15.53 ± 0.63	29.41 ± 5.96	45.11 ± 15.40	857.49 ± 274.21	59.50 ± 5.52	< LOQ	77.09 ± 34.13	26.49 ± 5.79	9.04 ± 2.08	302.33 ± 61.12
240 min	32705.70 ± 2751.59	1723.77 ± 440.73	8.22 ± 1.08	29.94 ± 8.95	69.11 ± 12.43	1006.76 ± 374.95	64.58 ± 14.77	21.05 ± 1.29	255.93 ± 47.07	208.44 ± 34.25	9.57 ± 2.02	429.12 ± 86.39
300 min	33091.08 ± 238.93	2088.79 ± 28.53	15.18 ± 4.90	23.67 ± 5.49	52.18 ± 6.86	997.47 ± 174.19	61.30 ± 5.34	< LOQ	182.66 ± 11.00	198.90 ± 17.23	10.01 ± 0.63	337.37 ± 0.95
Average	**34016.63**	**1874.82**	**14.54**	**26.76**	**54.23**	**1038.58**	**65.04**	**21.05**	**158.44**	**125.77**	**9.96**	**421.57**
Olive oil												
Unheated	4095.27 ± 199.57	1511.72 ± 287.02	18.47 ± 3.71	20.09 ± 3.14	47.74 ± 7.22	562.99 ± 45.91	14.55 ± 1.36	13.94 ± 4.44	362.57 ± 34.79	18.51 ± 0.45	< LOQ	214.21 ± 52.42
60 min	3286.22 ± 7.59	1218.35 ± 11.03	14.03 ± 1.70	27.53 ± 0.13	44.49 ± 3.81	365.54 ± 10.96	17.20 ± 1.25	< LOQ	201.86 ± 52.01	16.64 ± 1.61	< LOQ	413.62 ± 57.79
120 min	3675.23 ± 126.27	1393.34 ± 87.04	20.59 ± 0.99	25.24 ± 1.52	46.06 ± 4.95	458.06 ± 30.36	27.10 ± 2.00	< LOQ	94.16 ± 26.65	36.12 ± 8.48	< LOQ	511.56 ± 115.47
180 min	3500.53 ± 148.52	1362.72 ± 186.42	23.49 ± 0.82	23.29 ± 3.57	30.07 ± 3.70	370.59 ± 36.42	15.67 ± 0.64	< LOQ	40.77 ± 6.40	16.55 ± 1.50	< LOQ	395.84 ± 91.02
240 min	3581.00 ± 18.76	1337.85 ± 26.11	14.59 ± 5.40	24.03 ± 8.07	26.66 ± 4.73	356.72 ± 0.11	11.86 ± 1.59	< LOQ	44.33 ± 6.68	16.34 ± 0.13	< LOQ	368.73 ± 9.35
300 min	3762.80 ± 245.86	1416.08 ± 122.82	19.89 ± 1.94	22.20 ± 3.27	30.92 ± 2.00	393.09 ± 46.61	12.67 ± 1.41	< LOQ	111.58 ± 34.60	22.55 ± 7.00	< LOQ	230.76 ± 61.22
Average	**3650.18**	**1373.34**	**18.51**	**23.73**	**37.65**	**417.83**	**16.51**	**13.94**	**142.55**	**21.12**		**355.79**
Legal limit*	11100^{EFSA}	15500^{EFSA}	190^{EFSA}	23250^{EFSA}	1100^{PRI}	9000^{FNB}	5500^{EFSA}	217^{EFSA}	1940^{EFSA}	–	1800^{FNB}	8250^{PRI}
	Rapeseed oil											
Unheated	13458.20±840.71	1763.78±187.67	20.15±1.85	20.67±0.72	57.67±4.93	810.70±233.42	32.07±6.25	3.87±0.75	174.79±62.24	20.10±3.07	3.36±0.78	330.71±41.34
60 min	13838.44±103.16	1713.03±68.68	18.95±5.14	22.75±0.80	42.59±8.56	554.04±14.48	41.26±3.30	< LOQ	113.15±13.19	26.73±4.93	1.09±0.26	412.23±43.28
120 min	13670.70±515.76	1614.68±41.97	14.36±3.55	21.71±2.60	47.59±0.06	491.40±16.81	25.53±2.27	< LOQ	106.79±1.42	20.65±0.64	1.30±0.01	201.87±54.31
180 min	15396.30±795.74	1682.91±215.44	14.15±3.33	36.46±4.03	56.42±16.51	647.93±21.72	47.22±9.38	12.62±0.95	179.52±38.97	24.70±0.23	2.39±0.33	287.33±69.19
240 min	13770.44±595.30	1381.57±33.73	11.18±2.94	24.55±3.37	47.73±12.95	553.92±29.67	25.69±2.79	5.34±1.28	262.60±74.80	19.60±0.34	2.95±0.01	226.83±20.58
300 min	13376.74±669.06	1699.95±117.03	15.36±4.59	20.00±3.17	48.45±5.94	771.30±173.63	26.87±0.59	< LOQ	248.78±50.75	20.80±1.34	2.60±0.05	175.10±6.72
Average	**13918.47**	**1642.65**	**15.69**	**24.36**	**50.08**	**638.22**	**33.10**	**7.28**	**180.94**	**22.10**	**2.28**	**272.34**
	Sunflower oil											
Unheated	3421.89±680.34	1322.67±266.60	28.03±2.01	24.05±4.58	51.90±1.59	511.71±38.53	16.36±2.28	< LOQ	283.12±72.43	19.62±2.02	< LOQ	283.03±9.76
60 min	3513.23±90.48	1357.85±15.41	15.03±4.51	26.81±9.04	73.17±2.18	745.49±91.59	16.41±2.76	9.31±2.54	332.23±13.18	20.78±1.20	< LOQ	285.69±92.05
120 min	4678.84±753.92	1872.38±326.28	25.49±2.82	29.72±2.81	78.79±20.19	728.30±145.14	19.58±6.09	< LOQ	271.47±50.77	25.60±2.59	< LOQ	312.71±81.68
180 min	3314.30±279.27	1253.38±159.10	20.65±3.68	24.76±3.34	37.80±6.55	444.76±61.38	16.09±2.07	4.56±0.53	241.26±33.20	25.56±4.72	< LOQ	300.34±44.23
240 min	3734.48±610.62	1523.80±338.82	16.00±1.98	30.04±3.83	35.69±3.48	516.54±42.60	14.04±4.59	12.15±4.23	315.43±62.71	19.57±1.04	< LOQ	262.55±54.58
300 min	3397.12±36.68	1309.06±53.75	11.87±1.39	20.42±0.69	37.56±0.44	452.22±58.24	12.37±0.14	< LOQ	202.64±21.63	19.67±1.20	< LOQ	324.73±76.36
Average	**3676.64**	**1439.86**	**19.51**	**25.97**	**52.48**	**566.50**	**15.81**	**8.67**	**274.36**	**21.80**		**294.84**
Legal limit*	11100^{EFSA}	15500^{EFSA}	190^{EFSA}	23250^{EFSA}	1100^{PRI}	9000^{FNB}	5500^{EFSA}	217^{EFSA}	1940^{EFSA}	–	1800^{FNB}	8250^{PRI}

