



The impact of supercritical CO₂ conditions on extracting antioxidant compounds from tangerine leaves (*Citrus reticulata*) for enhancing oxidative stability in soybean oil

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ABSTRACT

Tangerine leaves were valorized as a source of natural antioxidants for protecting soybean oil against lipid oxidation. Initial Soxhlet extracts obtained using hexane (Hex-S), ethyl acetate (EtOAc-S), and ethanol (EtOH-S) showed that the Hex-S extract provided the highest oxidative stability, highlighting the relevance of nonpolar compounds in delaying lipid oxidation. To develop a more sustainable alternative to hexane extraction, supercritical CO₂ (SC-CO₂) extraction was optimized using a central composite design, assessing the effects of pressure (100, 200, and 300 bar) and temperature (40, 50, and 60 °C) on the extract's antioxidant performance. The optimal SC-CO₂ extract, obtained at 273 bar and 37 °C, extended the induction period of soybean oil oxidation to 5.2 h, outperforming both the Hex-S extract (4.4 h) and the control sample (3.8 h), and resulted in a lower p-anisidine value (13.36). These activities may be attributed to extracted bioactive compounds, such as linalool, thymol, and tangeretin.

1. Introduction

Consumers are increasingly concerned about the potential toxicological risks associated with synthetic antioxidants, including butylhydroxytoluene (BHT), tert-butyl hydroquinone (TBHQ), propyl gallate (PG), and butylhydroxyanisole (BHA), commonly used to prevent lipid oxidation in oils (Hashemi, Khorram, & Sohrabi, 2017). In this context, studies have focused on replacing synthetic antioxidants with natural ones extracted from agro-industrial waste (Alonso et al., 2026). Among the antioxidant molecules that have been used to enrich foods, notable examples include phenolic compounds, such as polymethoxyflavones, flavanones glycosides, (Chakroun et al., 2023; Safranko, Šubarić, Jerković, & Jokić, 2023), hydroxycinnamic acids (Medina, González, Iglesias, & Hedges, 2009), and volatile compounds such as terpenes and sesquiterpenes (Domínguez-Rodríguez et al., 2024).

Considering this growing interest in natural antioxidants, citrus fruits are among the most widely produced crops worldwide (Food and

Agriculture Organization of the United Nations (FAO), 2022). The global tangerine production in 2023/2024 reached 38.15 million metric tons (United State Department of Agriculture (USDA), 2024), resulting in approximately 15 million tons of waste, primarily comprising peels and leaves (Andrade et al., 2023). Traditionally, these residues, which contribute to environmental pollution (Fierascu, Fierascu, Avramescu, & Sieniawska, 2019), have been used as livestock feed or eliminated through combustion. However, burning these materials releases harmful chemical compounds, including greenhouse gases such as CO₂, CH₄, and N₂O (Lynch, Cain, Frame, & Pierrehumbert, 2021), posing a serious threat to human health and the environment. However, citrus leaves, considered low-value post-harvest by-products, contain bioactive compounds with significant potential to mitigate oxidative stress (Fahmy, Elhady, Bannan, Malatani, & Gad, 2022; Vladić et al., 2023). In particular, tangerine leaves stand out for their high concentration of phenolic compounds, phenolic acids, flavonoids, coumarins, and terpenoids, which have demonstrated remarkable antioxidant activity

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(Domínguez-Rodríguez et al., 2024).

Although traditional liquid-liquid and solid-liquid extraction techniques, such as Soxhlet, are effective for recovering various phytochemicals (Alasalvar & Yildirim, 2021; Saboon, Arshad, Amjad, & Akhtar, 2019), they present significant drawbacks: they require large amounts of solvents, involve long extraction times, can thermally degrade the target compounds (Galanakis, Tornberg, & Gekas, 2010), and pose health risks due to some solvent toxicity (Pimentel-Moral et al., 2018). Therefore, there is considerable interest in replacing traditional extraction techniques and organic solvents with advanced extraction technologies and green solvents (Domínguez-Rodríguez et al., 2024; Jiao et al., 2026; Leyva-Jiménez et al., 2020).

