Evaluation of Oxidation Parameters of Caffeic Acid Phenethyl Ester Comparing with Caffeic Acid, Ascorbyl Palmitate, and α-Tocopherol on the Thermal Oxidation Model

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Abstract: In this study, the antioxidative capacity of caffeic acid (CA), ascorbyl palmitate (AP), α-tocopherol (α-TO), and caffeic acid phenethyl ester (CAPE) was evaluated under the thermal oxidation model, in which 200 ppm of each compound was added to soybean oil, followed by thermal oxidation at 180°C for 32 h. Change of viscosity, acid value (AV), conjugated dienoic acid value (CDAV), p-anisidine value (p-AV), total polar materials (TPM), and the ratio of C18:2 to C16:0 (LA/PA) were evaluated during the reaction. All antioxidants showed significantly lower viscosity, TPM, and p-AV, and higher LA/PA, than the control (without antioxidant, CON), indicating that thermal oxidation was delayed. Among them, CAPE showed significantly lower viscosity, TPM, and p-AV, and higher LA/PA, than the other antioxidants (p < 0.05). In the correlation between the oxidation parameters measured from CON and CAPE, the correlation coefficient between p-AV and viscosity was rather low at r = 0.7603 (in CON) and r = 0.7338 (in CAPE), respectively.

Key words: caffeic acid phenethyl ester, caffeic acid, ascorbyl palmitate, α-tocopherol, thermal oxidation model, oxidation parameters

1 Introduction

Oil is used as a heat transfer medium in the frying process, which improves the flavor and texture inherent in the food after cooking. Soybean oil is commonly used as a frying oil because it is widely produced vegetable oil in the world¹ and contains essential fatty acids, such as linoleic acid (LA) and alpha-linolenic acid (LnA), that have more than one double bond, making it a desirable vegetable oil in both economic and nutritional terms. However, unsaturated fatty acids with double bonds are vulnerable to oxidation, and the more double bonds, the more oxidation occurs because the oxidation of oil is initiated by the abstraction of hydrogen from the methylene group adjacent to the double bond²⁻⁶. Oxidation of oil is accelerated by heat due to the faster generation, decomposition and polymerization of the primary (i.e., hydroperoxide) and secondary oxidants (i.e., carbonyl compounds, such as various aldehydes and ketones, etc.). Oxidation of oil causes physico-chemical changes, such as an increase in conjugated double bonds, color change, flavor reversion, and viscosity increase due to the polymerization reaction, etc.²⁻⁵. Accordingly, antioxidants are widely used in the food industry to maintain stability against oxidation. In particular, addition of natural or artificial antioxidants retards the thermal oxidation process, minimizing the deterioration of food quality. Tocopherol, which is a commonly used natural antioxidant, and ascorbyl palmitate, are typical lipid-soluble antioxidants. They can serve to inhibit the formation of radicals by donating hydrogen to the radicals produced in the oxidation process⁴. In addition, synthetic antioxidants such as butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT) and tert-butylhydroquinone (TBHQ) are used as food additives.

Caffeic acid phenethyl ester (CAPE) is a natural phenolic compound, which is composed of an ester of caffeic acid and phenethyl alcohol. Unlike caffeic acid, CAPE does not
have a carboxyl group, and thus has better oil solubility than CA. Because it is uneconomical to extract CAPE directly from natural substances, CAPE can be synthesized from caffeic acids and phenethyl alcohol\(^5\). In most studies, the antioxidant capacity of CAPE has been performed under biological or autoxidation conditions\(^6-9\), and few studies have been reported on the antioxidant capacity of CAPE under thermal oxidation condition of high temperatures so far. Therefore, we observed whether CAPE, which showed effective antioxidant capacity in the autoxidation, also retarded the thermal oxidation. Soybean oil (SBO) is widely used in the process of frying. Also, this oil will be easily oxidized because it contains a large amount of linoleic acid (containing two double bonds), allowing relatively easy monitoring of the oxidation degree. In this study, \(\alpha\)-tocopherol (\(\alpha\)-TO), an antioxidant widely used in the oil industry, caffeic acid (CA), which is known to have excellent free radical scavenging ability\(^10\), ascorbyl palmitate (AP), an antioxidant that can be used as a food additive\(^11\), and CAPE were added to SBO at a concentration of 200 ppm. The antioxidative capacity of each antioxidant was determined by analysis of viscosity, fatty acid composition, acid value (AV), conjugated diene acid value (CDAV), \(p\)-anisidine value (\(p\)-AV) and total polar materials (TPM). The correlations between these oxidation parameters were also examined when CAPE is added into SBO.

2 Experimental

2.1 Materials and chemicals

Soybean oil (SBO) was purchased from a local market (Daejeon, Korea). Caffeic acid, phenethyl alcohol, and dicyclohexylcarbodiimide (DCC) used for the synthesis of CAPE were purchased from Sigma-Aldrich Sigma-Aldrich Korea (Seoul, Korea). SupelcoseTM LC-Si SPE tubes (6 mL) and 14% BF\(_3\)-methanol solution were also obtained from Sigma-Aldrich Korea (Seoul, Korea). Thin layer chromatography (TLC) silica gel 60 F254 was provided by Merck KGaA (Darmstadt, Germany). \(\alpha\)-Tocopherol (\(\alpha\)-TO) and ascorbyl palmitate (AP) used as antioxidants were purchased from Sigma-Aldrich Sigma-Aldrich Korea (Seoul, Korea). Tetrahydrofuran (THF) and all solvents were analytical HPLC grade (Fisher Scientific Korea., Seoul, Korea).