Abbreviations: <LOQ, less than limit of quantification; EFSA, European Food Safety Authority; PRI, Population Reference Intake (European); FNB, Food and Nutrition Board; Al, aluminium; Ba, barium; Cd, cadmium; Cr, chromium; Cu, copper; Fe, iron; Mn, manganese; Ni, nickel; Pb, lead; Ti, titanium; V, vanadium; Zn, zinc. *Daily maximum legal limit of trace metals (μg) per average body weight (77.5 kg) are derived values per day. All values are presented as mean±SD μg trace metal per 1.0 kg oil.

the same types of LOPs measured in coconut, olive, and sunflower oils at 300 min. The suppression factor of LOPs was evaluated as the ratio of the mM concentrations of LOPs of continuously thermo-oxidised culinary oils without partial oil substitutions (reported by Le Gresley et al. (2019)) to that of partially substituted composites of the same type and brand of culinary oil at a given time point. This variability could be used to discern which partial substitution method, in relation to percentage quantity and substitutional time point, is optimal in a culinary environment for a given oil to reduce the evolution of certain types of LOPs.

In 75% (v/v) partially substituted rapeseed oil, the % suppression activity of aldehydic LOPs varied between 39.93% (4-oxo-alkanal) to 100% (unsaturated unidentified aldehyde (signal k) and (*Z*)-2-alkenals) (Supplementary Information Fig. S.14 (ii)). Furthermore, the % suppression activity of LOPs found at this level was predominantly, by far, the highest reported among all % partial substitutions for all culinary oils. Whilst 75% (v/v) partial oil substitutions of may be recommended, this option could be negated by high-cost implications. In addition, it could also be argued that replacing all oil may be a better option than replacing only 75% (v/v) of the thermo-oxidised oil.

According to data obtained from this study, partial oil substitutions could constitute one of the effective and safe means that could make use of unheated oils as a chemical-free technique to suppress the levels of toxic LOPs in a continuously, thermo-oxidised oil. This report is, therefore, a contribution to other research findings that make use of natural processes such as a naturally antioxidant-fortified, unrefined, cod liver oil isolated from pre-fermented cod livers (Percival et al., 2020b), and a chemical anti-foaming agents such as polydimethylsiloxane (PDMS) (Ampem et al., 2021) to significantly lower aldehydic LOP levels during high-temperature frying processes.

