Effects of tea polyphenols and tertiary butylhydroquinone on quality of palm oils and losses of endogenous vitamin E during batch frying and oxidative stability of fried instant noodles

Jun Li [a], Fangbo Yuan [a,b], Jiayou Teng [b], Fang Li [b], Penghui Zhou [b], Yanlan Bi [a,*]

[a] College of Food Science and Engineering, Henan University of Technology, Zhengzhou 450001, China
[b] Braisun Food Group, Xinzheng 451100, China

ARTICLE INFO

ABSTRACT

The effects of tea polyphenols (TP) on the quality of palm oils (PO) and losses of endogenous vitamin E during batch frying of instant noodles as well as oxidative stability of fried instant noodles were investigated. PO without antioxidant addition was negative control and with tertiary butylhydroquinone (TBHQ) addition positive control. TP and TBHQ addition inhibited the increase of peroxide, *p*-anisidine, and total oxidation values of PO and reduced tocopherol and tocotrienol losses with 200 mg/kg of TP having the best performance, but didn't affect acid value and triglyceride composition. 200 mg/kg of TP and 100 mg/kg of TBHQ inhibited unsaturated fatty acid losses. During frying, TBHQ was mainly volatilized but TP transformed. TP more effectively reduced tocopherol and tocotrienol losses than TBHQ, reducing PO deterioration. The extended lifecycles of PO and shelf life of fried instant noodles are attributed to nonvolatility of TP and antioxidative properties of its transformation products.

1. Introduction

Instant noodles are popular among consumers due to ready-to-eat convenience, easy portability, and low price, whose market size was expected to reach $74.85 billion at 2028 with a compound annual growth rate of approximately 6.8 % (Facts and Factors, 2022). According to the difference of processing patterns, instant noodles are grouped into fried and nonfried instant noodles (Park et al., 2019), among which fried ones dominate in the global instant noodle market due to excellent flavor. Fried instant noodles are generally required to have a shelf life of 2 ∼ 12 months. The shelf life of fried instant noodles largely depends upon the oxidative stability of frying oils due to 15 ∼ 20 % oils and fats contained in fried instant noodles (Rani et al., 2018). Thus, numerous efforts have been made on improving the oxidative stability of frying oils, which can not only extend the lifecycle of frying oils but also ensure different batches of fried instant noodles to reach the required shelf life.

Antioxidants are considered to be one of the most common and effective methods to improve the lifecycle of frying oils and the shelf life of fried instant noodles (Gulia et al., 2014). Akhtar et al. (2012) investigated the effects of 200 mg/kg of tertiary butylhydroquinone (TBHQ), butylated hydroxytoluene (BHT), butyl hydroxyanisole (BHA), or mixture of BHT plus BHA (1: 1, w/w) on the oxidative stability of sunflower oils during storage (30 ℃) and frying (180 ℃, 4 h per day), and found that all of them effectively improved the oxidative stability of sunflower oils with the order: TBHQ > BHT > BHT plus BHA > BHA. Shende et al. (2014) reported that soybean oils with 200 mg/kg of BHA after each cycle of frying (180 ℃) had a much higher induction period (IP) than that without BHA (24.3 vs. 10.9 h for cycle 0, 15.6 vs. 1.7 h for cycle 1, 9.9 vs. 0.5 h for cycle 2, 4.5 vs. 0.4 h for cycle 3, and 3.4 vs. 0.2 h for cycle 4), indicating the effectiveness of BHA in oxidative stability of soybean oils. In recent years, attention has been turning on natural antioxidants due to the concerns regarding the safety of synthetic antioxidants. Chung et al. (2006) found that the addition (10 and 20 %, v/v) of sesame oils not only largely improves the oxidative stability of soybean oils during frying (160 C), but also significantly reduces the losses of tocopherols (Ts, endogenously presented in soybean oils and sesame oils) in fried foods during storage (60 ℃, dark, 18 days), which is attributed to the protective effects of lignans endogenously presented in sesame oils. Kiran et al. (2015) reported that the addition of synthetic and natural antioxidants effectively reduces the formation of polar compounds in soybean oils during frying (180 ℃ and 2 h) with the effectiveness of them at 200 mg/kg following the order: rosemary

---

* Corresponding author.
 E-mail address: bylzry@126.com (Y. Bi).

extracts > Ts > γ-oryzanol > sesamol > TBHQ > BHT. The weaker antioxidation of synthetic antioxidants than natural antioxidants could be ascribed to the easy volatilization of synthetic antioxidants due to their small molecular weights (Aladedunye, 2014). From the above analysis, it can be seen that most studies focused on the improvement of oxidative stability of frying oils by antioxidants, while the fate (losses, protective effects of one to the other) of antioxidants (including exo- and en-dogenous ones) during frying remains still unknown as well as the improvement of shelf life of fried foods.

Tea polyphenols (TP), as natural antioxidants, mainly including catechin (C), epicatechin (EC), epigallocatechin (EGC), epicatechin gallate (ECG), and epigallocatechin gallate (EGCG), have good biological and antioxidative activities (Guo et al., 2019; Musial et al., 2020), thus extensively adding into food products. However, most studies regarding antioxidative activities of TP mainly centered on room- or low-temperature storage (Lorenzo et al., 2014, 2014b), while studies regarding antioxidative activities of TP under high-temperature frying conditions are rare. In addition, previous studies (Sang et al., 2003; Valcic et al., 1999, 2000) taking peroxyl radicals as initiators at low temperature (50 C) indicated that transformation products of TP also still have antioxidative activities theoretically due to the presence of phenolic hydroxyl groups. However, there is no relevant report regarding the fate of TP during frying as well as its transformation products. In fried instant noodle industry, the most common frying medium is palm oils, especially in China, due to its high thermal and oxidative stability (Wu et al., 2018), whose endogenous antioxidants are vitamin E including Ts and tocotrienols (TTs) (Absalome et al., 2020).

The objective of the work, therefore, was to investigate the effects of TP on the quality of palm oils and losses of endogenous vitamin E during batch frying of instant noodles as well as oxidative stability of fried instant noodles. Palm oils with TBHQ addition was used as comparison.

2. Materials and methods

2.1. Materials and chemicals

Fractionated refined palm oils (melting point of 33 ℃, no exogeneous antioxidants), wheat flour, wheat gluten, tapioca starch, and saline solution were kindly provided from Braisun Food Group (Xinzheng, China). TBHQ (purity ≥ 99 %), α-, β-, γ-, and δ-Ts (purity ≥ 98 %) and TTs (purity ≥ 98 %), C (purity ≥ 95 %), EC (purity ≥ 97 %), EGC (purity ≥ 98 %), ECG (purity ≥ 98 %), and EGCG (purity ≥ 98 %) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China). TP (purity > 10 %) was kindly provided from National Research Center for Engineering Technology for Utilization Ingredients from Botanicals (Hunan, China). All chemicals and solvents were obtained from a local supplier, in which acetonitrile, methanol, acetic acid, isopropanol, *n*-hexane, and isooctane were HPLC grade, and others were analytical grade.

2.2. Preparation of fresh wet noodle blocks

2.4 kg of wheat flour, wheat gluten, and tapioca starch (20: 3: 1, w/w/w) and 0.8 kg of saline solution were mixed in a blender (JHMZ-200, Beijing Dongfu Jiuheng Instrument Technology Co., Ltd.) for 1 min at low-speed mode, 10 min at high-speed mode, and then 6 min again at low-speed mode, followed by rising for 10 min. After that, the dough was repeatedly rolled out three times and sheeted to a thickness of 0.90 ~ 0.92 mm, followed by cutting into noodles (0.90 ~ 0.92 mm thickness × 1.5 mm width) and steaming for 7 min. After cooling down, noodles were cut into noodle blocks with each block weighing about 100 g. Finally, approximately 3 kg of fresh wet noodle blocks was achieved.

2.3. Frying of wet noodles

7.5 kg of fractionated refined palm oils was poured into a Topkich

fryer (Guangzhou Top Kitchen Instrument Co., Ltd., China) with a surface-to-volume ratio of 0.138 cm^{-1}, followed by heating to 150 C. Two fresh wet noodle blocks were individually placed into two square frying boxes, submerged into palm oils for 2 min of frying, fished out to drain the excessive oils out, and sealed into zipper bags after cooling down, which was called one frying cycle. Frying oils were statically kept at 150 ℃ for 30 min before next frying cycle. 6 h of frying per day was conducted, which was equivalent to 13 frying cycles per day. Frying oils were spontaneously cooled down to room temperature after each day of frying and reheated to 150 ℃ next day. Frying was conducted totally for 5 days with the surface-to-volume ratio of the oil increasing to 0.222 cm^{-1} at the end. 50 g of frying oils was sampled every 3 h for the first 3 days and every 6 h for the last 2 days, followed by storing in a 4 ℃ refrigerator until further analysis. No fresh palm oils were added during the entire frying process.