2.2 Synthesis of CAPE

CAPE was prepared by the chemical esterification reaction of CA and phenethyl alcohol using the method described in previous studies\(^5,8,9\). In short, CA (54 mg), phenethyl alcohol (180 mg), and 1.2 mL of THF were

Fig. 1 Preparation and identification of caffeic acid phenethyl ester (CAPE). (a) Separation by thin layer chromatogram; (b) molecular structure and \(^1\)H-NMR spectroscopic result; (c) HPLC chromatogram.
mixed in the test tube, and 108 mg of dicyclohexylcarbodi-
imide as a catalyst was added to conduct the esterification
reaction for 8 h at room temperature. Ethyl acetate and
petroleum ether (1:5, v/v) eluted the reactant through LC-Si
SPE, thereafter the fractions were selected to collect
CAPE (Fig. 1a). After evaporating the elution solvent, re-
crystallization was performed to increase the purity of
CAPE.

2.3 Thermal oxidation

The antioxidative capacity of each compound on thermal
oxidation was investigated. SBO (40 g) was taken in each
100-mL screw cap vial and each antioxidant (CAPE, CA,
α-TO, and AP) was added into the vial with 200 ppm (8
mg), respectively. Each vial with different antioxidants was
homogenized using sonication (JeioTech UCP-10, Daejeon,
Korea) for 20 min at 50°C. Finally, the vials without caps
were placed in an oil bath at 180°C for thermal oxidation,
in which the reaction was performed for 8 h per day.
Finally, each heated oil (5 mL) was taken for further studies
after thermal oxidation of 4, 8, 16, 24, and 32 h, respective-
ly. Fresh SBO was not replenished to the vial after thermal
oxidation according to AOAC official method and its content was
expressed as g fatty acid/100 g oil in duplicate analysis
(FID) were used. The temperatures of the injector and de-
tector were 225°C and 285°C, respectively. The oven tem-
perature was initially maintained at 100°C for 4 min, raised
to 240°C at 3°C/min, then finally held for 15 min. The split
ratio was 200:1 and the carrier gas was He (1 mL/min, con-
stant flow mode). The identification of FAME in the ana-
lyzed chromatogram was performed by comparing its re-
tention time with the Supelco 37 component FAME
mixture (10 mg/mL, Sigma-Aldrich/Merck KGaA, Darm-
stadt, Germany). Fatty acid composition was calculated
according to AOAC Official method and its content was ex-
plored using the AOCS method Cd 18-90.

2.6 Acid value (AV), conjugated dienoic acid value
(CDAV), and p-anisidine value (p-AV)

Acid value (AV), conjugated dienoic acid value (CDAV), and
p-anisidine value (p-AV) were measured. AV was ana-
lyzed using the AOAC method Cd 3a-63 and CDAV was
determined using the AOCS method Ti la-64. p-AV was mea-
sured with the AOCS method Cd 18-90.

2.7 Total polar materials (TPM) analysis

TPM was analyzed using the Testo 270 deep-frying oil
tester (Testo Inc., Germany). Testo is a device that deter-
mines the total amount of polar materials as a percent-
age. The Testo instrument was calibrated with a vegeta-
ble reference oil of 3.9% TPM at 50°C. This reference oil
was provided by Testo to adjust to Testo cooking oil
testers.

2.8 Statistical analysis and chemical kinetics

The analytical results were evaluated statistically using
ANOVA (SAS institute., v. 9.4, Cary, NC, USA) and Pearson
correlation coefficients (Microsoft Excel, 2016, Microsoft
Inc., Redmond, WA, USA). Duncan’s multiple range test
was carried out to evaluate the statistical significance at
the $p<0.05$ level. All data were expressed with mean and
standard deviation of duplicate analysis. The rate constants
(k) were obtained from the slopes of the equations gener-
ated by plotting oxidation products and oxidation time (h).
They make it possible to compare the degree of oxidation
over time in oxidation parameters. R square ($R^2$) obtained
by adjusting the data to an equation represents a linear
correlation coefficient.

3 Results and Discussion

3.1 Synthesis of CAPE

CAPE fractions from LC-Si SPE (silica bonding, solid
phase extraction) were collected (Fig. 1a), and the 1H-NMR
spectroscopic data of chemically synthesized CAPE are
presented in Fig. 1b, which were consistent with previous
studies. The HPLC analysis also suggested that CA
reacted with phenethyl alcohol and was successfully converted to CAPE after the esterification reaction. In the chromatogram (Fig. 1c), CAPE (retention time = 9.8167 min) was eluted later than CA (retention time = 3.35 min) because the hydrophilic carboxyl group of CA participated in the esterification reaction, resulting in reduced hydrophilicity of CAPE, which was separated later from the octadecyl carbon chain (C18)-bonded column in the reversed-phase HPLC system. Therefore, further experiments were carried out using the CAPE thus obtained.

