GRASAS Y ACEITES 74 (4)
October-December 2023, e525
ISSN-L: 0017-3495
https://doi.org/10.3989/gya.1105222

Retarding sunflower oil oxidation during the deep-fat frying of potato chips using micro-encapsulated *Convolvulus arvensis* Linn leaf phenolic extract

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Submitted: 07 November 2022; Accepted: 24 April 2022; Published online: 11 January 2024

SUMMARY: In this research, the extraction of polyphenols from *Convolvulus arvensis* (CA) leaves was optimized using ethanol (80%) at plant/solvent ratios and extraction times which varied between 1/10 to 1/30 (w/v) and 20 to 120 min, respectively. The extract with the highest polyphenol content was obtained at a ratio of 1/30 and 90 min. At 120 ppm, the preceding extract in either lyophilized (LyCAE) or encapsulated (EnCAE) form was evaluated as an antioxidant during the frying process using sunflower oil in comparison to TBHQ. Frying oil quality indices including refractive index, smoke point, acid value, anisidine value, polar and polymer compounds were monitored throughout frying times. FTIR spectroscopy was used to investigate the changes in *trans*-fatty acids, hydroperoxides and aldehyde contents. The results showed that the phenolic extract, especially in EnCAE form, exhibited superior antioxidant activity over TBHQ, which consequently led to the utilization of this phenolic extract as an antioxidant in frying oils.

KEYWORDS: *Convolvulus arvensis; Deep fat frying; Frying oil quality; FTIR spectroscopy; Micro-encapsulation.*

RESUMEN: ***Retrasar la oxidación del aceite de girasol durante la fritura de patatas utilizando extracto fenólico de hojas de*** **Convolvulus arvensis** ***Linn microencapsulado.*** En esta investigación se optimizó la extracción de polifenoles de hojas de *Convolvulus arvensis* (CA) utilizando etanol (80%) en las relaciones planta/solvente y tiempos de extracción entre 1/10 y 1/30 (p/v) y entre 20 y 120 min, respectivamente. El extracto con mayor contenido en polifenoles se obtuvo con una relación 1/30 durante 90 min. El extracto anterior en forma liofilizada (LyCAE) o encapsulada (EnCAE) se evaluó como antioxidante a 120 ppm durante el proceso de fritura utilizando aceite de girasol, en comparación con TBHQ. Los índices de calidad del aceite para freír, incluidos el índice de refracción, punto de humo, índice de acidez, índice de anisidina, compuestos polares y poliméricos, se monitorearon a lo largo de los tiempos de fritura. Se utilizó espectroscopia FTIR para investigar los cambios en el contenido de ácidos grasos *trans*, hidroperóxidos y aldehídos. Los resultados mostraron que el extracto fenólico, especialmente en forma de EnCAE, mostró una actividad antioxidante superior al TBHQ, lo que condujo a la utilización de este extracto fenólico como antioxidante en los aceites para freír.

PALABRAS CLAVE: *Aceite de fritura; Calidad del aceite de fritura; Convolvulus arvensis; Espectroscopia FTIR; Microencapsulación.*

Citation/Cómo citar este artículo: Hammad KSM, Elkharsa MM, El-Nikeety MMA, Hallabo SAS. 2023. Retarding sunflower oil oxidation during the deep-fat frying of potato chips using micro-encapsulated *Convolvulus arvensis* Linn leaf phenolic extract. *Grasas Aceites* **74** (4), e525. https://doi.org/10.3989/gya.1105222

1. INTRODUCTION

The frying process is often conducted at high temperatures (170-190 °C), which provides good conditions for the occurrence of oil deterioration reactions such as hydrolysis, oxidation, and polymerization. As a result, many harmful components are generated (Li *et al*., 2021). More than 400 components were identified in frying oils after the frying process, which can be absorbed by the fried food according to their nature and concentration. Due to the dangerous health effects of some of these components, several treatments were investigated to stop or reduce their generation during frying (Choe and Min, 2007). In addition, the reactions that lead to the formation of these compounds also cause changes in the physical and chemical indices of frying oil such as acid value (AV), smoke point (SP), refractive index (RI), total polar compounds (TPCs), total polymers (TPs), para-anisidine value (*p*-AV), conjugated dienes and trienes (K_{232} and K_{270}) (Li *et al*., 2021).

Antioxidants, especially synthetic ones, have been broadly implemented to extend the use-life of frying oil. However, some synthetic antioxidants such as tertiarybutyl hydroquinone (TBHQ) have been strictly regulated (Urbančič *et al.,* 2014). In addition, the long-term intake of synthetic antioxidants has been reported to be toxic or carcinogenic (Li *et al.,* 2021). Moreover, synthetic antioxidants are heat sensitive and the frying temperature (180 °C) can easily destroy or evaporate them (Guo *et al.,* 2016). As a response to the aforementioned drawbacks of synthetic antioxidants, several studies have been performed to examine various plant extracts as a source of natural antioxidants (Farag *et al.,* 2007; Biswal *et al.,* 2021). Recent studies have reported that natural antioxidants exhibited high antioxidant activities and thermal stability which guarantee a longer use-life of the oil (Carelli *et al*., 2005).