2.4. Determination of acid value, peroxide value, p-anisidine value, and total oxidation value, and total polar compounds content

The AV of frying oils was determined according to the AOCS method 3d-63 (2017). The PV of frying oils was determined according to the AOCS method Cd 8b-90 (2017). The *p*-AnV of frying oils was determined according to the AOCS method Cd 18-90 (2017). The TOTOX of frying oils was calculated using the Equation 1. The content of TPC was determined using a Testo 270 cooking oil tester (Testo Instruments International Trading (shanghai) Co., Ltd.).

$$TOTOX = 2 \times PV + p\text{-}AnV \tag{1}$$

2.5. Determination of fatty acid profile

Fatty acid profile of frying oils was determined using the methylation method recommended by the AOCS method Ce 2-66 (2017). An 6890 N gas chromatography (Agilent, USA) equipped with a flame ionization detector (FID) was employed with the following conditions: an SGE BXP-70 capillary column (30 m × 0.25 mm × 0.25 μm) was used as the separation unit with the temperature initially set at 170 ℃, raised to 210 ℃ with a rate of 2 ℃/min, and then kept at 210 C for 5 min; the temperatures of injector and FID were set at 250 and 300 ℃, respectively; split ratio was set at 10:1; nitrogen was used as the carrier gas with a flow rate of 0.4 mL/min; the flow rates of hydrogen and air were 30 and 400 mL/min, respectively.

2.6. Determination of glyceride profile

Glyceride profile of frying oils was determined according to the previous study reported by Wang et al. (2011). An 7890B high-temperature gas chromatography (Agilent, USA) equipped with a FID was employed with the following conditions: an DB-1ht capillary column (30 m × 0.25 mm × 0.1 μm) was used as the separation unit with the temperature initially set at 100 ℃, raised to 220 ℃ at 50 ℃/min, to 290 ℃ at 15 ℃/min, and to 320 ℃ at 40 ℃/min, kept at 320 ℃ for 8 min, raised to 360 at 20 ℃/min, and then kept at 360 ℃ for 10 min; the temperatures of injector and FID were both set at 350 ℃; split ratio was set at 20:1; nitrogen was used as the carrier gas with a flow rate of 4 mL/min; the flow rates of hydrogen and air were 60 and 400 mL/min, respectively.

2.7. Determination of tea polyphenols and TBHQ

TP and TBHQ in frying oils were extracted using methanol. 2 g of frying oils weighed into a 20-mL test tube, followed by adding 4 mL of methanol, agitating for 3 min, and centrifuging for 4 min at 3000 r/min. After that, methanol phase was transferred into a 10-mL volumetric flask. The extraction was repeated two more times with 3 mL of

methanol each. All of methanol phases were combined and diluted to 10 mL with methanol, followed by filtration using a 0.45 μm organic membrane before quantitative analysis.

Quantitative analysis of TP was performed using an e2695 HPLC equipped with an 2489 ultraviolet detector (Waters, USA). The conditions were as follows: SunFire C18 (4.6 mm × 250 mm, 5 μm) was used as the separation unit with the column temperature set at 35 ℃; injection volume was 20 μL; acetonitrile (solvent A) and 4 % acetic acid water (solvent B) were used as the mobile phase; elution program was isocratic mode of 5 % solvent B for 10 min, and linear gradient from 5 to 21 % solvent B for 5 min and from 21 to 31 % for 10 min; flow rate was 0.8 mL/min; and detection wavelength was set at 280 nm.

Quantitative analysis of TBHQ was same as that of TP except for mobile phase and gradient elution: methanol (solvent A) and 0.5 % acetic acid water (solvent B) were used as the mobile phase; elution program was linear gradient from 40 to 80 % solvent B for 8 min and from 80 to 100 % for 7 min, and then isocratic mode of 100 % solvent B for 5 min.

2.8. Determination of tocopherols and tocotrienols

0.1 ~ 1 g of frying oils was dissolved in *n*-hexane and diluted to 10 mL, followed by filtration using a 0.45 μm organic membrane before quantitative analysis.

Quantitative analysis of Ts and TTs was performed using an 2695 HPLC equipped with an 2475 fluorescence detector (Waters, USA). The conditions were as follows: SunFire prepsilica (4.6 mm × 250 mm, 5 μm) was used as the separation unit with the column temperature set at 30 ℃; injection volume was 20 μL; isopropanol and *n*-hexane (0.5: 99.5, v/v) were used as the mobile phase; isocratic elution was used with a flow rate of 1.0 mL/min; and excitation and emission wavelengths were set at 290 and 330 nm, respectively.

2.9. Analysis of transformation products of tea polyphenols

Transformation products of TP in frying oils were extracted using methanol. 2 g of frying oils was weighed into a 20-mL test tube, followed by adding 5 mL of methanol, agitating for 3 min, and centrifuging for 4 min at 3000 r/min. After that, methanol phase was transferred into a 10-mL volumetric flask. The extraction was repeated twice with 5 mL of methanol each. All of methanol phases were combined and diluted to 10 mL with methanol, followed by filtration using a 0.45 μm organic membrane before analysis.

Transformation products of TP were analyzed using an 1290 Infinity II UPLC equipped with an 6546 LC/Q-TOF MS detector (Agilent, USA). The conditions were as follows: ZORBAX Eclipse Plus C18 (50 mm × 2.0 mm, 1.8 μm) was used as the separation unit with the column temperature set at 35 C; injection volume was 2 μL; 0.5 % acetic acid water (solvent A) and acetonitrile (solvent B) were used as the mobile phase; flow rate was 0.3 mL/min; elution program was the isocratic mode of 80 % solvent B; ion polarity was under the negative mode; gas and shear gas temperatures were set at 180 and 350 ℃, respectively; flow rates of drying gas and sheath gas were set at 8 and 11 L/min, respectively; Nebulizer was 35 psi; nozzle, capillary, and fragmentor voltages were set at 1000, 3500, and 175 V, respectively; and mass range was at 50 ~ 1050 *m/z*.

2.10. Determination of oxidative stability of frying oils and fried instant noodles

Oxidative stability of frying oils was determined using an 892 Rancimat (Metrohm, Switzerland) with the following conditions: 5 g of frying oils, deionized water of 60 mL, air flow rate of 20 L/h, and heating temperature of 110 ℃.

According to the manual of Racimat from Metrohm (2023), typical examples of applications for direct measurements of oxidative stability include butter cookies, instant noodles, potato chips, microwave popcorn, and nuts. The only preparation required is a reduction in the size of the sample particles. Moreover, its feasibility had been evaluated by Wei and Zhou (1999) where fried instant noodles were taken directly for the measurements of oxidative stability. In the work, thus, fried instant noodle blocks were chopped into crumbs with particle sizes of less than 5 mm. The oxidative stability of fried noodle blocks was also determined using an 892 Rancimat (Metrohm, Switzerland) with the following conditions: 3 g of fried instant noodle crumbs, deionized water of 60 mL, air flow rate of 10 L/h, and heating temperature of 120 ℃.

Induction period (IP) of each sample was recorded to express its oxidative stability.

2.11. Statistical analysis

All experiments were independently conducted at least in duplicate. Data were presented with mean plus and minus standard deviation. Significance with *p*-value of 0.05 as cut-off was analyzed with Duncan multiple comparison using SPSS 20.0. Principal component analysis (PCA) was statistically analyzed using The Unscrambler X (version 10.4, CAMO software, Norway).

3. Results and discussion

3.1. Effects of tea polyphenols on acid value of palm oils during batch frying

The acid value (AV) of frying oils is usually used as one of indicators for discarding frying oils (Table S1). In Germany and Japan, the cutoff point is required to be less than 2.0 mg KOH/g. In China, it is required to be less than 5.0 mg KOH/g regulated by the safety standard (GB 2716–2018, 2018) of edible oils, but not more than 1.8 mg KOH/g regulated by the safety standard (GB 17400–2015, 2015) of instant noodles. Thus, the effects of TP (50–200 mg/kg) on AV of palm oils during batch frying of instant noodles were investigated with palm oils without addition of exogenous antioxidants as negative control and palm oils with addition of 100 mg/kg of TBHQ as positive control (Fig. 1A).