Supercritical fluid extraction (SFE), specifically, supercritical CO₂ (SC-CO₂) is a sustainable extraction alternative because CO₂ is a non-toxic, cheap, and renewable solvent that possesses physicochemical properties that allows an easy penetration in plant tissues (Manjare & Dhingra, 2019), exhibiting rapid mass transfer from the surface of particles to the fluid (Sovová, 2012). Additionally, SC-CO₂, a selective nonpolar solvent (Romano et al., 2020), is widely used in the food industry due to its critical point at 31 °C and 74 bar, enabling extractions at near-ambient temperatures. In this context, SC-CO₂ extraction offers a key advantage: it leaves no solvent residues in the final extracts. Moreover, the selectivity of this technique can be adjusted by modifying the temperature, pressure, or both factors (Aresta, Cotugno, De Vietro, Massari, & Zamboni, 2020).

The use of SC-CO₂ to recover bioactive compounds from tangerine leaves remains limited, with a focus on obtaining phenolic compounds using ethanol as a co-solvent (Jamilah, Abdulkadir, Suhaila, & Md Zaidul, 2011). Thus, the use of SC-CO₂ extraction for recovering bioactive compounds from tangerine agro-industrial waste to develop a novel oil preservative represents an opportunity aligned with the principles of green chemistry (De Marco et al., 2019). Therefore, this study aimed to replace the traditional Soxhlet extraction technique by optimizing SC-CO₂ extraction conditions (pressure and temperature) to achieve extracts that effectively prevent lipid oxidation in soybean oil while minimizing color alteration. This effort aimed to develop a novel natural antioxidant ingredient from Arrayana variety tangerine leaves (*Citrus reticulata*).

2. Material and methods

2.1. Chemicals

The analytical grade hexane (purity 99%), ethyl acetate (purity 99.7%), and ethanol (purity 99.5%) were purchased from Sigma-Aldrich (St. Louis, MO, USA) and TCI-Tokyo chloroform (purity 99.5%), isooctane (purity 99%), and ethyl ether (purity 99%) were obtained from Macron Fine Chemicals TM (Madrid, Spain). Tert-butylhydroquinone (TBHQ), potassium iodide (KI), and sodium thiosulfate (Na₂S₂O₃) were obtained from PanReac. The Milli-Q water was produced in a Millipore system (Billerica, MA, USA).

2.2. Materials preparation and characterization

Refined bleached, and deodorized (RBD) soybean oil without antioxidants was purchased from GRASCO (Bogotá, Colombia). The leaves of the Arrayana variety tangerine (*C. reticulata*) were supplied by producers from the Department of Tolima, Colombia. The leaves were harvested from randomly selected, healthy trees of the *Citrus* genus, family Rutaceae, during their harvest period in April 2024. Collection criteria included uniform size and color. After collection, the plant material was packed and stored in a cool, dry place for transport to the processing site. This storage period did not exceed 48 h. Upon arrival, the tangerine leaves were dried to a constant weight under reduced pressure at 0.07 bar and 40 °C in a drying oven for 48 h. Then, the dried leaves were ground in an electric mill and sieved using Tyler series

sieves, mesh #14 (1.4 mm). The samples were stored in the dark at 4 °C until further processing.

The proximate composition analysis of the tangerine leaves was assessed by the moisture, ash, protein, total carbohydrate, and fat content in triplicate. The moisture content was determined by AOAC Method No. 935.29, while ash content was measured by AOAC Method No. 972.15. The protein content in the leaves was determined using the Bradford method (Karimi et al., 2022), total carbohydrate content was determined following the UV-sulfuric acid assay (Ehnert, Seehase, Müller-Renno, Hannig, & Ziegler, 2021), and fat content was determined by the cold extraction method with chloroform:methanol (Pohndorf et al., 2016). Therefore, tangerine leaves presented 84.5 ± 0.3 g/100 g, 41.6 ± 2.3 g/100 g, 13.5 ± 0.1 g/100 g, 9.2 ± 0.7 g/100 g, and 7.0 ± 0.1 g/100 g of moisture, carbohydrate, protein, ash, and fat content, respectively.