3.2 Viscosity, conjugated dienoic acid value (CDAV), and acid value (AV)

Viscosity is the most common parameter used to evaluate physical changes in thermal oxidized oils. When the oil is heated at high temperatures and oxidized to form a polymer with a high molecular weight, viscosity increases as the amount of the polymer increases\(^{15,17}\). Therefore, the higher the viscosity of frying oil, the more oxidation can be generally expected. In Table 1, the viscosity in all samples rapidly increases as the thermal oxidation progresses continuously, showing a significant difference (\(p < 0.05\)). The initial viscosity (99.3 mPa·s) increased up to 460.7 mPa·s after 32 h thermal oxidation in CON (SBO without antioxidant). When SBO with each antioxidant (i.e., CA, CAPE, \(\alpha\)-TO, and AP) was compared with CON, the viscosity was low, suggesting that the addition of antioxidant had a significant effect on the reduction of high-molecular weight polymer formation due to thermal oxidation. The viscosity of CON after 8 h thermal oxidation was 136.3 mPa·s. This value was similar to the result of an intermittent frying performed for 2 h everyday for 4 days (8 frying hours, 180°C), resulting in viscosity of 103.8 mPa·s, diene value of 1.57, and \(\rho\)-anisidine value of 172.4\(^{10}\). The rate constant (\(k\)) for the viscosity of CON was the highest (10.96) during the 32-h thermal oxidation. A relatively high correlation (\(R^2 > 0.90\)) between viscosity and thermal oxidation time was observed. This result means that the viscosity increases linearly with the oxidation time at 180°C. Among them, CAPE had the lowest viscosity at all oxidation times (8, 16, 24, and 32 h) of 120.5, 175.3, 242.1, and 370.9 mPa·s, suggesting that CAPE is the most effective to retard the polymer formation. In addition, the rate constant was the lowest (8.20) among the oils to which antioxidants were added. The viscosity of \(\alpha\)-TO and AP was lower than that of CA until the 24-h oxidation, but CA conversely showed lower viscosity (407.6 mPa·s) than \(\alpha\)-TO (418.4 mPa·s) and AP (436.6 mPa·s) after the final 32-h oxidation. This results showed that CAPE was effective in depressing polymer formation during thermal oxidation. Polymeric compounds were intermolecularly formed by thermal polymerization such as carbon-to-carbon (C-C) linkages and oxygen bridges (C-O-C) at high temperatures\(^{10}\). The polymeric compounds formed have a high molecular weight and increase the viscosity.

As oxidation of the oil progresses, oxidation products with a conjugated double bond increase\(^{20,21}\). During the initial oxidation stage, the hydrogen atoms are released from the unsaturated fatty acids to generate free radicals, and hydroperoxides are formed. Among them, hydroperoxides with a conjugated double bond accumulate rapidly because of their thermodynamic stability\(^{21}\), which are further utilized to form conjugated oxidation products. Therefore, CDAV can be used as an indicator of measuring

| Thermal oxidation time (h) | CON | CA | CAPE | \(\alpha\)-TO | AP |
|---------------------------|-----|----|------|-------------|----|
| 0                         | 99.3 ± 0.3 |
| 8                         | 136.3 ± 0.2\(^{a}\) | 135.7 ± 0.5\(^{a}\) | 129.5 ± 0.4\(^{ab}\) | 130.1 ± 0.4\(^{ab}\) | 130.6 ± 0.3\(^{ab}\) |
| 16                        | 201.2 ± 0.2\(^{a}\) | 191.9 ± 0.4\(^{ab}\) | 175.3 ± 0.4\(^{cd}\) | 176.5 ± 0.5\(^{cd}\) | 176.3 ± 0.3\(^{cd}\) |
| 24                        | 290.4 ± 0.8\(^{ab}\) | 274.9 ± 0.8\(^{ab}\) | 242.1 ± 0.7\(^{cd}\) | 261.9 ± 1.2\(^{cd}\) | 269.6 ± 1.8\(^{cd}\) |
| 32                        | 460.7 ± 1.5\(^{a}\) | 407.6 ± 0.4\(^{cd}\) | 370.9 ± 1.0\(^{ae}\) | 418.4 ± 0.1\(^{ae}\) | 436.6 ± 1.4\(^{ab}\) |
| \(k\)                      | 10.96 | 9.45 | 8.20  | 9.63        | 10.17 |
| \(R^2\)                    | 0.92  | 0.94 | 0.92  | 0.90        | 0.90  |

Note: All data are shown as mean ± standard deviation (\(n = 2\)). Means with different letters (A–D) within the same column are significantly different (\(p < 0.05\)) according to Duncan’s multiple range test. Means with different letters (a–c) within the same row are significantly different (\(p < 0.05\)) according to Duncan’s multiple range test. \(k\) is rate constant, and \(R^2\) is r square (correlation coefficient).
the degree of oil oxidation. In Table 2, the CDAV of CON significantly increased (p < 0.05) as oxidation progressed from 0 h (0.43%) to 32 h (3.67%). When the antioxidant was added, CAPE showed the lowest CDAV (1.02%) at the initial 4-h oxidation, thereafter, it increased up to 3.12% at 32 h. The CDAV of CA, α-T0, and AP also ranged from 1.16% to 1.43% at 4 h. After 4 h, the CDAV of CAPE was lowest at all oxidation times (i.e., 8, 16, 24, and 32 h), and was about 15% lower than that of CON after 32 h, at which time the CDAV was in the order of CON (3.67%) ≥ CA (3.44%) ≥ AP (3.30%) ≥ CAPE (3.12%). Correlation coefficients of CDAV with thermal oxidation time ranged from 0.93 to 0.95, indicating a linear increase in CDAV over oxidation time. The rate constant (k) for the CDAV was the lowest (0.08) in CAPE during the 32-h thermal oxidation.