Regardless of whether or not antioxidants were added, and the amount added, the AV of palm oils increased significantly ($p < 0.05$) with the prolongation of frying time. However, there was no significant ($p > 0.05$) difference between the AVs of palm oils supplemented with TP and TBHQ during batch frying. The causes of AV increase during frying could be the small molecular acids that are from the decomposition of hydroperoxides formed by the oxidation of oils and fats, and the free fatty acids that are from the hydrolysis of glycerides due to the introduction of moisture by foods. However, the composition analysis of fatty acids (Figure S1 and Table 1) and glycerides (Fig. 2) showed that no small molecular acids were detected, which is attributed to the easy volatilization of small molecular acids and steam distillation. Thus, the contribution of small molecular acids was tiny in AV increase during frying. Two fresh wet noodle blocks (100 g/block) with a moisture content of 30 % were fried at each frying cycle, which was equivalent to the introduction of 60 g of water moisture into frying oils. Finished instant noodles had a moisture content of 2 ~ 3 %. The increase of AV of palm oils without antioxidant addition (negative control) was only 0.12 mg KOH/g within the first 6 h of frying, which indicates that more than 90 % moisture in wet noodle blocks was evaporated rapidly and directly at frying temperature and only small part of moisture participated in the hydrolysis of glycerides. The composition analysis of glycerides (Fig. 2) showed that as the prolongation of frying time, the relative contents of free fatty acids and diglycerides increased, while the relative contents of triglycerides decreased, which further indicates that the hydrolysis of glycerides due to the introduction of moisture by foods was the main cause of AV increase during frying.
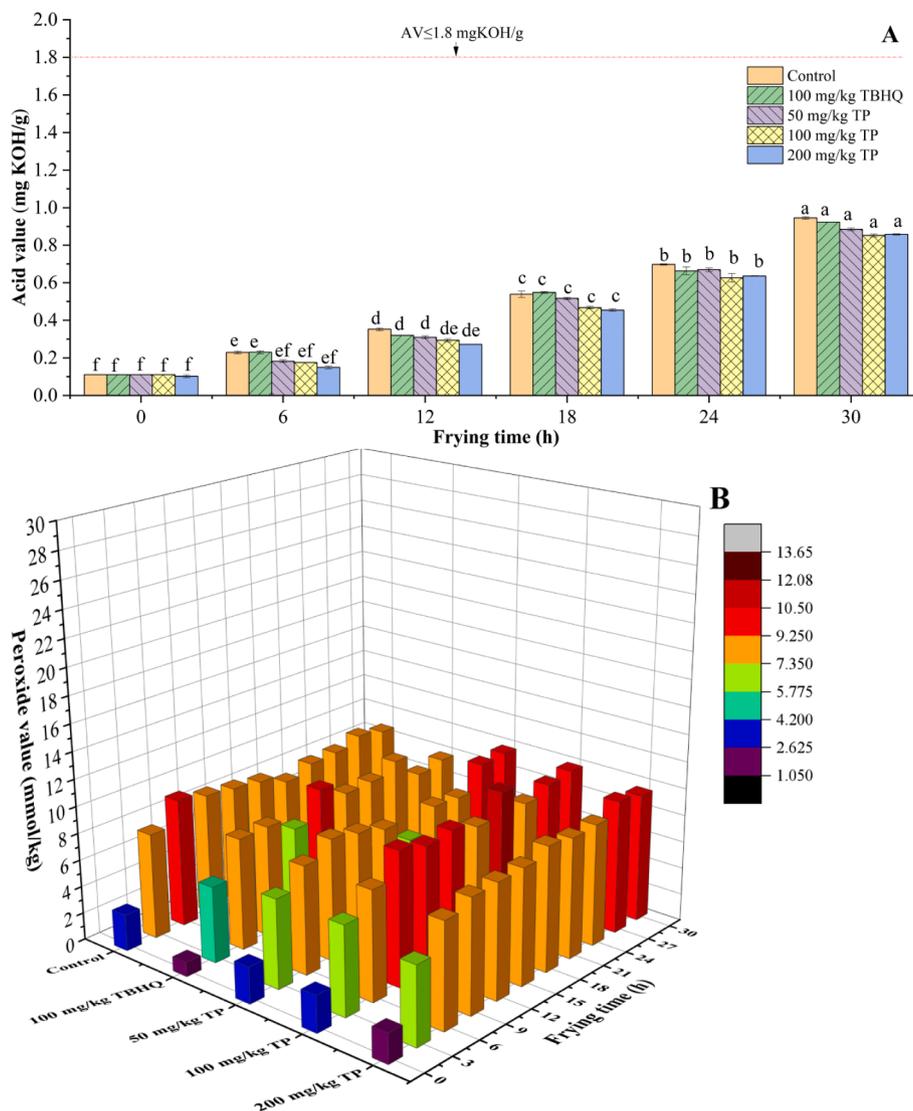
Fig. 1. Effects of tea polyphenols (TP) and tertiary butylhydroquinone (TBHQ) on acid value (A), peroxide value (B), *p*-anisidine value (C), total oxidation value (D), the contents of total polar compounds (E) of palm oils during batch frying. The different lowercase letters indicated that the values in each graph have significant difference ($p < 0.05$).

3.2. Effects of tea polyphenols on peroxide value of palm oils during batch frying

The international Food Standards (CODEX, 2023) point out that the peroxide value (PV) of refined oils should be not more than 5 mmol/kg. The safety standard (GB 2716-2018) of edible oils in China points out that the PV of edible oils should be not more than 9.85 mmol/kg. Neither doesn't point out the requirement for the PV of oils and fats during frying. The safety standard (GB 17400-2015) of instant noodles in China points out that the PV of oils and fats in instant noodles should be not more than 9.85 mmol/kg. Thus, the effects of TP (50–200 mg/kg) on the PV of palm oils during batch frying of instant noodles were investigated with palm oils without addition of exogenous antioxidants as negative control and palm oils with addition of 100 mg/kg of TBHQ as positive control (Fig. 1B).

Regardless of whether or not antioxidants were added and the amount added, the PV of palm oils increased significantly ($p < 0.05$) within the first 6 h of frying, and showed a fluctuating change between 7.27 and 10.66 mmol/kg after 6 h. The fluctuation of PV is attributed to the instability of hydroperoxides resulting in simultaneous occurrence of

formation and decomposition of hydroperoxides during frying (Gertz, 2014). Within the first 6 h of frying, the PVs of palm oils with TP presented a decreasing trend with the amount of TP increasing from 50 to 200 mg/kg, and was less than that of both negative and positive control. For example, when frying time reached 6 h, the PVs were 8.02 mmol/kg for palm oils with 50 mg/kg of TP, 8.08 mmol/kg for palm oils with 100 mg/kg of TP, 7.79 mmol/kg for palm oils with 200 mg/kg of TP, 8.26 mmol/kg for positive control, and 9.51 mmol/kg mmol/kg for negative control, respectively. This indicates that the addition of TP and TBHQ can effectively inhibit the increase of PV and the performance of TP was better than that of TBHQ.

3.3. Effects of tea polyphenols on p-anisidine value of palm oils during batch frying

The decomposition of hydroperoxides generates a large amount of small molecular components such as aldehydes and carbonyls (Gertz, 2014). *p*-Anisidine value (*p*-AnV) is a typical indicator for evaluation of secondary oxidative products. The effects of TP (50–200 mg/kg) on *p*-AnV of palm oils during batch frying of instant noodles were
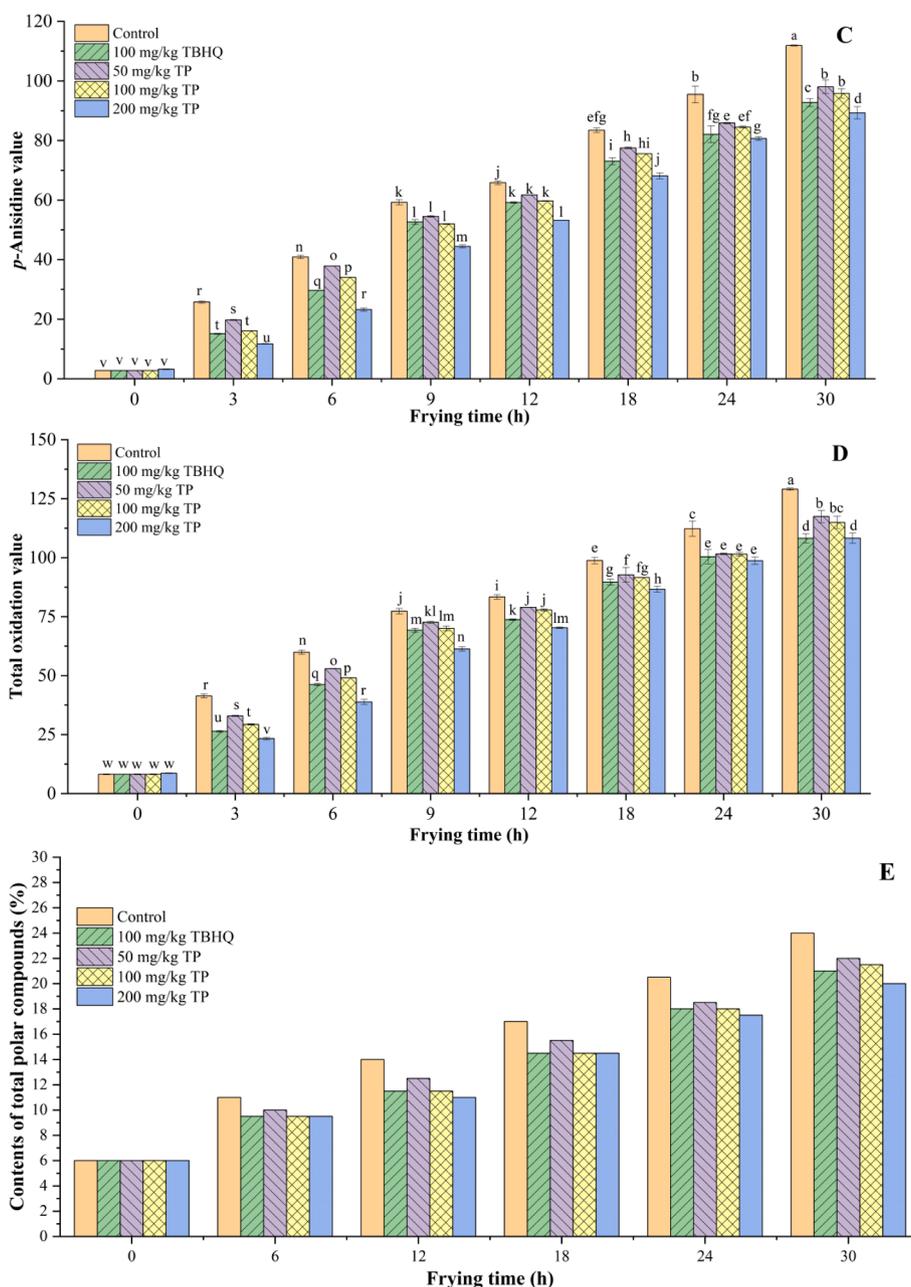
Fig. 1. (continued).