The optimal antioxidant concentration of frying oils is crucial (Wang *et al.,* 2020). According to Guo *et al.* (2016), this concentration can only be determined after frying with oils, containing the antioxidants for at least five hours. Indeed, recent studies showed that utilizing these antioxidants, specially plant extracts in the form of micro-capsules or nano-capsules, enhanced their functional characteristics (Biswal *et al.,* 2021). The enhancement in micro-encapsulation techniques (physical, physiochemical or chemical) generated antioxidant microcapsules that have improved the ability to protect the antioxidant against degradation, control its release and mask its taste (Ozkan *et al*., 2019).

Convolvulus arvensis Linn (CA), commonly known as field bindweed, is an annual or sometimes perennial weed native to Europe and Asia and is used for many purposes. Data in the literature show that CA has antibacterial, antidiarrheal, antioxidant, vasorelaxant, immunostimulant, hepato-protective, and diuretic effects (Al-Snafi, 2020). On the other hand, the literature is scarce on the utilization of CA extract as an antioxidant in food systems. Indeed, there is no previous study which investigates the ability of using CA extract to reduce or prevent degradation in frying oils. Therefore, the current study was conducted to optimize the extraction conditions of CA leaf phenolic compounds and identify these compounds present in the extract, in addition to studying the antioxidant activity of the selected extract formulated in two different forms (lyophilized and micro-encapsulated). The effects of formulated CA extracts on the chemical, physical and thermal characteristics of sunflower oil during the deep-fat frying of potato chips were investigated.

2. MATERIALS AND METHODS

2.1. Plant material

Convolvulus arvensis (CA) leaves were collected from the gardens of the Faculty of Agriculture, Cairo University, Egypt. *Convolvulus arvensis* voucher number (000194 WM 194. 09-,05-,02 – 09) was placed in the herbarium of Orman Botanic Garden, Giza, Egypt. Antioxidant-free sunflower oil was kindly supplied by Arma company, 10th of Ramadan, Egypt.

2.2. Chemicals and reagents

Folin–Ciocalteu reagent, Quercetin, *P*-anisidine, Isooctane, Gallic acid, methyl alcohol, silica gel and TBHQ (Tert-Butylhydroquinone) were purchased from Sigma–Aldrich Co., St. Louis, USA.

2.3. Extraction of polyphenols

The plant leaves were dried at 45 °C, milled up to 50 mesh and stored at room temperature. The ex-

traction of polyphenols was performed according to Elsayed *et al.* (2020) with a slight modification. Aqueous ethanol (80%) at solid-to-solvent ratios of 1/10, 1/20 and 1/30 (*w/v*) were used to extract the phenolic compounds using a benchtop lab stirrer (Heidolph, Germany) at maximum speed. Extraction was conducted for 20, 30, 60, 90 and 120 min. The optimum extract with the highest total polyphenols yield was concentrated under vacuum at 45 °C using the EYELA Rotary Evaporator (Tokyo Rikakikai Co., LTD, Japan). The concentrated phenolic extract was divided into two parts. One of them was lyophilized (Edward freeze dryer, England) and the other one was microencapsulated.

2.4. Microencapsulation

Microencapsulation of the optimal CA leaf extract was prepared using the mini spray drier BUCHI B-290 (BÜCHI, Flawil, Switzerland) according to the method described by Sukri *et al.* (2021). Firstly, equal weights of gum Arabic and maltodextrin were dissolved in deionized water with the assistance of vigorous mixing and then the optimal extract was added. When the process was finished the extract represented 20% of the total solid (20g extract/ 80 g encapsulating material). The preceding mixture was magnetically stirred for 5 min before sonication for 20 min using UP200S ultrasound homogenizer (IKA Hielscher GmbH, Berlin, Germany) at 200 W. The spray dryer was operated under the following conditions: mixture flow rate = 8 ml/min, inlet air temperature = 130 °C, outlet temperature = 80 °C and drying air flow rate = 85% of the suction fan controller.

2.5. Total phenolic content (TPC)

The total phenolic content of the plant extracts was determined by Folin-Ciocalteu reagent according to the Elsayed *et al.* (2020) method using UNICO UV-Visible spectrophotometer (UNICO Instruments Co., LTD, U.S.A.) at 750 nm. The results were expressed as mg Gallic acid equivalent per gram plant dry weight (mg GAE/g DW).

2.6. Total flavonoid content (TFC)

The total flavonoid content was determined using the aluminum chloride colorimetric method at 510 nm according to Formagio *et al.* (2014). The results were expressed as milligrams Quercetin equivalent/ gram of dry weight (mg QE/g DW).

2.7. HPLC analysis

An agilent1260 infinity HPLC Series (Agilent, USA) equipped with a Quaternary pump and a Kineted® 5µm EVO C_{18} column 100 mm x 4.6 mm, (Phenomenex, USA) were used to identify phenolic and flavonoid compounds. The separation was achieved using a ternary linear elution gradient with (A) HPLC grade water 0.2% H_3PO_4 (v/v), (B) methanol and (C) acetonitrile at a flow rate of 0.7 mm/min. The detection wavelength was set at 284 nm. The injection volume was 20 µl and the column temperature was held at 30 °C. The compounds were identified by comparing their retention times with those of authentic standards. Calibration curves were used to calculate the concentrations of the compounds.