The content of free fatty acids is shown as the acid value (AV) in Table 2. While the AV of SBO before oxidation was not detected (ND), AV gradually increased as the oxidation proceeded. In the case of SBO with added antioxidant (i.e., CA, CAPE, α-T0, and AP), the AV showed no significant difference (p > 0.05) among the groups until the first 8 h, but a difference was observed thereafter. After 32 h of oxidation, the AV of CON was the highest at 0.48, whereas the lowest AV was observed in α-T0 (0.34). In the cases of AP, CAPE, and CA, AVs of 0.39–0.44 were observed. AV increased linearly with the thermal oxidation time (correlation coefficients ranged from 0.97 to 0.99).

In this experiment, triacylglycerol hydrolysis would have rarely occurred because SBO itself was heated. Therefore it can be said that the increase in AV was caused by thermal oxidation because our experiment excluded the presence of any food or water that could promote hydrolysis. According to previous studies20–25), even though AV is one of the methods for measuring oil rancidity, having a high correlation with other oxidation parameters, it is not recommended to use it as the only indicator to determine the shelf-life of frying oil. In addition, the AV would not exactly determine the quality of frying oils as well as the sensory quality of fried foods. Fritsch also suggested that if the quality of frying oil is only evaluated by using the AV, an incorrect judgment, such as discarding the usable oil, may occur26). In addition, Onal and Ergin explained that it was not accurate to evaluate the degree of oxidation with

| Thermal oxidation time (h) | CON     | CA | CAPE | α-T0 | AP |
|---------------------------|---------|----|------|------|----|
| 0                         | 0.43 ± 0.01 |
| 4                         | 1.25 ± 0.03<sup>Db</sup> | 1.16 ± 0.04<sup>Ac</sup> | 1.02 ± 0.01<sup>Ba</sup> | 1.43 ± 0.01<sup>Ba</sup> | 1.18 ± 0.04<sup>Bc</sup> |
| 8                         | 1.92 ± 0.09<sup>Da</sup> | 1.78 ± 0.05<sup>Babc</sup> | 1.70 ± 0.06<sup>Ba</sup> | 1.87 ± 0.01<sup>Db</sup> | 1.79 ± 0.01<sup>Dabc</sup> |
| 16                        | 2.64 ± 0.05<sup>Ca</sup> | 2.58 ± 0.09<sup>Cab</sup> | 2.35 ± 0.18<sup>Gb</sup> | 2.63 ± 0.06<sup>Ca</sup> | 2.50 ± 0.07<sup>Ca</sup> |
| 24                        | 3.08 ± 0.02<sup>Bb</sup> | 3.01 ± 0.00<sup>Db</sup> | 2.88 ± 0.03<sup>Ba</sup> | 3.22 ± 0.03<sup>Db</sup> | 3.03 ± 0.1<sup>Bb</sup> |
| 32                        | 3.67 ± 0.02<sup>Aa</sup> | 3.44 ± 0.17<sup>Ab</sup> | 3.12 ± 0.13<sup>Ac</sup> | 3.67 ± 0.04<sup>Ab</sup> | 3.30 ± 0.09<sup>Bbc</sup> |
| k                         | 0.09     | 0.09 | 0.08  | 0.09 | 0.09 |
| R²                        | 0.95     | 0.94 | 0.94  | 0.94 | 0.93 |

| AV                         | ND<sup>11</sup> |
|---------------------------|----------------|
| 0                         | 0.11 ± 0.02<sup>Da</sup> | 0.10 ± 0.00<sup>Da</sup> | 0.08 ± 0.02<sup>Da</sup> | 0.08 ± 0.02<sup>Da</sup> | 0.08 ± 0.02<sup>Ca</sup> |
| 8                         | 0.14 ± 0.00<sup>Da</sup> | 0.13 ± 0.00<sup>Da</sup> | 0.13 ± 0.00<sup>Da</sup> | 0.10 ± 0.00<sup>Da</sup> | 0.12 ± 0.02<sup>Ca</sup> |
| 16                        | 0.25 ± 0.02<sup>Ca</sup> | 0.22 ± 0.02<sup>Cab</sup> | 0.19 ± 0.02<sup>Cab</sup> | 0.17 ± 0.00<sup>Ba</sup> | 0.20 ± 0.05<sup>Ca</sup> |
| 24                        | 0.35 ± 0.02<sup>Ba</sup> | 0.30 ± 0.00<sup>Bb</sup> | 0.27 ± 0.00<sup>Bb</sup> | 0.22 ± 0.00<sup>Bb</sup> | 0.26 ± 0.02<sup>Bbc</sup> |
| 32                        | 0.48 ± 0.02<sup>Aa</sup> | 0.44 ± 0.00<sup>Babc</sup> | 0.42 ± 0.02<sup>Ab</sup> | 0.34 ± 0.00<sup>Bd</sup> | 0.39 ± 0.02<sup>Ac</sup> |
| k                         | 0.01     | 0.01 | 0.01  | 0.01 | 0.01 |
| R²                        | 0.99     | 0.98 | 0.97  | 0.97 | 0.98 |

<sup>11</sup>not detected.

Note: All data are shown as mean ± standard deviation (n = 2). Means with different letters (A–E) within the same column are significantly different (p < 0.05) according to Duncan’s multiple range test. Means with different letters (a–c) within the same row are significantly different (p < 0.05) according to Duncan’s multiple range test. k is rate constant, and R² is r square (correlation coefficient).
AV alone because the oil decomposes into volatile compounds that are more volatile than free fatty acids, which are lost due to evaporation or react to form a non-volatile compound during the oxidation reaction.  