investigated with palm oils without addition of exogenous antioxidants as negative control and palm oils with addition of 100 mg/kg of TBHQ as positive control (Fig. 1C).

Regardless of whether or not antioxidants were added and the amount added, the *p*-AnV of palm oils increased significantly ($p < 0.05$) during 30 h of frying. The *p*-AnV of palm oils increased from 2.77 to 23.24–40.90 within the first 6 h of frying, which further confirms the simultaneous occurrence of formation and decomposition of hydroperoxides during frying. Compared to negative control, palm oils with TP and positive control both had smaller *p*-AnV. Within the first 6 h of frying, the performance of TP and TBHQ in inhibiting *p*-AnV increase followed the order: 200 mg/kg of TP > 100 mg/kg of TBHQ > 100 mg/kg of TP > 50 mg/kg of TP. Although 200 mg/kg of TP still remained the best performance in inhibiting *p*-AnV increase with the further prolongation of frying time from 9 to 30 h, the performance of 100 mg/kg of TP and 100 mg/kg of TBHQ tended to be comparable.

3.4. Effects of tea polyphenols on total oxidation value of palm oils during batch frying

Considering the instability of hydroperoxides especially under high-temperature heating and frying conditions as well as expression of *p*-AnV only as secondary oxidation products of oils and fats, total oxidation value (TOTOX) is proposed to be an indicator that can more comprehensively evaluate the degree of oxidation of oils and fats. The effects of TP (50–200 mg/kg) on TOTOX of palm oils during batch frying of instant noodles were investigated with palm oils without addition of exogenous antioxidants as negative control and palm oils with addition of 100 mg/kg of TBHQ as positive control (Fig. 1D).

After 30 h of frying, the TOTOX of palm oils increased from initial 8.16–8.61 to 108.20–129.06, and the significant lower TOTOX of palm oils with TP and positive control than negative control also indicates the effectiveness of TP and TBHQ in inhibiting the oxidation of palm oils during batch frying. With the first 12 h of frying, 200 mg/kg of TP had

Table 1
Fatty acid composition of palm oils during batch frying.

Fatty acids	Before frying	After 12 h of frying						After 30 h of frying				
		A	B	C	D	E		A	B	C	D	E
Lauric acid	0.09 ± 0.00a	0.09 ± 0.02a	0.08 ± 0.00a	0.09 ± 0.00a	0.08 ± 0.00a	0.08 ± 0.00a		0.09 ± 0.02a	0.09 ± 0.01a	0.07 ± 0.00a	0.09 ± 0.00a	0.08 ± 0.00a
Myristic acid	0.79 ± 0.00c	0.82 ± 0.01ab	0.82 ± 0.01ab	0.79 ± 0.03c	0.81 ± 0.01ab	0.82 ± 0.00ab		0.84 ± 0.01a	0.82 ± 0.01ab	0.84 ± 0.01a	0.84 ± 0.01a	0.84 ± 0.02a
Palmitic acid	42.54 ± 0.05h	43.73 ± 0.00f	43.75 ± 0.03f	43.87 ± 0.02e	43.73 ± 0.02f	43.52 ± 0.01g		45.27 ± 0.04c	45.13 ± 0.03d	45.56 ± 0.04a	45.42 ± 0.02b	45.05 ± 0.01d
Stearic acid	5.00 ± 0.07d	5.03 ± 0.00cd	5.00 ± 0.00d	4.97 ± 0.00d	4.96 ± 0.01d	4.98 ± 0.03d		5.15 ± 0.01ab	5.10 ± 0.01bc	5.20 ± 0.01a	5.13 ± 0.03ab	5.20 ± 0.00a
Oleic acid	41.82 ± 0.01a	41.33 ± 0.02d	41.37 ± 0.02d	41.38 ± 0.01cd	41.46 ± 0.00c	41.62 ± 0.00b		40.97 ± 0.02f	41.01 ± 0.06f	41.01 ± 0.00f	41.03 ± 0.03f	41.23 ± 0.04e
Linoleic acid	8.81 ± 0.04a	8.03 ± 0.01b	8.06 ± 0.02b	7.91 ± 0.02d	7.96 ± 0.01cd	8.01 ± 0.03bc		6.80 ± 0.00f	6.89 ± 0.01e	6.41 ± 0.00i	6.52 ± 0.04h	6.62 ± 0.01g
SFA	48.43 ± 0.06i	49.66 ± 0.04f	49.65 ± 0.02f	49.73 ± 0.03e	49.58 ± 0.02g	49.40 ± 0.02h		51.34 ± 0.02c	51.14 ± 0.03d	51.67 ± 0.03a	51.48 ± 0.03b	51.18 ± 0.01d
MUFA	41.82 ± 0.01a	41.33 ± 0.02bc	41.37 ± 0.02bc	41.38 ± 0.02b	41.46 ± 0.01b	41.62 ± 0.01a		40.97 ± 0.03d	41.01 ± 0.04d	41.01 ± 0.01d	41.03 ± 0.02d	41.23 ± 0.02c
PUFA	9.36 ± 0.05a	8.60 ± 0.03b	8.60 ± 0.03b	8.50 ± 0.02c	8.57 ± 0.02bc	8.58 ± 0.03b		7.30 ± 0.02e	7.47 ± 0.02d	6.95 ± 0.02h	7.10 ± 0.03g	7.19 ± 0.01f
UFA	51.18 ± 0.08a	49.93 ± 0.03de	49.96 ± 0.02d	49.88 ± 0.01f	50.03 ± 0.01c	50.20 ± 0.02b		48.27 ± 0.12i	48.48 ± 0.02g	47.96 ± 0.13k	48.13 ± 0.03j	48.42 ± 0.00h
Other	0.99 ± 0.07	0.98 ± 0.06	0.93 ± 0.05	0.97 ± 0.01	1.00 ± 0.02	0.98 ± 0.07		0.90 ± 0.04	0.96 ± 0.04	0.91 ± 0.02	0.98 ± 0.03	0.96 ± 0.05

SFA: saturated fatty acids; MUFA: monounsaturated fatty acids; PUFA: polyunsaturated fatty acids; UFA: unsaturated fatty acids; A: palm oils without addition of exogeneous antioxidants; B: palm oils with 100 mg/kg of TBHQ; C: palm oils with 50 mg/kg of tea polyphenols; D: palm oils with 100 mg/kg of tea polyphenols; E: palm oils with 200 mg/kg of tea polyphenols. The different lowercase letters indicated that the values in each row have significant difference ($p < 0.05$).

the best performance in inhibiting TOTOX increase, followed by 100 mg/kg of TBHQ. However, as the frying time extended from 18 to 30 h, the performance of 200 mg/kg of TP and 100 mg/kg of TBHQ in inhibiting TOTOX increase tended to be comparable. In addition, within the first 9 h of frying, the performance of TP in inhibiting TOTOX increase enhanced as the concentrations of TP increased. However, the performance of 100 mg/kg of TP and 50 mg/kg of TP tended to be comparable with the further prolongation of frying time from 12 to 30 h, which is attributed to the gradual losses of TP and transformation products as well as Ts and TTs (discussed in Section 3.9).