2.8. Frying process

According to the permissible concentration of TBHQ in vegetable oils (CODEX, 2019 CXS 210-1999) and previous studies (Wang *et al.,* 2020), lyophilized and microencapsulated leaf extracts were separately added to sunflower oil at 120 mg gallic acid equivalent/kg oil and TBHQ was added at the same level (120 ppm). Sunflower oil without added antioxidants was used as a control. Frying was performed in a deep-frying pan. The surface/ oil volume ratio was 0.28 cm^{-1}. One kilogram of oil was heated to 180 ± 10 °C. Fifty g of potato chips were fried for five min every 20 min, which was consecutively repeated for 8 hours per day. This frying process was repeated for four consecutive days with the same oil without replenishment. A 50 ml sample of the oil was collected both in the fresh state and at the end of every frying day. Oil samples were stored at -18 °C for analysis. All the frying processes were done twice.

2.9. Frying oil quality indices

2.9.1. Acid value (AV), smoke point (SP), refractive index (RI), conjugated dienes (K232) and conjugated trienes (K270)

Acid value, smoke point and refractive index were determined according to AOCS (2009). Conjugated dienes (K_{232}) and conjugated trienes (K_{270})

were determined according to the European Commission (2013).

2.9.2. p-*Anisidine value (*p-*AV)*

The *p*-AV was determined according to AOCS (2009). Isooctane was used as a blank. The experiment was performed in triplicate and values were calculated according to the following equation:

$$p\text{-AV} = \frac{25 \times (1{,}2\ A_s - A_b)}{wt}$$

Where (A_s) is the absorbance at 350 nm of the fat solution in isooctane after reacting with the *p*-anisidine reagent, (A_b) is the absorbance of the fat solution without the addition of reagent and (Wt) is the weight of the sample in grams.

2.9.3. Total polar compounds (TPCs %)

One gram of oil was fractionated in a silica gel column chromatography. The PC were recovered with diethyl ether (150 mL) after the non-polar components had been eluted with the same volume of a mixture of petroleum ether (b.p. 40-60 ºC) -diethyl ether (87:13, v/v) according to Waltking and Wessels (1981).

2.9.4. Total polymer content (PCs%)

The polymer content was determined in 1 g of oil by methylation under reflux with a solution of 1% (v/v) concentrated sulfuric acid in methanol, followed by separation of the methanol-insoluble fraction. The insoluble fraction was transferred to a preweighed flask with petroleum ether. The solvent was evaporated to constant weight, according to Pei-Fan and Nawar (1986).

2.10. Infrared spectroscopy (FTIR)

The IR absorption spectra in potassium bromide disks of oil sample were taken in the region (4000-400 Cm^{-1}). A FTIR spectrometer (NICOLET 380 FT-IR, Thermo Scientific, made in China) was used. Data were manipulated by a computer equipped with Professional Windows XP Software.

2.11. Statistical analysis

The data are presented as mean values ± SD. The data were subjected to analysis of variance (ANOVA) followed by Tukey's test using significance level of 0.05 (XLSTAT, Addinsoft, USA).

3. RESULTS AND DISCUSSION

3.1. Phenolic content of *Convolvulus arvensis*

The yield of phenolic compounds was proven to be highly dependent on extraction process parameters. Thus, the effect of plant/solvent ratio and extraction time on the yield of phenolic compounds was investigated. Results in Figure 1(a) illustrate that decreasing plant/solvent ratio caused a significant ($p < 0.05$) increase in the yield of total polyphenol contents (TPC) at various extraction times. Extending extraction time from 20 to 90 min at different plant/solvent ratios (except plant/solvent ratio of 1/10)