3.3 \( p \)-Anisidine value (\( p \)-AV) and total polar materials (TPM)

As hydroperoxides generated from primary oxidation are very unstable at high temperatures of thermal oxidation, the hydroperoxide rapidly decomposes to produce secondary degradation products, such as aldehydes, ketones, esters, acids, alcohols and short chain hydrocarbons. \( p \)-Anisidine value evaluates the degree of secondary oxidation of the oil by measuring the absorbance at 350 nm after the decomposed secondary degradation product reacts with anisidine. According to a previous study, the correlation between heating time and \( p \)-AV was high when cottonseed oil was heated at 155–195°C, showing an increase of \( p \)-AV over the heating time. In Fig. 2, \( p \)-AV increased exponentially during the thermal oxidation from 0 h to 4 h after which it gradually increased in all samples. For example, CON showed a value of 1.6 at 0 h, and 149 at 32 h.

![Fig. 2](image)

Fig. 2 \( p \)-Anisidine value (\( p \)-AV) of soybean oil (CON) and soybean oil with 200 ppm of caffeic acid (CA), caffeic acid phenethyl ester (CAPE), alpha-tocopherol (\( \alpha \)-TO) and ascorbyl palmitate (AP), during the 32-h thermal oxidation at 180°C. All data are shown as mean ± standard deviation (\( n = 2 \)). Means with different letters (a–e) are significantly different (\( p < 0.05 \)) according to Duncan’s multiple range test.

![Fig. 3](image)

Fig. 3 Total polar materials % (TPM %) of soybean oil (CON) and soybean oil with 200 ppm of caffeic acid (CA), caffeic acid phenethyl ester (CAPE), alpha-tocopherol (\( \alpha \)-TO) and ascorbyl palmitate (AP) during the 32-h thermal oxidation at 180°C. All data are shown as mean ± standard deviation (\( n = 2 \)). Means with different letters (a–d) are significantly different (\( p < 0.05 \)) according to Duncan’s multiple range test.
### Table 3
Changes in the major fatty acid composition (g fatty acid/100 g oil) of soybean oil (CON) and soybean oil with 200 ppm of caffeic acid (CA), caffeic acid phenethyl ester (CAPE), alpha-tocopherol (α-T0), and ascorbyl palmitate (AP) during the 32-h thermal oxidation at 180°C.

| Thermal oxidation time (h) | PA       | OA       | LA       | LnA     |
|---------------------------|----------|----------|----------|---------|
| 0                         | 10.4 ± 0.1 | 23.5 ± 0.1 | 48.3 ± 0.3 | 4.9 ± 0.0 |
| 4                         | 10.9 ± 0.1 | 23.2 ± 0.3 | 46.8 ± 0.6 | 4.7 ± 0.0 |
| 8                         | 11.0 ± 0.1 | 22.9 ± 0.3 | 44.2 ± 0.5 | 4.2 ± 0.0 |
| 16                        | 11.0 ± 0.1 | 22.2 ± 0.3 | 39.1 ± 0.4 | 3.4 ± 0.0 |
| 24                        | 10.8 ± 0.1 | 21.4 ± 0.1 | 34.6 ± 0.2 | 2.7 ± 0.0 |
| 32                        | 10.9 ± 0.1 | 20.9 ± 0.4 | 30.5 ± 0.5 | 2.2 ± 0.0 |
| k                         | 0.01     | -0.08    | -0.57    | -0.09   |
| R²                        | 0.16     | 1.00     | 1.00     | 0.99    |

| Thermal oxidation time (h) | PA       | OA       | LA       | LnA     |
|---------------------------|----------|----------|----------|---------|
| 4                         | 11.0 ± 0.0 | 23.4 ± 0.1 | 47.6 ± 0.1 | 4.8 ± 0.0 |
| 8                         | 10.9 ± 0.1 | 22.7 ± 0.3 | 44.1 ± 0.7 | 4.2 ± 0.0 |
| 16                        | 11.0 ± 0.2 | 22.3 ± 0.6 | 39.8 ± 1.0 | 3.5 ± 0.1 |
| 24                        | 10.8 ± 0.1 | 21.4 ± 0.3 | 35.4 ± 0.5 | 2.8 ± 0.0 |
| 32                        | 10.8 ± 0.3 | 20.7 ± 0.7 | 31.1 ± 1.0 | 2.3 ± 0.0 |
| k                         | 0.00     | -0.09    | -0.56    | -0.09   |
| R²                        | 0.06     | 0.99     | 0.99     | 0.99    |

| Thermal oxidation time (h) | PA       | OA       | LA       | LnA     |
|---------------------------|----------|----------|----------|---------|
| 4                         | 11.0 ± 0.1 | 23.5 ± 0.2 | 48.2 ± 0.3 | 4.9 ± 0.0 |
| 8                         | 11.0 ± 0.0 | 23.1 ± 0.0 | 45.2 ± 0.1 | 4.4 ± 0.0 |
| 16                        | 10.9 ± 0.2 | 22.5 ± 0.5 | 40.9 ± 0.9 | 3.7 ± 0.1 |
| 24                        | 10.9 ± 0.2 | 21.8 ± 0.6 | 36.7 ± 1.1 | 3.0 ± 0.0 |
| 32                        | 10.8 ± 0.1 | 21.0 ± 0.3 | 32.0 ± 0.4 | 2.4 ± 0.0 |
| k                         | 0.00     | -0.08    | -0.53    | -0.08   |
| R²                        | 0.07     | 0.98     | 0.99     | 0.99    |