3.5. Effects of tea polyphenols on total polar compounds in palm oils during batch frying

The total polar compounds (TPC) of oils and fats increases during frying due to the occurrence of oxidation, polymerization, and decomposition of oils and fats (Farhoosh et al., 2009; Farhoosh and Tavassoli-Kafrani, 2010). Thus, TPC are used as one of indicators for evaluating the degree of oxidative deterioration of frying oils, which is required to be not more than 24–30 % depending on different countries (Donner and Richter, 2000; Osawa and Gonçalves, 2012). The effects of TP (50–200 mg/kg) on TPC in palm oils during batch frying of instant noodles were investigated with palm oils without addition of exogenous antioxidants as negative control and palm oils with addition of 100 mg/kg of TBHQ as positive control (Fig. 1E).

Regardless of whether or not antioxidants were added and the amount added, the TPC in palm oils increased significantly ($p < 0.05$) during 30 h of frying, but none of them exceeded 24–30 %. The initial TPC of palm oils was 6 %. After 30 h of frying, the TPC increased by 18 % for negative control, 15 % for positive control, 16 % for palm oils with 50 mg/kg of TP, 15.5 % for 100 mg/kg of TP, and 14 % for 200 mg/kg of TP. The whole performance of TP and TBHQ followed the order: 200 mg/kg of TP > 100 mg/kg of TBHQ ≈ 100 mg/kg of TP > 50 mg/kg of TP.

3.6. Effects of tea polyphenols on fatty acid composition of palm oils during batch frying

The effects of TP (50–200 mg/kg) on fatty acid composition of palm oils during batch frying of instant noodles were investigated with palm oils without addition of exogenous antioxidants as negative control and palm oils with addition of 100 mg/kg of TBHQ as positive control (Figure S1 and Table 1).

The main fatty acids of palm oils were palmitic acid (42.54 %), oleic acid (41.82 %), linoleic acid (8.81 %), stearic acid (5.00 %), and small amounts of lauric acid and myristic acid. Palm oils had 48.43 % of saturated fatty acids and 41.82 % of monounsaturated fatty acid, which is the one of causes for its high oxidative stability. During 30 h of frying, the relative contents of myristic acid, palmitic acid, and stearic acid increased significantly ($p < 0.05$), while the relative contents of oleic acid and linoleic acid decreased significantly ($p < 0.05$). The insignificant change of the relative content of lauric acid could be ascribed to its tiny amount in fatty acid profile of palm oils. Compared to the fatty acid profile of negative control, the fatty acid profiles of palm oils with TP and TBHQ showed that 200 mg/kg of TP and 100 mg/kg of TBHQ both effectively inhibited the decrease of the relative contents of unsaturated fatty acids and the increase of the relative contents of saturated fatty acids due to the reduced degree of oxidation, which is consistent with the results of AV, PV, p-AnV, TOTOX, and TPC. In addition, the performance of 200 mg/kg of TP and 100 mg/kg of TBHQ was comparable in affecting fatty acid profile. However, 50 mg/kg of TP and 100 mg/kg of TP did not significantly affect fatty acid profile.

3.7. Effects of tea polyphenols on glyceride composition of palm oils during batch frying

The changes of glyceride composition of palm oils with and without TP and TBHQ during frying are shown in Fig. 2.

After 30 h of frying, the relative contents of free fatty acids and diglycerides in palm oils increased significantly ($p < 0.05$) from initial 2.20–2.76 to 3.34–3.59 % and 4.44–5.02 to 7.35–8.02 %, respectively, while the relative contents of triglycerides in palm oils decreased significantly ($p < 0.05$) from initial 92.61–92.90 % to 88.25–89.13 %.
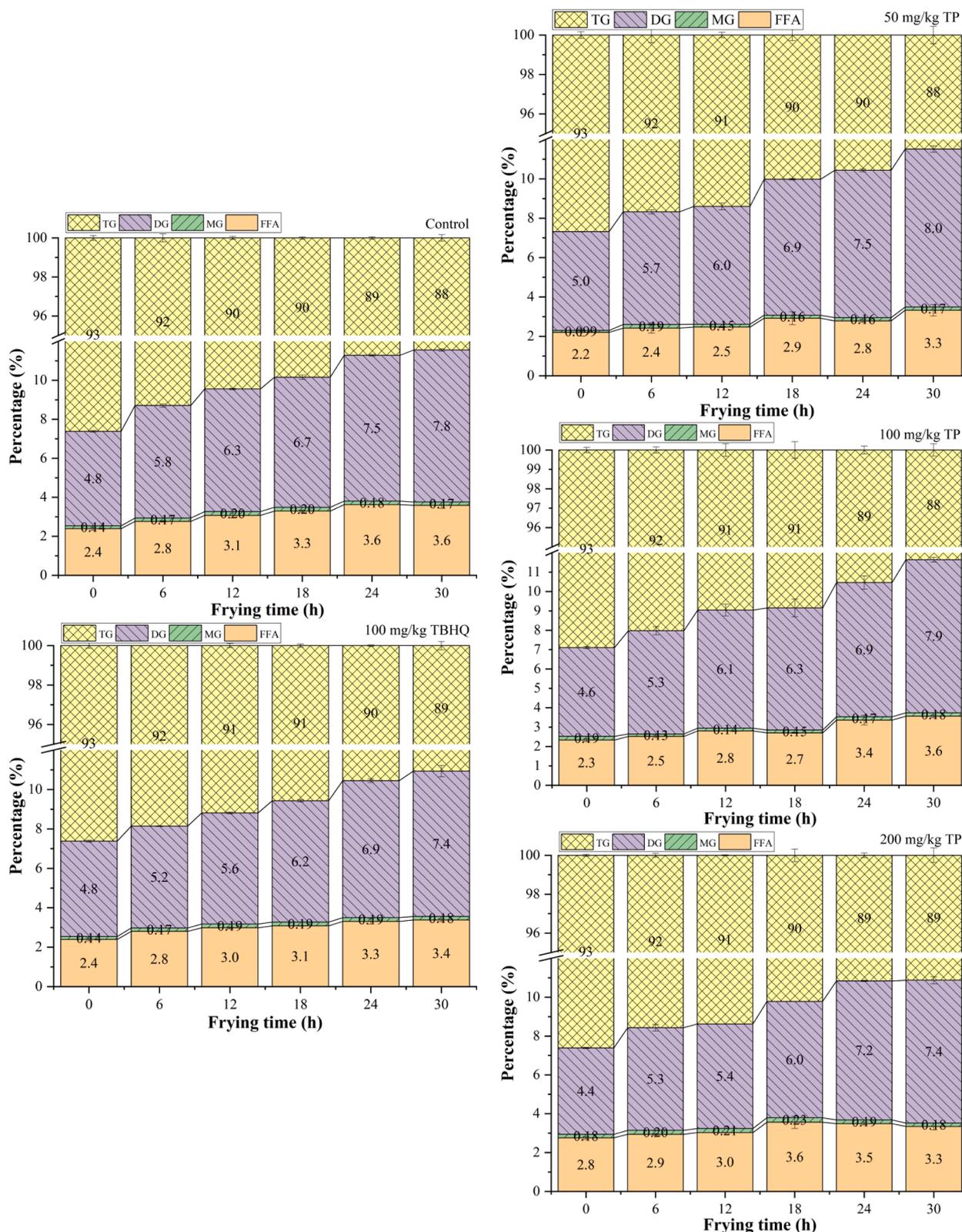
Fig. 2. Effects of tea polyphenols (TP) and tertiary butylhydroquinone (TBHQ) on glyceride composition of palm oils during batch frying (FFA: free fatty acids; MG: monoglycerides; DG: diglycerides; TG: triglycerides). The different lowercase letters indicated that the values have significant difference ($p < 0.05$).

This indicates the hydrolysis of triglycerides into diglycerides and free fatty acids during frying. The relative contents of monoglycerides in palm oils remained almost unchanged, which could be because the hydrolysis of diglycerides into monoglycerides and free fatty acids and the hydrolysis of monoglycerides into glycerol and free fatty acids were

equivalent as well as the degree of oxidation of palm oils was low (only 3.5 % decrease in the relative contents of triglycerides). There was no significant difference among the glyceride composition of the five palm oils (negative control, positive control, and palm oils with 50, 100, or 200 mg/kg of TP).

3.8. Principal component analysis of palm oils

To investigate the quality changes during batch frying of palm oils added with different antioxidants, principal component analysis was carried out and the results are shown in Fig. 3.