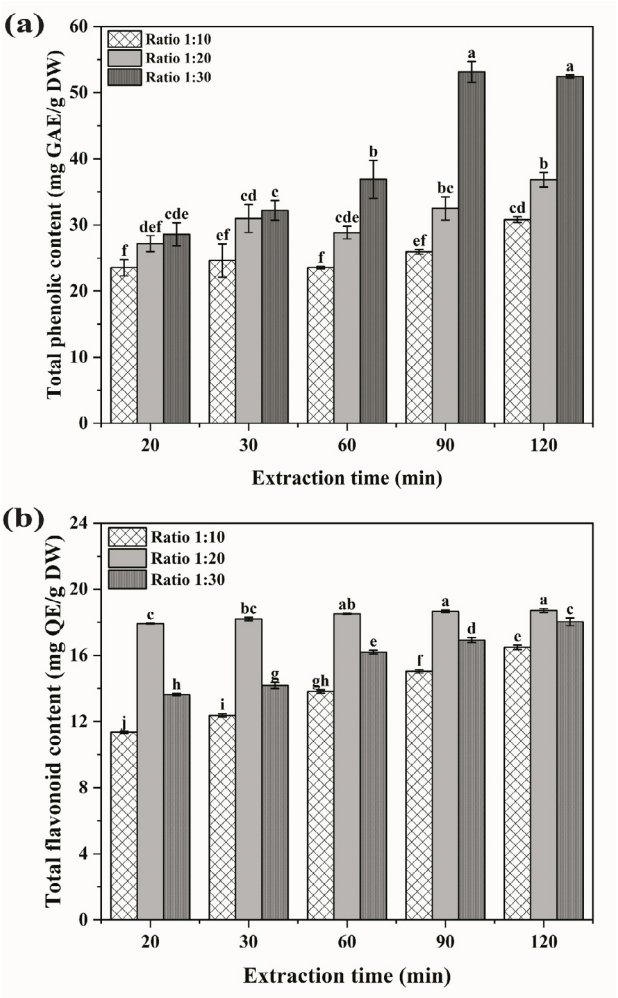

Figure 1. Effect of plant: solvent ratio (w/v) and extraction time on bioactive compound contents in *Convolvulus arvensis* leaves. The results are expressed as mean ± standard deviation (n = 3). Bars with different letters represent significant difference ($p < 0.05$, one-way ANOVA with Tukey test).

caused a significant ($p < 0.05$) increase in the yield of TPC, whereas further increase in extraction time had an insignificant ($p > 0.05$) effect on the yield of TPC. The highest TPC yield was 53.15 ±1.58 mg GAE/g DW, which was obtained at a plant/solvent ratio of 1/30 and extraction time of 90 min. These results agree with those reported by Ćujić *et al.* (2016). They reported that decreasing plant/solvent ratio from 1/10 to 1/80 caused a significant increase in the TPC from 53 to 83 mg GAE/g DW, respectively. They also reported that increasing the extraction time caused an increase in TPC. In a similar trend, Chirinos *et al.* (2007) reported that the TPC of mashua tubers (*Tropaeolum tuberosum*) was increased by increasing extraction time from 0 to 60 min, and a further increase in extraction time from 60 to 120 min had no significant effect on the yield of TPC.

The total flavonoid content (TFC) of CA leaf ethanolic extracts obtained under various extraction conditions are presented in Figure 1(b). What stands out in Figure 1(b) is that the highest yields of TFC were achieved at a plant/solvent ratio of 1/20 for various extraction times. Furthermore, at this plant/solvent ratio (1/20) extending the extraction time to higher than 60 min had no significant ($p > 0.05$) effect on the yield of TFC. In contrast to the TPC extraction pattern, decreasing plant/solvent ratio to 1/30 significantly ($p < 0.05$) reduced the yield of TFC at various extraction times. Moreover, it could be noted that for all plant/solvent ratios, except (1/20), extending extraction time from 20 to 120 min significantly ($p < 0.05$) increased the yield of TFC. The highest TFC yield was 18.72 ± 0.12 mg QE/g DW, which was obtained at a plant/solvent ratio of 1/20 and extraction time of 120 min. Similar results were reported by Chirinos *et al.* (2007), who studied the effect of different extraction times (from zero to 140 minutes) on the yield of TFC. They reported that the TFC yield increased significantly when the extraction time was increased from zero to 60 min, and then it became stable during additional extraction times.

The results indicated that the TPC of the LyCAE was 55.40 ± 0.43 mg GAE/g; whereas it was 9.30 ± 0.22 mg GAE/g for the EnCAE.

3.2. Identification of the phenolic and flavonoid compounds in *Convolvulus arvensis* extract

The phenolic compounds in the optimal ethanolic extract with the highest yield of polyphenols from CA leaves are listed in Table 1. The predominant phenolic compounds were benzoic acid and rosmarinic acid (164.39 and 134.58 µg/g DW, respectively), while quercetin and rutin (173.25 and 155.55 µg/g DW, respectively) were dominant flavonoids.

Elzaawely and Tawata (2012) showed that benzoic acid, syringic acid, *p*-hydroxy benzoic acid, vanillin and ferulic acid were the major identified phenolic acids in the CA leaf acidic ethyl acetate extract. This difference in the phenolic composition of the extracts could be attributed to plant species and solvent type.

Table 1. HPLC analysis of the ethanolic extract of CA leaves extracted with a ratio of 1:30 (w/v) for 90 minutes

Compound name	µg/g dried leaves
Phenolics	
Pyrogallol	0. 50
Quinol	0. 44
Gallic acid	4. 56
p-Hydroxy benzoic acid	32.29
Chlorogenic acid	61.45
Vanillic acid	16.80
Caffeic acid	60.56
Syringic acid	7.62
p-Coumaric acid	73.88
Benzoic acid	164.39
Ferulic acid	6.96
o-Coumaric acid	11.64
Resveratrol	66.29
Cinnamic acid	41.20
Rosmarinic acid	134.58
Flavonoids	
Naringenin	75.04
Myricetin	28.26
Kampherol	69.53
Catechin	8. 97
Rutin	155.55
Ellagic acid	57.12
Quercetin	173.25