| Thermal oxidation time (h) | PA       | OA       | LA       | LnA     |
|---------------------------|----------|----------|----------|---------|
| 4                         | 11.0 ± 0.1 | 23.4 ± 0.2 | 47.5 ± 0.3 | 4.7 ± 0.0 |
| 8                         | 10.9 ± 0.1 | 23.0 ± 0.4 | 45.0 ± 0.7 | 4.4 ± 0.0 |
| 16                        | 11.0 ± 0.2 | 22.6 ± 0.4 | 41.1 ± 0.7 | 3.7 ± 0.0 |
| 24                        | 10.9 ± 0.2 | 21.8 ± 0.5 | 36.2 ± 0.8 | 2.9 ± 0.0 |
| 32                        | 10.8 ± 0.1 | 20.8 ± 0.2 | 31.0 ± 0.3 | 2.2 ± 0.0 |
| k                         | 0.01     | -0.08    | -0.55    | -0.09   |
| R²                        | 0.10     | 0.97     | 0.99     | 1.00    |

| Thermal oxidation time (h) | PA       | OA       | LA       | LnA     |
|---------------------------|----------|----------|----------|---------|
| 4                         | 11.1 ± 0.0 | 23.5 ± 0.1 | 47.9 ± 0.1 | 4.8 ± 0.0 |
| 8                         | 11.0 ± 0.1 | 23.1 ± 0.2 | 45.4 ± 0.3 | 4.4 ± 0.0 |
| 16                        | 11.0 ± 0.1 | 22.5 ± 0.4 | 40.9 ± 0.6 | 3.7 ± 0.0 |
| 24                        | 11.0 ± 0.3 | 21.9 ± 0.7 | 36.0 ± 1.2 | 2.9 ± 0.1 |
| 32                        | 10.7 ± 0.1 | 20.6 ± 0.2 | 30.4 ± 0.3 | 2.2 ± 0.0 |
| k                         | 0.00     | -0.09    | -0.58    | -0.09   |
| R²                        | 0.01     | 0.96     | 0.99     | 0.99    |

Note: All data are shown as mean ± standard deviation (n = 2). k is rate constant, and R² is r square (correlation coefficient). LA is linoleic acid (C18:2), PA is palmitic acid (C16:0), LnA is linolenic acid (C18:3), OA is oleic acid (C18:1).
4 h, and then further increased to 346 after 32 h, showing a non-linear increase of $p$-AV with respect to time. An increase of $p$-AV in similar tendency was observed previously\(^\text{20}\). In the case of SBO with added antioxidant (i.e., CA, CAPE, $\alpha$-TO, and AP), $p$-AV showed a similar trend to that of CON during the 32-h oxidation. Finally, the value of $p$-AV after the 32-h oxidation was in the order of CON $(346) > \alpha$-TO $(322) > CA (318) > AP (314) > CAPE (302)$. Therefore, CAPE showed the lowest $p$-AV at all oxidation times $(p<0.05)$.

The content of total polar materials (TPM) is known to be a reliable parameter of the quality of the oil used for frying food, indicating the presence of newly produced compounds with higher polarity than triacylglycerol. Therefore, TPM is more influenced by the type of oil than by the type of food, because the fatty acid composition of oil (e.g., short chain fatty acid and unsaturated fatty acid) and its content affect the rate of hydrolysis and oxidation\(^\text{16,30}\). In Fig. 3, TPM % increased linearly with increasing heating time in all samples. In the case of CON, TPM increased to 74% at 32 h, and the order of TPM of samples containing antioxidants after the 32-h oxidation was AP $(72\%) > \alpha$-TO $(70\%) > CA (67.5\%) > CAPE (64.3\%)$. Some of the polar compounds derived from thermally oxidized oils are toxic in animal experiments and, therefore, the TPM % of frying oil is recommended to be less than 24–27% in many European countries\(^\text{14,32}\). In our results, CON, CA, $\alpha$-TO, and AP were 22.5–23% TPM at 8 h, but CAPE was 19.3%, which was the slowest TPM production during the thermal oxidation among the antioxidants used. Generally, the formation of polar components during the oxidation is facilitated by the high temperature and the large amount of unsaturated fatty acids\(^\text{21,29}\). In previous research, the total polar component (%) of the frying canola oil was studied at 185°C and 215°C with replenishment of oil. After 7 days, total polar component (%) at 215°C was 2.6 times higher than that at 185°C\(^\text{25}\).