The contribution of PC1 was 100 %, indicating that the extracted principal components can represent most of information from the original sample. Fig. 3A illustrated a good differentiation of palm oils with different frying times, indicating that palm oils underwent significant quality changes during frying. Fig. 3B showed the effect of different indicators on the samples, in which TG decreased but AV, *p*-AnV, TOTOX, TPC, FFA, and DG increased with the prolongation of frying time, while the change in MG was not apparent. Obvious differences were observed in the PV of palm oils between the before and during batch frying but was not in the PV of palm oils between the different times of batch frying, which is attributed to the decomposition of hydroperoxides at the frying temperature. It was noteworthy that palm oils showed a left–right distribution in Fig. 3A with ones with TP and positive control (with TBHQ) on the left but negative control on the right, which suggests that the negative control encountered more severe quality deterioration during batch frying. Overall, 200 mg/kg of TP had better performance in protecting the quality of palm oils during batch frying.

3.9. Losses of tea polyphenols, tocopherols, and tocotrienols in palm oils during batch frying

The losses of TP and the effects of TP on the losses of Ts and TTs in

palm oils during batch frying are presented in Fig. 4 with palm oils without addition of exogenous antioxidants as negative control and palm oils with addition of 100 mg/kg of TBHQ as positive control. After 3 h of frying, the losses of TP and TBHQ in palm oils with 50, 100, and 200 mg/kg of TP and 100 mg/kg of TBHQ reached 100, 100, 91.88, and 90.49 %, respectively (Fig. 4A). After 6 h of frying, the losses of TP and TBHQ in palm oils with 200 mg/kg of TP and 100 mg/kg of TBHQ also reached 100 %, respectively. The rapid loss of TBHQ in palm oils during frying is due to easy volatilization, steam distillation, and partial transformation as reflected by high-performance liquid chromatography (HPLC) analysis (Figure S2), which is consistent with previous reports (Hamama and Nawar, 1991; Li et al., 2014, 2017). Same as the losses of most of natural antioxidants, the loss of TP under frying conditions could result from transformation rather than volatilization. To clarify it, 200 g of palm oils with 200 mg/kg of TP was heated at 150 ℃ for 4 h under the reflux condensation mode. Results (Figure S3) showed no volatiles was observed on the surface of condenser, but the color of palm oils became darker after heating, which indicates that transformation was the main pathway for the loss of TP under frying conditions as reflected by HPLC analysis (Figure S4). To further reveal the transformation products of TP, palm oils with 200 mg/kg of TP were taken out after 6 h of frying and analyzed using an ultra-high-performance liquid chromatography-mass spectrometry (UPLC-MS). Molecular weights of 290 (EC), 296, 306 (EGC), 320, 448, 458 (EGCG), 472, 526, 578, 626, 642, and 794 were detected as shown in Figure S5. This is consistent with previous reports (Li et al., 2006; Sang et al., 2003; Valcic et al., 1999, 2000) where the transformation of TP has been reported through the following pathways: double bond between C4′ and C5′ on B ring of EGC is oxidized to double
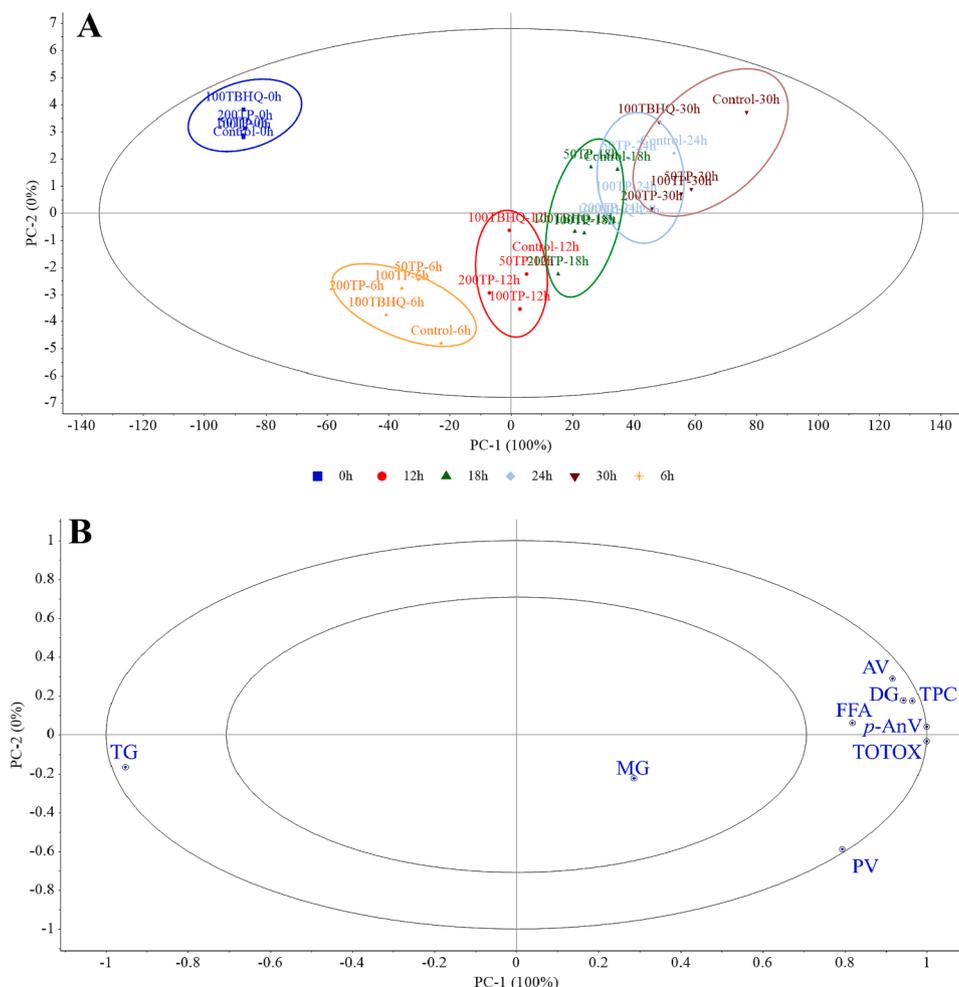
Fig. 3. Principal component analysis scores (A) and loadings (B) of palm oils.
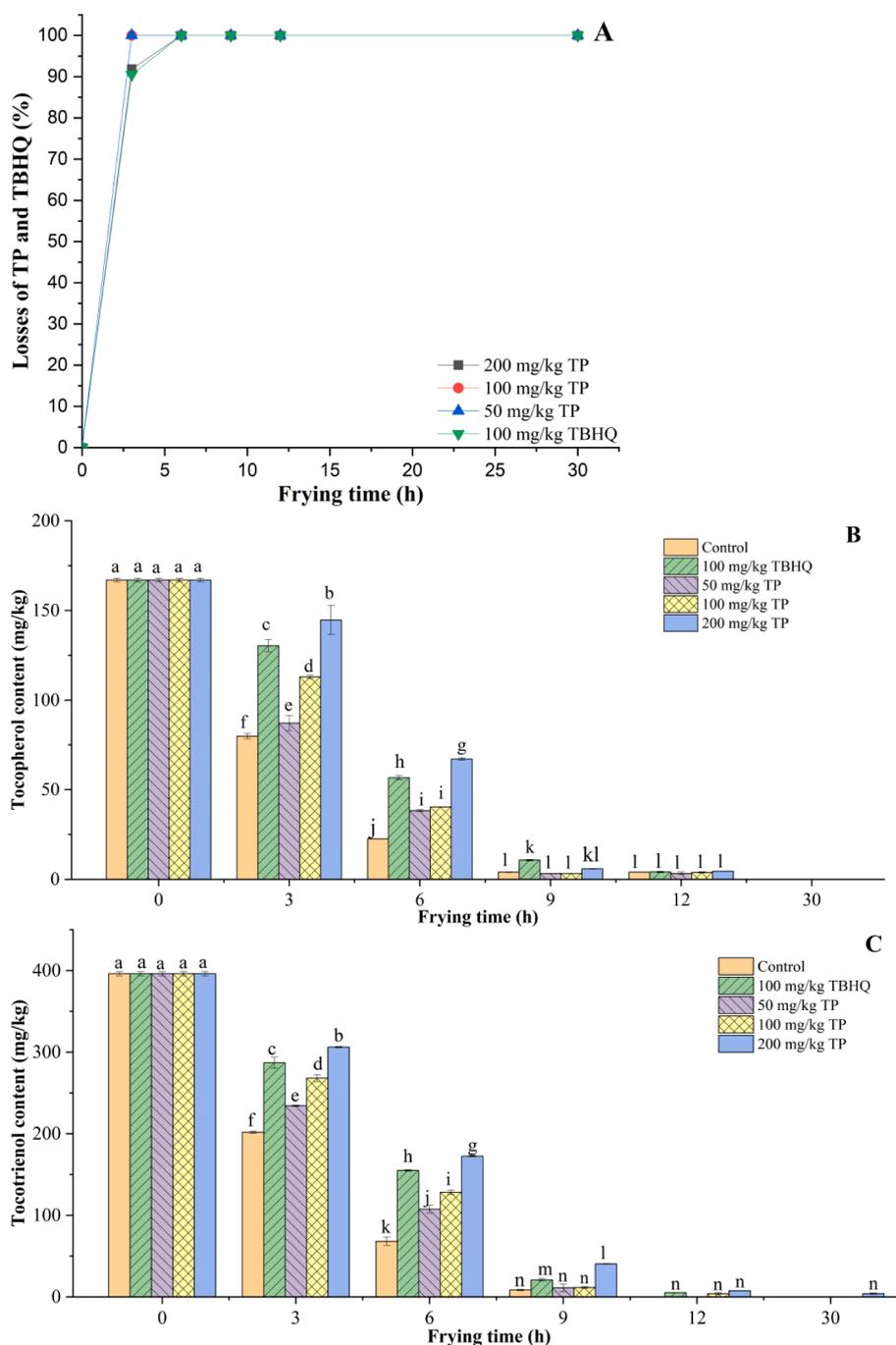
Fig. 4. Losses of tea polyphenols (TP) and tertiary butylhydroquinone (TBHQ) (A) and effects of TP and TBHQ on tocopherols (B) and tocotrienols (C) in palm oils during batch frying. The different lowercase letters indicated that the values in each graph have significant difference ($p < 0.05$).