3.2. Trace metal ion levels

Quantification of trace metals in culinary oils is important for two major reasons: (1) their potential nutritional value, and (2) their catalytic role in the production of toxic lipid oxidation products. The trace metal ions of Co, Mo, and Tl were undetectable in all culinary oils. Furthermore, 3.23 ± 0.79 μg As in 1.00 kg oil was found in sunflower oil at a 300 min thermo-oxidation time-point. Accordingly, the decreasing order of magnitude of trace elements found were (Table 2):

Coconut oil: Al > Ba > Fe > Zn > Pb > Ti > Mn > Cu > Cr > Ni > Cd > V

Rapeseed oil: Al > Ba > Fe > Zn > Pb > Cu > Mn > Cr > Ti > Cd > Ni > V

Olive and sunflower oil: Al > Ba > Fe > Zn > Pb > Cu > Cr > Ti > Cd > Mn > Ni > V

Amongst the trace metals determined in the culinary oils, Al of coconut oil (31–38 $mg.kg^{-1}$) and rapeseed oil (13–15 $mg.kg^{-1}$) were above the specified daily maximum legal limit of elements (μg) per average body weight of 77.5 kg (Creff formula) set by European Population Reference Intake (PRI), Food and Nutrition Board (FNB), and European Food Safety Authority (EFSA) (EFSA, 2009; EFSA, 2010) (Table 2). Therefore, Al present in the coconut and rapeseed oil products tested exceeded the daily maximum legal limit by 2.82–3.40- and 1.21–1.39-fold, respectively. The high levels of Al in these oils could explain the higher amount of Al quantified in oil extracted from French fries purchased from restaurant X, which was 13.7 $mg.kg^{-1}$, a value 1.24-fold greater than the daily maximum legal limit (Le Gresley et al., 2021). High levels of Al may be deleterious to human health since they have been implicated in Alzheimer's disease (Bastos & Pereira, 2010).

Trace metal ions such as Fe^{3+} and Cu^{2+} abstract ^1H form lipids to produce alkyl radicals by redox reactions (Choe & Min, 2007). In addition, they also produce $^1O_2$ and hydroxy radical from triplet oxygen ($^3O_2$) and hydrogen peroxide, respectively (Andersson, 1998; Choe & Min, 2006). The lipid alkyl radical, $^1O_2$, and hydroxy radical formed further accelerate LOPs formation. The trend observed for all trace metal ions, however, did not suggest a direct relationship between continuous culinary oils thermo-oxidation with their increasing concentrations (Table 2).

4. Limitations

The glassware employed for the thermo-oxidation of the culinary oils did not contribute towards the observed LOP levels (Gutteridge et al., 1985; Díaz et al., 2006; Bastos & Pereira, 2010; Llorent-Martínez et al., 2011; Lorrain et al., 2012; Trindade et al., 2015). Notwithstanding, trace metal ions could play a vital role in the autocatalysis of UFAs, however, this was not observed for the partial oil substitutions. Transition metal ions, in some cases, could act as antioxidants by neutralising primary carbon-centred pentadienyl radicals, and/or peroxyl radicals (Scott, 1993) and in a recent study, trace metals analysed in oil extracts of French fries from the fast-food restaurants involved were also found to act as anti- rather than pro-oxidants (Le Gresley et al., 2021). However, the passive transfer of these trace metal ions and LOPs into fried foods as demonstrated by Le Gresley et al. (2021) raises health concerns. If not monitored and carefully regulated, this could potentially intensify the adverse health effects, putatively stemming from the excessive consumption of LOPs and fried food intake in humans (Grootveld et al., 2014).

5. Conclusions

Partially substituting thermally stressed culinary oils is effective in suppressing the evolution of LOPs in thermally stressed culinary oils. Nonetheless, the % suppression activity by partial substitutions is dependent on the unsaturation degree of the oil, as well as the % level of oil to be substituted, as expected. Coconut oil was least impacted by partial substitutions, and this was ascribable to its 3.90% UFA groups and 15.08 units IV. Sunflower oil, regardless of the % partial substitutions, still proved to be the most susceptible culinary oil to thermo-oxidation, as we might expect from its high PUFA content. Indeed, the concentrations of LOPs generated were higher in sunflower than in coconut, olive, and rapeseed oils. Amongst the UFA-rich oils, aldehydic LOPs were greatly suppressed in partially substituted rapeseed oil. Furthermore, data acquired from the evaluation of % suppression activity indicated that certain LOPs could evolve faster than others during partial oil substitutions. The effect of partial substitutions in suppressing LOPs in the studied culinary oils was in order of 50% > 25% > 10%. By implication, partial substitutions of culinary oil potentially offer to be an effective chemical-free scientific technique in suppressing LOPs at 180℃. Furthermore, an ICP-OES investigation of culinary oils revealed that the concentrations of trace metal ions did not influence the types and levels of LOPs in the studied culinary oils.

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CRediT authorship contribution statement

Gilbert Ampem: Formal analysis, Investigation, Data curation, Writing – original draft, Writing – review & editing, Visualization. **Adam Le Gresley:** Methodology, Validation, Data curation, Writing – original draft, Writing – review & editing, Visualization, Supervision, Project administration. **Martin Grootveld:** Conceptualization, Methodology, Validation, Resources, Writing – review & editing. **Simon De Mars:** Formal analysis, Investigation. **Declan P. Naughton:** Conceptualization, Methodology, Validation, Resources, Writing – review & editing, Writing – review & editing, Supervision, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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