### 3.4 Change of fatty acid composition

When the thermal oxidation was carried out at 180°C for 32 h, quantitative changes in the fatty acid expressed in g fatty acid/100 g oil are shown in Table 3. As expected, the change in polyunsaturated fatty acids (PUFAs) was larger than that of saturated fatty acids (SFAs) and monounsaturated fatty acids (MUFA) in the CON and all samples containing antioxidants because PUFAs are more readily degraded by thermal oxidation than SFAs and MUFA. During the thermal oxidation process, the structure of some fatty acids constituting oil is changed by chemical reactions including cyclization, polymerization, pyrolysis, and oxidation\(^\text{4}\). Because unsaturated fatty acids, such as linoleic acid (LA, C18:2) and linolenic acid (LnA, C18:3), are unstable to thermal oxidation and are likely to undergo structural changes, while saturated fatty acids such as palmitic acid (PA, C16:0) are stable, a change in the content of unsaturated fatty acids, or the ratio of unsaturated fatty acids to saturated fatty acids, can be used as an indication of the degree of oxidation\(^\text{15,34}\). In the case of CON, LA (C18:2), the main unsaturated fatty acid constituting SBO, decreased from 48.3 before oxidation to 30.5 g/100 g oil after 32 h. Furthermore, LnA (C18:3) showed a marked decrease of approximately 55% over the same oxidation time. However, the decrease was less in the samples containing antioxidants, especially CAPE. The contents of LA and LnA were higher in CAPE than those of CA, $\alpha$-TO, and AP after 32 h, showing 32 and 2.4 g/100 g oil, respectively. LA and LnA decreased linearly with the thermal oxidation time (correlation coefficients ranged from 0.99 to 1.00). The reduction rate constants of the LA and LnA in CAPE were 0.53 and 0.08, respectively, indicating that CAPE is more efficient on thermal oxidation.

Based on the result from content of fatty acids, LA/PA and LnA/PA were obtained and compared among the CON and all samples containing antioxidants (Table 4). In the case of CON after 32 h, LA/PA and LnA/PA decreased from 4.66 and 0.48 before oxidation to 2.8 and 0.2, respectively. Such a decrease was observed in all samples containing antioxidant where LA/PA and LnA/PA gradually decreased as the oxidation proceeded. After 32-h oxidation, CAPE showed a higher LA/PA than CA, $\alpha$-TO, and AP, and the order of LA/PA was CAPE $(2.96) > CA (2.88) > \alpha$-TO $(2.87) > AP (2.83) > CON (2.8) \ (p<0.05)$, suggesting that CAPE is the most effective at retarding the thermal oxidation. Similarly, CAPE showed higher LnA/PA than CA, $\alpha$-TO, and AP, and CON $(p>0.05)$ at 32 h oxidation. Such antioxidative capacity is attributed to the structural characteristics of CAPE, which has an ortho-dihydroxyl group within its catechol ring, inhibiting oxidation as a hydrogen donor\(^\text{2,35}\).

### 3.5 Correlation between oxidation parameters in CON and CAPE under thermal oxidation

The correlation between the oxidation parameters (TPM, CDAV, $p$-AV, viscosity, AV, and LA/PA) observed from thermal oxidation for 32 h was examined; in which CAPE, which showed the best oxidation parameters, and CON are presented in Table 5. In this study, TPM had a correlation coefficient ($r$) of 0.94 or higher with CDAV, viscosity, AV, and LA/PA, but a somewhat lower $r$ with $p$-AV. For example, TPM showed a relatively high correlation with viscosity in both CON ($r=0.9732$) and CAPE ($r=0.9821$) as the thermal oxidation progressed. After 32 h, TPM % of the CON with the highest viscosity $(460.7 \text{ mPa·s})$ and CAPE with the lowest viscosity $(370.9 \text{ mPa·s})$ were 74 and 64.3, respectively, and this tendency was also observed during the reaction (Table 1 and Fig. 3). In a previous study, there was a high correlation between TPM and viscosity in frying oil, and this increase in viscosity and TPM was mainly attributed to the increase in polymers during
In the content of palmitic acid (C16:0) ppm of caffeic acid (CA), caffeic acid phenethyl ester (CAPE), alpha-tocopherol (α-T0), and ascorbyl palmitate (AP) during the 32-h thermal oxidation at 180°C.

Table 4  The ratio of C18:2/C16:0 (LA/PA) and C18:3/C16:0 (LnA/PA) in soybean oil (CON) and soybean oil with 200 ppm of caffeic acid (CA), caffeic acid phenethyl ester (CAPE), alpha-tocopherol (α-T0), and ascorbyl palmitate (AP) during the 32-h thermal oxidation at 180°C.

| Thermal oxidation time (h) | 0   | 4   | 8   | 16  | 24  | 32  | k    | R²  |
|---------------------------|-----|-----|-----|-----|-----|-----|------|-----|
| CON                       | 4.28b | 4.02b | 3.57c | 3.19d | 2.80d | −0.06 | 0.99 |
| CA                        | 4.31b | 4.05b | 3.63b | 3.27c | 2.88b | −0.05 | 0.99 |
| CAPE                      | 4.66 |     |     |     |     |     |      |     |
| α-T0                      | 4.30b | 4.12a | 3.75a | 3.31b | 2.87b | −0.05 | 0.99 |
| AP                        | 4.32b | 4.11a | 3.73a | 3.27c | 2.83a | −0.06 | 1.00 |
| LnA/PA                    | 0.48 |     |     |     |     |     |      |     |
| CAPE                      | 0.44 | 0.40 | 0.34 | 0.28 | 0.22 | −0.01 | 1.00 |
| α-T0                      | 0.43 | 0.40 | 0.34 | 0.27 | 0.21 | −0.01 | 1.00 |
| AP                        | 0.44 | 0.40 | 0.34 | 0.26 | 0.20 | −0.01 | 1.00 |

Note: All data are shown as mean ± standard deviation (n = 2). Means with different letters (a–d) within the same column are significantly different (p < 0.05) according to Duncan’s multiple range test, which was performed on LA/PA. LA is linoleic acid (C18:2), PA is palmitic acid (C16:0), LnA is linolenic acid (C18:3). k is rate constant, and R² is r square (correlation coefficient).