carboxyl groups under the action of radicals, followed by forming seven-membered ring of anhydride; B ring of EGC can also be oxidized and polymerized to double flavanone (Figure S6). The transformation of EGCG is same as that of EGC. Under the action of radicals, hydroxyl group at C3′ on B ring of EC are etherified at C8 on A ring of EC; two EC molecules are polymerized to procyanidins through linkage between C6′ on B ring and C6/C8 on A ring, which can be further oxidized to ethers (Figure S7).

Regardless of whether or not antioxidants were added and the amount added, the contents of Ts and TTs in palm oils decreased significantly ($p < 0.05$) with the prolongation of frying time and were almost not left after 9 h of frying (Fig. 4B and C). The addition of TP and TBHQ, especially 200 mg/kg of TP and 100 mg/kg of TBHQ, effectively

reduced the losses of Ts within the first 6 h of frying and the losses of TTs within the first 9 h of frying. The protective effects of TP and TBHQ on losses of Ts and TTs in palm oils during frying followed the order: 200 mg/kg of TP > 100 mg/kg of TBHQ > 100 mg/kg of TP > 50 mg/kg of TP.

3.10. Effects of tea polyphenols on induction periods of palm oils and fried instant noodles

The effects of TP on IPs of palm oils and fried instant noodles are presented in Fig. 5. The addition of 100 mg/kg of TBHQ and 50, 100, and 200 mg/kg of TP enhanced the IPs of palm oils not yet used for frying from initial 15.54 to 19.95, 16.89, 22.08, and 26.89 h,
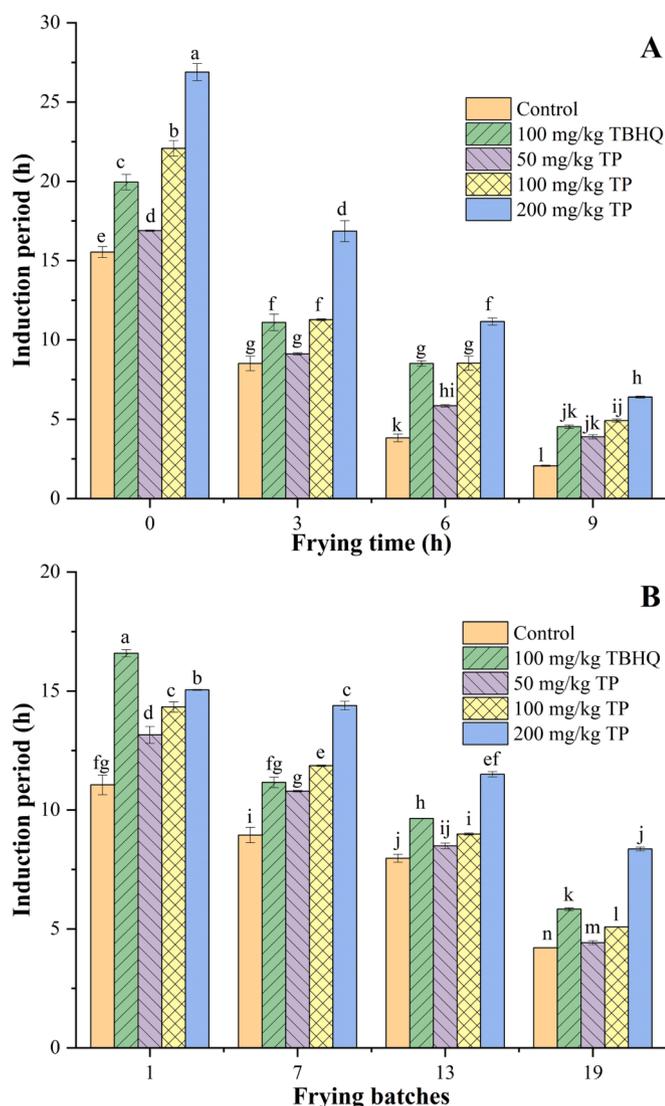
Fig. 5. Effects of tea polyphenols (TP) and tertiary butylhydroquinone (TBHQ) on induction periods of palm oils (A) and fried instant noodles (B). The different lowercase letters indicated that the values in each graph have significant difference ($p < 0.05$).

respectively (Fig. 5A). After 3 h of frying, negative control, positive control, and palm oils with 50, 100, and 200 mg/kg of TP had IPs of 8.51, 11.10, 9.12, 11.28, and 16.86 h, respectively. After 9 h of frying, negative control, positive control, and palm oils with 50, 100, and 200 mg/kg of TP had IPs of 2.07, 4.53, 3.90, 4.92, and 6.40 h, respectively. These results indicate that the addition of TBHQ and TP enhanced the IPs of palm oils and the enhanced degree increased with the increased concertation of TP.

The addition of 100 mg/kg of TBHQ and 50, 100, and 200 mg/kg of TP significantly enhanced the IPs of fried instant noodles (Fig. 5B). Fried instant noodles from first cycle of frying had IPs of 11.06 (negative control), 16.59 (positive control), 13.16 (50 mg/kg of TP), 14.33 (100 mg/kg of TP), and 15.05 (200 mg/kg of TP) h, respectively. The best performance of them in improving IPs of fried instant noodles from first cycle of frying was 100 mg/kg of TBHQ, followed by 200 mg/kg of TP, 100 mg/kg of TP, 50 mg/kg of TP. However, with the increase of frying cycles, 200 mg/kg of TP showed better performance in improving IPs of fried instant noodles than 100 mg/kg of TBHQ. This is because easy volatilization and steam distillation led TBHQ to be rapidly lost, reducing the protective effects on palm oils and fried instant noodles, while transformation products of TP still have antioxidative activities,

extending the IPs of palm oils and fried instant noodles.

The protective effects of TP and TBHQ on palm oils and fried instant noodles followed the order: 200 mg/kg of TP > 100 mg/kg of TBHQ > 100 mg/kg of TP > 50 mg/kg of TP.

3.11. Effects of tea polyphenols on color of fried instant noodles

The effects of tea polyphenols on color of fried instant noodles are showed in Figure S8 with no addition of exogenous antioxidants as negative control and 100 mg/kg of TBHQ as positive control. Results showed that there was significant difference among fried instant noodles from the five palm oils (negative control, positive control, and palm oils with 50, 100, or 200 mg/kg of tea polyphenols) under the naked-eye observation. Zhang and Chen (2014) pointed out that the generation of color of foods during frying is mainly due to nonenzymatic browning such as Maillard reactions which is associated with the nature of foods for frying and parameter conditions of frying. Thus, the addition of tea polyphenols and TBHQ did not affect the color of fried instant noodles.

4. Conclusions

TP was added into batch frying of instant noodles to stabilize palm oils, reduce the losses of endogenous vitamin E, and improve the oxidative stability of fried instant noodles with TBHQ as comparison. 200 mg/kg of TP had better capacity of stabilizing palm oils, inhibiting the oxidization of fried instant noodles, and protecting Ts and TTs from being lost than 50 and 100 mg/kg of TP and 100 mg/kg of TBHQ. Palm oils with TP addition became darker during heating due to the formation of transformation products of TP. TP and TBHQ in palm oils were rapidly lost during batch frying with transformation being the main pattern for TP loss and volatilization being the main pattern for TBHQ loss.

CRediT authorship contribution statement

Jun Li: Formal analysis, Writing – original draft, Funding acquisition. **Fangbo Yuan:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Software, Visualization. **Jiayou Teng:** Resources, Supervision. **Fang Li:** Resources, Supervision. **Penghui Zhou:** Resources, Supervision. **Yanlan Bi:** Conceptualization, Funding acquisition, Methodology, Project administration, Supervision, Validation, Writing – review & editing.