The values refer to a single determination

3.3. Frying oil quality indices

3.3.1. Acid value (AV)

The change in AV with frying times is illustrated in Figure 2(a), which clearly shows an increasing trend in the AV of sunflower oils with increasing

frying time for various treatments. Compared to the control sample, sunflower oils containing TBHQ or either LyCAE or EnCAE significantly ($p < 0.05$) exhibited low AV After 32 h of frying. The control sample exhibited the highest AV (2.04 ± 0.02 mg KOH/g oil), whereas the AV of oil samples incorporated with LyCAE and TBHQ were 1.72 ± 0.02 and 1.62 ± 0.01 mg KOH/g oil, respectively. The oil with EnCAE recorded the lowest AV (0.86 ± 0.02 mg KOH/g oil). These results revealed that the TBHQ and EnCAE decreased the AV of frying oil by 20.38 and 57.67%, respectively, after frying for 32 h.

This finding is consistent with that of Asadi and Farahmandfar (2020), who added the phenolic extract of *Teucrium polium* at 200 ppm to canola oil during frying. They found that the *Teucrium polium* extract decreased the acid value by 47.6% after 30 h of frying. The superiority of EnCAE in the reduction of AV could be attributed to the protective effect of the encapsulation process on the stability of antioxidant compounds. According to Munin and Edwards-Lévy (2011), the encapsulation of polyphenols has a good influence on their stability against light and heat.

3.3.2. Smoke point (SP)

The change in smoke point of sunflower oil during frying is shown in Figure 2(b), which reveals that there was a marked decline in the smoke point of sunflower oil during frying for all treatments. At the end of frying (32 h), the control sample exhibited the lowest ($p < 0.05$) smoke point (193.5 ± 0.5 °C); whereas the sample treated with EnCAE exhibited the highest ($p < 0.05$) smoke point (236 ± 5 °C). These results agree with those previously reported by Farag *et al*. (2007). They found that sunflower oil samples enriched with phenolic extract (olive leaf juice extract) at concentrations of 800 and 1600 and 2400 ppm polyphenols showed a higher smoke point than oil samples enriched with BHT and the control ones after frying for 25 h.

3.3.3. Refractive index (RI)

Figure 2 (c) shows that there was a significant ($p < 0.05$) increase in the refractive index during frying for all treatments. It can be clearly noted that after frying for 32 h, the sunflower oil sample containing EnCAE showed the lowest ($p < 0.05$) refractive index