Table 5 Correlation coefficients (r) of oxidation parameters in soybean oil (CON) and soybean oil with 200 ppm of caffeic acid phenethyl ester (CAPE) during the 32-h thermal oxidation at 180°C.

|                  | TPM  | CDAV | p-AV | Viscosity | AV  |
|------------------|------|------|------|-----------|-----|
|                  | CON  | CAPE | CON  | CAPE      | CON |
| CDAV             | 0.9595 | 0.9417 | −    | −         | −   |
| p-AV             | 0.8790 | 0.8533 | 0.9760 | 0.9762    | −   |
| Viscosity        | 0.9732 | 0.9821 | 0.8769 | 0.8528    | 0.7603 | 0.7338 | −    | −    | −    |
| AV               | 0.9878 | 0.9811 | 0.9760 | 0.9437    | 0.9188 | 0.8807 | 0.9578 | 0.9732 | −    | −    |
| LA/PA            | 0.9865 | 0.9865 | 0.9915 | 0.9797    | 0.9447 | 0.9226 | 0.9289 | 0.9454 | 0.9940 | 0.9876 |

¹Correlations were negative.

Note: CDAV is conjugated diene acid value, AV is acid value, p-AV is p-anisidine value, TPM is total polar materials, LA/PA is ratio of C18:2 to C16:0, LA is linoleic acid (C18:2), and PA is palmitic acid (C16:0).

the thermal oxidation⁶⁰. Therefore, it can be concluded that the correlation between the TPM % and the viscosity was affected by the produced polymers. In addition, as presented, the correlation between TPM and the other parameters ranged from 0.9878 (r of between TPM and AV in CON) to 0.8533 (r of between TPM and p-AV in CAPE) in this study.

The correlation between TPM and LA/PA was also high. Warner and Mounts stated that since unsaturated fatty acids in oil are more oxidative than SFAs, reduction of unsaturated fatty acid content during thermal oxidation should be associated with an increase in polar compounds¹¹. During 32 h of thermal oxidation, the decrease in the content of palmitic acid (C16:0) was negligible, but the LA (C18:2) decreased from 48.3% (0 h) to 30.5% (32 h) in the CON. Such a decrease was also observed in CAPE, which was 32.0% after the 32-h oxidation, but the reduction rate was lower than CON. Thus, the decrease in LA/PA and the increase in TPM % also showed a high correlation in both CON and CAPE (r = 0.9865).

In principle, the double bond of linoleic acid (cis, cis-9,12-octadecadienoic acid) is in the form of non-conjugation, where the position of the double bond is changed during oxidation, resulting in a structural change to a conjugated diene³⁶–³⁸. In our previous study, oxidized SBO with high LA content resulted in the formation of a conjugated form of aldehyde such as (E,E)-2,4-alkadienals, which could be identified by proton nuclear magnetic resonance (¹H-NMR)⁶, ¹⁸, ⁴⁰. Therefore, CDAV had a very high correlation with LA/PA (r = 0.9915 in CON and r = 0.9797 in CAPE) because a conjugated double bond would be formed from the oxidized LA and LnA. In addition, CDAV was more
correlated with p-AV and AV than viscosity. However, p-AV, which measures the secondary oxidation products, showed a relatively lower correlation with viscosity (0.7603 in CON and 0.7338 in CAPE) and TPM (0.8790 in CON and 0.8533 in CAPE) than other parameters. This is because rapid secondary oxidation caused by heat resulted in an exponential increase in p-AV (i.e., aldehyde) that were much faster than viscosity and TPM (i.e., a polar compound) up to 4 h, thereafter, the increase in p-AV was less than viscosity and TPM until 32 h. On the other hand, viscosity and TPM increased gradually during the thermal oxidation for 32 h. Therefore, relatively low correlations among p-AV, viscosity, and TPM were observed.

4 Conclusion

In this study, the antioxidative capacity of CA, AP, α-T, and CAPE was evaluated under the thermal oxidation condition. After 32 h, all antioxidants used in this experiment showed significantly lower viscosity, TPM, p-AV, and higher LA/PA than CON (p < 0.05), indicating that the thermal oxidation was retarded. In particular, CAPE showed significantly lower viscosity, TPM, p-AV, and higher LA/PA than other antioxidants (p < 0.05) after the 32-h reaction. CAPE was synthesized by esterifying CA and phenethyl alcohol. Therefore, the carboxyl group, which is a hydrophilic group in CA, is not present in CAPE, but instead has a phenethyl group. As a result, the structural conversion to CAPE showed higher solubility than CA in oil, resulting in different antioxidant capacity in this study. CAPE showed relatively low rate constants in viscosity (polymer formation), CDAV (conjugated dienes formation), and reduction of LA and LnA contents. It can be concluded that the addition of CAPE to the fried oils offers the higher thermal oxidation stability. In the correlation between the oxidation parameters measured from CON and CAPE, p-AV showed a relatively lower correlation with viscosity (r = 0.7603 in CON and r = 0.7338 in CAPE) and TPM (r = 0.8790 in CON and r = 0.8533 in CAPE) than other parameters because p-AV, which increased rapidly up to the first 4 h, was less likely to increase thereafter, compared to viscosity and TPM.

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Conflicts of Interest

The authors declare no conflict of interest.

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