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.

Data availability

Data will be made available on request.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fochx.2023.101049.

References

Absalome, M. A., Massara, C. C., Alexandre, A. A., Gervais, K., Chantal, G. G. A., Ferdinand, D., … Jean-Paul, C. (2020). Biochemical properties, nutritional values, health benefits and sustainability of palm oil. *Biochimie, 178*, 81–95.

Akhtar, H., Tariq, I., Mahmood, S., Hamid, S., & Khanum, R. (2012). Effect of antioxidants on stability, nutritional values of refined sunflower oil during accelerated storage and thermal oxidation in frying. *Bangladesh Journal of Scientific and Industrial Research, 47*, 223–230.

Aladedunye, F. A. (2014). Natural antioxidants as stabilizers of frying oils. *European Journal of Lipid Science and Technology, 116*, 688–707.

AOCS. Acid Value of Fats and Oils. In Official Methods and Recommended Practices of the American Oil Chemists' Society, 7th ed.; Champaign, IL: AOCS Press. Official Method Cd 3d-63, 2017.

AOCS. p-Anisidine Value. In Official Methods and Recommended Practices of the American Oil Chemists' Society, 7th ed.; Champaign, IL: AOCS Press. Official Method Cd 18-90, 2017.

AOCS. Peroxide Value, Acetic Acid, Isooctane Method. In Official Methods and Recommended Practices of the American Oil Chemists' Society, 7th ed.; Champaign, IL: AOCS Press. Official Method Cd 8b-90, 2017.

AOCS. Preparation of Methyl Esters of Fatty Acids. In Official Methods and Recommended Practices of the American Oil Chemists' Society, 7th ed.; Champaign, IL: AOCS Press. Official Method Ce 2-66, 2017.

Chung, J., Lee, Y., & Choe, E. (2006). Effects of sesame oil addition to soybean oil during frying on the lipid oxidative stability and antioxidants contents of the fried products during storage in the dark. *Journal of Food Science, 71*, C222–C226.

CODEX. https://www.fao.org/fao-who-codexalimentarius/sh-proxy/en/?lnk=1&url=https%253A%252F%252Fworkspace.fao.org%252Fsites%252Fcodex%252FStandards%252FCXS%2B210-1999%252FCXS_210e.pdf, 2023 [access April 18, 2022].

Donner, M. G., & Richter, W. O. (2000). 3rd International symposium on deep-fat frying—optimal operation. *European Journal of Lipid Science and Technology, 102*, 306–308.

Facts and Factors. Global Demand for Instant Noodles Market Size. https://www.globenewswire.com/news-release/2022/01/17/2367865/0/en/Global-Demand-for-Instant-Noodles-Market-Size-Poised-to-Reflect-6-8-CAGR-by-2028-to-Reach-USD-74-85-Billion-Facts-Factors.html, 2022 [access April 1, 2022].

Farhoosh, R., Einafshar, S., & Sharayei, P. (2009). The effect of commercial refining steps on the rancidity measures of soybean and canola oils. *Food Chemistry, 115*, 933–938.

Farhoosh, R., & Tavassoli-Kafrani, M. H. (2010). Polar compounds distribution of sunflower oil as affected by unsaponifiable matters of Bene hull oil (BHO) and tertiary-butylhydroquinone (TBHQ) during deep-frying. *Food Chemistry, 122*, 381–385.

GB 17400-2015. National Food Safety Standards: Instant Noodles, 2015.

GB 2716-2018. National Food Safety Standards: Edible Oils, 2018.

Gertz, C. (2014). Fundamentals of the frying process. *European Journal of Lipid Science and Technology, 116*, 669–674.

Gulia, N., Dhaka, V., & Khatkar, B. S. (2014). Instant noodles: Processing, quality, and nutritional aspects. *Critical Reviews in Food Science and Nutrition, 54*, 1386–1399.

Guo, T., Song, D., Cheng, L., & Zhang, X. (2019). Interactions of tea catechins with intestinal microbiota and their implication for human health. *Food Science and Biotechnology, 28*, 1617–1625.

Hamama, A. A., & Nawar, W. W. (1991). Thermal decomposition of some phenolic antioxidants. *Journal of Agricultural and Food Chemistry, 39*, 1063–1069.

Kiran, C. R., Sasidharan, I., Soban Kumar, D. R., & Sundaresan, A. (2015). Influence of natural and synthetic antioxidants on the degradation of Soybean oil at frying temperature. *Journal of Food Science and Technology, 52*, 5370–5375.

Li, D., Wan, X., Yang, C., & Wang, H. (2006). Oxidation mechanism of tea catechins (in Chinese). *Natural Product Research and Development, 18*, 171–181.

Li, J., Bi, Y., Liu, W., Sun, S., Liu, C., & Ma, S. (2014). Effect of acid value on TBHQ and BHT losses in heating oils: Identification of the esterification products of TBHQ and free fatty acids. *Journal of the American Oil Chemists' Society, 91*, 1763–1771.

Li, J., Bi, Y., Yang, H., & Wang, D. (2017). Antioxidative properties and interconversion of tert-butylhydroquinone and tert-butylquinone in soybean oils. *Journal of Agricultural and Food Chemistry, 65*, 10598–10603.

Lorenzo, J. M., Batlle, R., & Gomez, M. (2014). Extension of the shelf-life of foal meat with two antioxidant active packaging systems. *LWT-Food Science and Technology, 59*, 181–188.

Lorenzo, J. M., Sineiro, J., Amado, I. R., & Franco, D. (2014). Influence of natural extracts on the shelf life of modified atmosphere-packaged pork patties. *Meat Science, 96*, 526–534.

Metrohm. https://www.metrohm.com/en/products/stability-measurement/Stability-measurement-Rancimat-Thermomat.html, 2023 [access April 1, 2023].

Musial, C., Kuban-Jankowska, A., & Gorska-Ponikowska, M. (2020). Beneficial properties of green tea catechins. *International Journal of Molecular Sciences, 21*, 1744.

Osawa, C. C., & Gonçalves, L. A. G. (2012). Changes in breaded chicken and oil degradation during discontinuous frying with cottonseed oil. *Food Science and Technology, 32*, 692–700.

Park, E., Kim, H. Y., Shin, H. Y., Jeon, Y. I., Kim, J. M., Kim, S., & Kim, J. Y. (2019). Change in textural properties, starch digestibility, and aroma of nonfried instant noodles by substitution of konjac glucomannan. *Cereal Chemistry, 96*, 784–791.

Rani, S., Singh, R., Kaur, B. P., Upadhyay, A., & Kamble, D. B. (2018). Optimization and evaluation of multigrain gluten-enriched instant noodles. *Applied Biological Chemistry, 61*, 531–541.

Sang, S., Tian, S., Wang, H., Stark, R. E., Rosen, R. T., Yang, C. S., & Ho, C. T. (2003). Chemical studies of the antioxidant mechanism of tea catechins: Radical reaction products of epicatechin with peroxyl radicals. *Bioorganic & Medicinal Chemistry, 11*, 3371–3378.

Shende, S., Patel, S., Arora, S., & Sharma, V. (2014). Oxidative stability of ghee incorporated with clove extracts and BHA at elevated temperatures. *International Journal of Food Properties, 17*, 1599–1611.

Valcic, S., Burr, J. A., Timmermann, B. N., & Liebler, D. C. (2000). Antioxidant chemistry of green tea catechins. New oxidation products of (−)-epigallocatechin gallate and (−)-epigallocatechin from their reactions with peroxyl radicals. *Chemical Research in Toxicology, 13*, 801–810.

Valcic, S., Muders, A., Jacobsen, N. E., Liebler, D. C., & Timmermann, B. N. (1999). Antioxidant chemistry of green tea catechins. Identification of products of the reaction of (−)-epigallocatechin gallate with peroxyl radicals. *Chemical Research in Toxicology, 12*, 382–386.

Wang, L., Wang, Y., Hu, C., & Zhang, Y. (2011). Analysis of acylglycerols by high temperature gas chromatography (in Chinese). *China Oils and Fats, 36*, 75–79.

Wei, A., & Zhou, R. (1999). Oxidation degree of palm oil fried instant noodles determined by Rancimat method. *Journal of Zhengzhou Grain College, 20*, 39–41.

Wu, X., Wu, S., Ji, M., & Yoong, J. H. (2018). Influence of red palm oil on the physicochemical and sensory qualities of flavouring oil gravy for instant noodles. *RSC Adv., 8*, 1148–1158.

Zhang, C., & Chen, D. (2014). Advance in flavor study of the deep-fried food (in Chinese). *J. Food Safety Quality, 5*(10), 3085–3091.