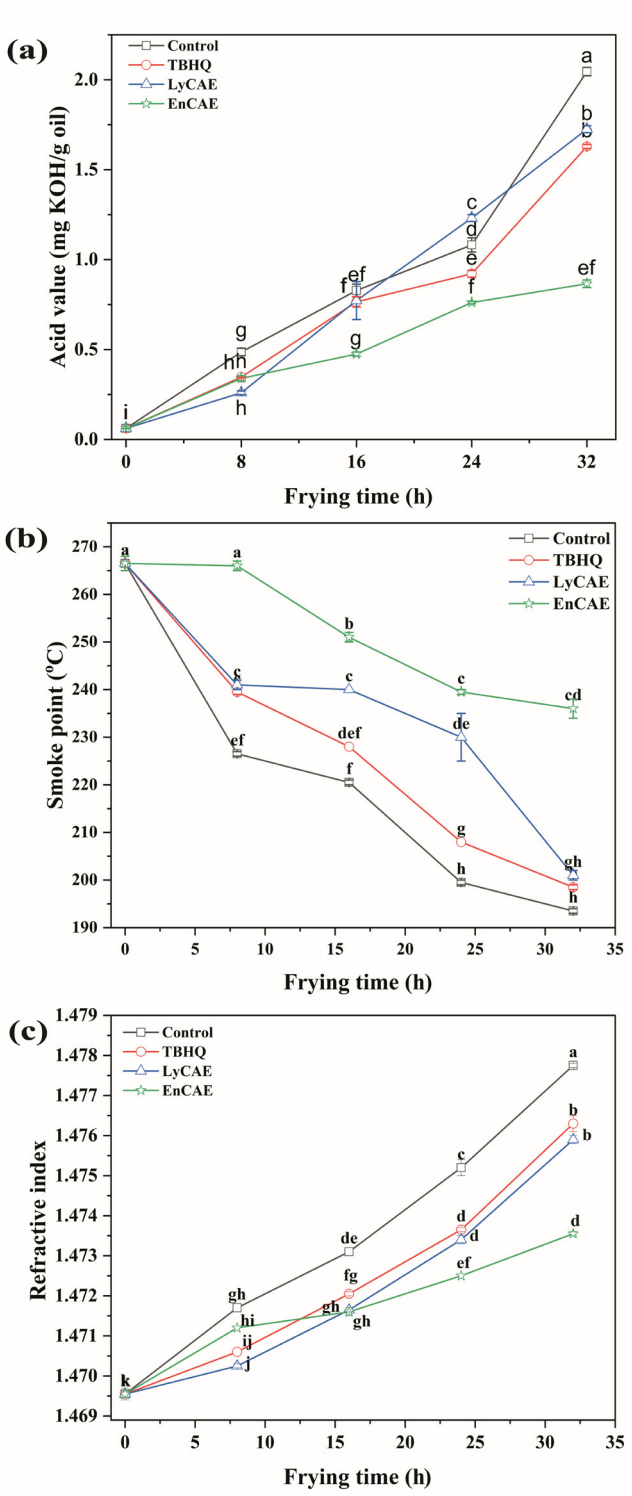

Figure 2. The change in acid value (a), smoke point (b), and refractive index (c) of sunflower oil samples containing TBHQ (TBHQ), lyophilized *Convolvulus arvensis* extract (LyCAE), and microencapsulated *Convolvulus arvensis* extract (EnCAE) throughout the frying process. The results are expressed as mean ± standard deviation (n = 3). Error bars with different letters represent significant difference ($p < 0.05$, one-way ANOVA with Tukey test).

value (1.4736); however, the control sample exhibited the highest ($p < 0.05$) refractive value (1.4778). Moreover, the same data reveal that TBHQ, LyCAE and EnCAE decreased the change in RI of various oil samples by 18.29, 23.17 and 51.22%, respectively. These results are consistent with those of Farag *et al*. (2007), who found that adding phenolic extract (olive leaf juice and pomposia extract, respectively) to frying oils reduced the increase in RI values in comparison to the control sample.

3.3.4. p-*Anisidine value* (p-*AV)*

p-AV is a measure of the level of non-volatile carbonyl secondary oxidation compounds produced during the frying process (Wu *et al.,* 2022). Figure 3(a) shows that sunflower oil samples containing TBHQ, LyCAE and EnCAE significantly ($p < 0.05$) exhibited lower *p*-AV than the control sample after frying for 32 h. TBHQ reduced the increase in *p*-AV by 10.05% compared to the control, while the LyCAE and EnCAE reduced it by 67.49 and 88.07%, respectively. This difference in *p*-AV between LyCAE- and EnCAE-treated samples could be attributed to the high stability of the phenolic extract resulting from the encapsulation process (Munin and Edwards-Lévy, 2011). In a similar trend, Wu *et al.* (2022) found that adding *Camellia oleifera* seed cake into soybean oil reduced its *p*-AV at various frying times in comparison to the control sample.

3.3.5. *Conjugated dienes (K_{232}) and trienes (K_{270})*

After frying for 32 h, it could be clearly noted that there were significant ($p < 0.05$) differences in CD and CT contents among various treatments (Figure 3(b)). The addition of EnCAE to sunflower oil significantly ($p < 0.05$) inhibited the formation of both CD and CT during frying. Moreover, the addition of CAE in either lyophilized or encapsulated form prevented the formation of CD and CT to levels lower than those generated during frying with oil

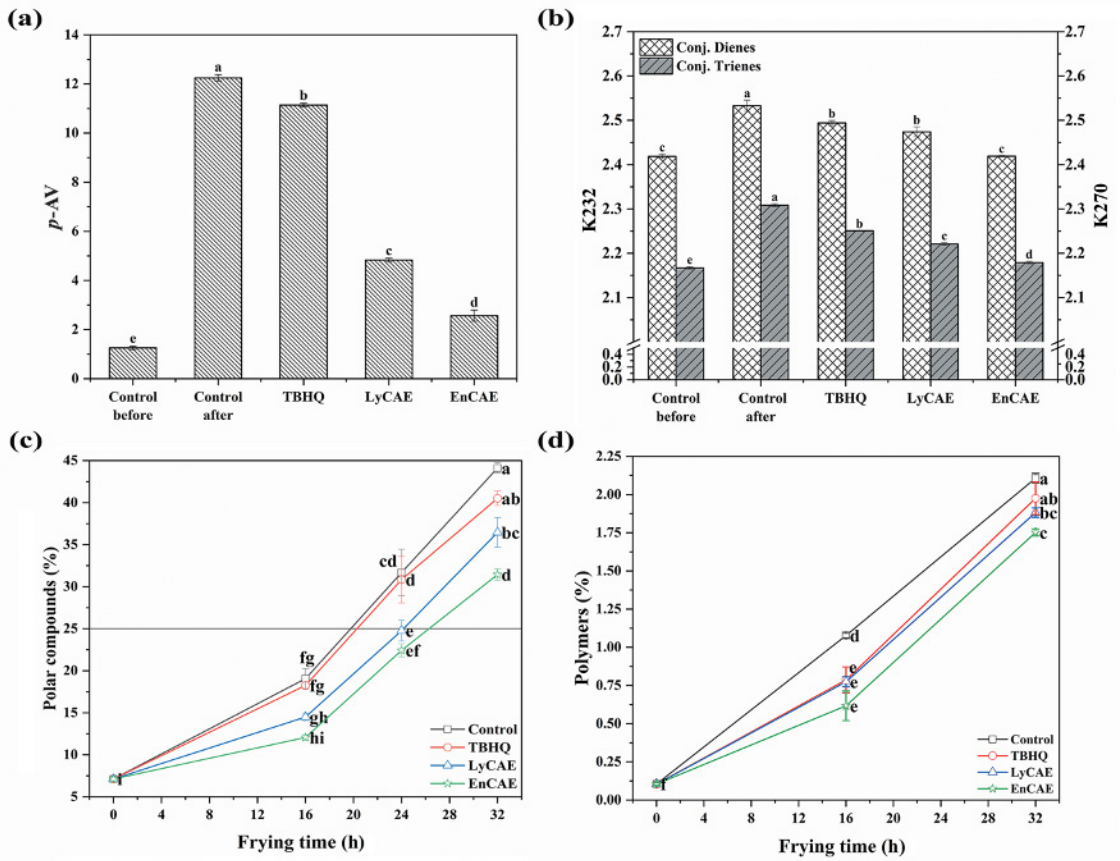

Figure 3. The *p*-anisidine value (a), conjugated dienes and trienes (b) in oil samples after frying for 32 h and the change in polar compound % (C), and polymer % (d) of sunflower oil samples containing TBHQ (TBHQ), lyophilized *Convolvulus arvensis* extract (LyCAE), and microencapsulated *Convolvulus arvensis* extract (EnCAE) throughout the frying process. The results are expressed as mean ± standard deviation (n = 3). Error bars with different letters represent significant difference ($p < 0.05$, one-way ANOVA with Tukey test).

containing TBHQ. This high antioxidant activity of CAE could be attributed to its phenolic compounds, especially rosmarinic acid, which have previously shown protective effects against the oxidation of vegetable oils during frying. Li *et al.* (2021) reported the potent effect of rosmarinic acid in retarding the soybean oil oxidation processes during frying. They also found a negative correlation between the level of rosmarinic acid and the formation of both CD and CT. The EnCAE was superior in preventing the formation of CD and CT. The role of encapsulation is limited to the enhancement of the antioxidant action through controlling the release and protecting the activity of the antioxidants in the frying oil (Sharma *et al.,* 2019).

3.3.6. Total polar compounds (TPCs %)

Due to the severe conditions of the frying process, many complex compounds with high polarity are formed. These compounds can be named and determined as the TPC % value (Wang *et al.,* 2020). Figure 3(c) shows that throughout frying times, oil samples containing various antioxidants exhibited lower TPC % values than the control sample, indicating that these antioxidants play a role in retarding or reducing TP formation during the deep-fat frying of potato chips, as reported by Frankel (2005). Indeed, the addition of CA leaf extract in either LyCAE or EnCAE to frying oils significantly ($p < 0.05$) extended their lifetime to 24 h as the generated TPC % in oil samples containing these antioxidants were acceptable (< 25%) (Firestone, 2007).

Despite all the oil samples exhibiting high TPC % values (> 25%) at the end of the frying process, the oil sample containing EnCAE showed the significantly ($p < 0.05$) lowest TPC % value (31.44 ± 0.68%). The addition of TBHQ, LyCAE and EnCAE to frying oil significantly ($p < 0.05$) inhibited the formation of TPC % in the control sample at the end of the frying process by 8.18, 17.38 and 28.74%, respectively. Our results are consistent with those of Li *et al.* (2021), who found that at the end of frying process, mixing the frying soybean oil with 200 ppm rosemary extract and rosmarinic acid inhibited the formation of TPC % by 19.52 and 24.66%, respectively. Wu *et al.* (2022) found that adding TBHQ or *Camellia oleifera* seed cake phenolic extract (200 ppm) to soybean oil had almost the same effect on the formation of TPC % during frying process. TBHQ and phenolic extract inhibited the formation of TPC% by 19.61 and 19.81%, respectively.

3.3.7. Total polymers (TP %)

During the frying process, monomer free radicals react to generate polymers. The levels of polymer compounds (TP %) is a good measure for frying oil quality since they increase with prolonged frying time. TP % has been proved to be decreased by mixing antioxidants with frying oil, mainly natural polyphenols (Wang *et al.,* 2020).

Based on Figure 3(d), TBHQ, LyCAE and EnCAE all have a good effect on decreasing the formation of polymeric compounds in sunflower oil during frying. After frying for 32 h, the sunflower oil sample containing EnCAE exhibited the lowest significant ($p < 0.05$) TP %, followed by LyCAE, TBHQ, and control samples in the same order. Indeed, EnCAE, LyCAE and TBHQ reduced the formation of TP % by 16.88, 10.70 and 6.26%, respectively, in comparison to the control sample. These results agree with those reported by Wang *et al.* (2020). They found that adding carvacrol methyl ether and TBHQ to sunflower oil reduced the TP % by 60.7 and 39.29%, respectively, during Chinese *youmotou* frying at 180 ^{o}C for 30 h.

3.4. FTIR analysis

The FTIR spectra of fresh oil and various frying oil samples at the end of the frying process were measured in the range of 4000 – 400 cm^{-1}, as shown in Figure 4. IR spectral bands shown at 3470, 1164, and 968 cm^{-1} are assigned to a hydroperoxide group, a carbonyl group, and trans double bonds, respectively, (Guillen and Cabo, 1997*;* Hammad *et al.,* 2021), which were used to assess the effect of the frying process on the quality of oil at the end of the frying process. Considering spectral band of 3470, the control sample showed the highest absorbance value at the end of the frying process; whereas samples containing various antioxidants showed absorbance values closed to those of fresh oil (before frying process).

In addition, control samples at the end of frying process showed the highest absorbance value at 1164 cm^{-1}, which indicates the increase in the formation of the aldehyde functional group in the absence of various antioxidants. The thermal oxidation of oil gener-

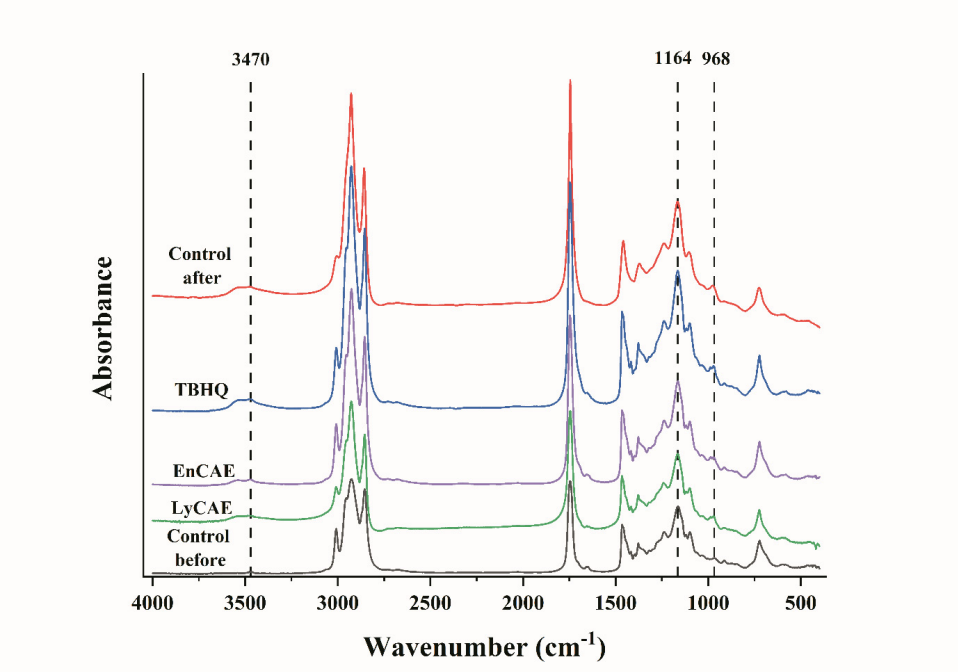

Figure 4. FT-IR spectrum of sunflower oil samples containing TBHQ (TBHQ), lyophilized *Convolvulus arvensis* extract (LyCAE), and microencapsulated *Convolvulus arvensis* extract (EnCAE) after the frying process (32 h). The values refer to a single determination.

ates hydroxyl groups which are represented in peaks in the range of 3000 cm^{-1} to 3600 cm^{-1}, especially after multiple frying cycles. Ahmad *et al. (*2022) reported that the C-O and carbonyl (C = O) bonds of aliphatic esters are responsible for the spectrum peaks near 1150 cm^{-1} and 1750 cm^{-1}, respectively. On the other hand, frying oil containing EnCAE exhibited the lowest absorbance value followed by LyCAE and TBHQ in the same order. At IR spectral band of 968 cm^{-1}, frying oil containing EnCAE exhibited the lowest absorbance value followed by TBHQ and LyCAE in the same order, which indicates the inhibiting effect of these antioxidants on the formation of trans double bonds. The absorbance of oils at 968 cm^{-1} reflects the trans double bond C-H (Guillen and Cabo, 1997). Moreover, multiple frying at various intervals may make oxygen more availableonce the frying oil cools, which could lead to similar peaks in the edible oils (Ahmad *et al.,* 2022).

4. CONCLUSIONS

According to the results, the process variable that had the greatest impact on the yield of the phenolic compounds was the plant/solvent ratio. The maximum TPC yield (53.15 mg GAE/g DW) was obtained by extracting with 80% ethanol for 90 minutes at a plant/solvent ratio of 1/30 (w/v). The HPLC analysis of the extract showed benzoic acid and rosmarinic acid as the main polyphenols while quercetin and rutin were the major flavonoids. This study set out to assess the feasibility of utilizing CA leaf extract as a natural antioxidant to prevent sunflower oil degradation during the deep-fat frying of potato chips in comparison to synthetic TBHQ. At a concentration of 120 ppm, TBHQ, lyophilized and encapsulated CA leaf extract (LyCAE and EnCAE) were individually added to sunflower oil. The findings clearly indicate that both LyCAE and EnCAE exhibited superior antioxidant activity over TBHQ regarding the physical, chemical, and thermal properties of oil. The excessive antioxidant activity of CA leaf extract may be attributed to its high content of rosmarinic acid. In addition, the encapsulation of CA leaf extract promoted its influence much more. This can be due to the protection and enhancement of the polyphenols due to encapsulation. CA leaf extract is a promising antioxidant for oil, particularly during frying. Hence, it can be used as a natural additive in frying oils.

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