2.3. Traditional extraction of compounds with preservative effects on soybean oil

Soxhlet extractions were performed with hexane (Hex-S), ethyl acetate (EtOAc-S), and ethanol (EtOH-S) to obtain different compound groups from tangerine leaves. Extractions were conducted under reduced pressure, using 75 mL of each solvent, Hex-S, EtOAc-S, and EtOH-S, and 1.5 g of grounded tangerine leaves at a solid to solvent ratio of 1:50 (w/v). The extraction conditions were: Hex-S at 450 mbar and 35 °C, EtOAc-S at 550 mbar and 40 °C, and EtOH-S at 600 mbar and 45 °C. Each extraction was carried out for 10 h. Solvents were then removed from each extract under reduced pressure using a rotary evaporator. The dry basis percentage yield (%) for each extract was determined by weight difference. The dry extracts were directly added to soybean oil at 1000 ppm to observe their protective effects through a stability study.

2.4. Sustainable extraction of preservative compounds from tangerine leaves using SC-CO₂

A new SC-CO₂ sustainable extraction process to replace traditional extractions was developed to obtain compounds with preservative effects in soybean oil and low changes in the oil color from tangerine leaves. This study was performed using a rotational central composite design (RCCD), including four axial points and five central points, for a total of 13 assays (shown in Table S1 in the supplementary material). The variables evaluated were pressure (58, 100, 200, 300, and 341 bar) and temperature (35, 40, 50, 60, and 64 °C) on yield, compounds preservative effects on soybean oil, and changes in oil color, being the Induction Time (IT), acid value (AV), peroxide value (PV), *p*-anisidine value (pAV), and oil color used as response variables. The response variables were evaluated at each point of the experimental design to identify the optimal extract, and subsequently, the same response variables were assessed in the optimal extract. These measurements were carried out every 5 days over a period of 20 days in the extracts stored at 60 °C.

The extraction was conducted using a Speed Helix supercritical fluid extractor from Applied Separations (Allentown, PA, USA) with pure CO₂ as the solvent (Carbueros Metálicos, Air Products Group, Madrid, Spain). For each extraction, 15.0 g of dried tangerine leaves were combined with 7.5 g of glass beads and placed in a 300 mL stainless steel extraction cell. Filter paper was used at both ends of the cell to contain the sample. A kinetic study was performed, obtaining an optimal extraction time of 40 min with a constant CO₂ flow rate of 9 L/min. To protect the collected extracts from light exposure, vials were wrapped in aluminum foil. Then, the dry extracts were added to soybean oil at 1000 ppm to observe their protective effects through a stability study. A central composite design was implemented, conducting a total of 13 experiments. The conditions of each experiment and the results are presented in the Supplementary Tables S1 and S2.

2.5. Oxidative stability study of soybean oil

To evaluate the preservative effects of Soxhlet and SC-CO₂ extracts on soybean oil, two oxidative stability tests were performed: 1) using the Schaal oven storage test at 60 °C and (Nielsen, 2019); 2) by the induction time (IT) test using the 892 Professional Rancimat® method of Metrohm.

1) Dry, solvent-free extracts were added to refined, bleached, and deodorized (RBD) soybean oil samples at a concentration of 1000 ppm. As a positive control, the synthetic antioxidant TBHQ was added at 200 ppm, and an untreated oil sample served as the control. The added extract oils were then placed in an oven at 60 °C for 20 days. Aliquots of the oils were collected every 5 days and analyzed for acid value (AV, expressed as % oleic acid), peroxide value (PV), p-anisidine value (pAV), and total oxidation value (TOTOX). The AV was determined following the AOCS Cd 3d-63 method, while PV was measured according to AOAC method 965.33. The pAV was assessed using AOAC method 18–90. A blank test was run under the same conditions as the samples. The TOTOX value, representing total oxidation by combining primary (PV) and secondary (pAV) oxidation products, was calculated using Eq. 1 (Gutiérrez, Quiñones-Segura, Sanchez-Reinoso, Díaz, & Abril, 2017). All analyses were conducted in triplicate to ensure reproducibility.

$$TOTOX = (2 \times PV) + pAV. \quad (1)$$

2) The oxidative stability of soybean oil was assessed by measuring the IT using the Metrohm 892 Professional Rancimat® method. The IT test defines the time elapsed before the onset of detectable rancidity or rapid lipid oxidation, reflecting the period required to form the secondary oxidation products. Each extract from tangerine leaves was added to 3.0 g soybean oil sample at 1000 ppm. Soybean oil without antioxidants served as the control sample, while TBHQ, a synthetic antioxidant, was used at 200 ppm as a positive control according to Codex Alimentarius limits. Results were expressed as IT and each test was performed in triplicate. During the test, samples were exposed to a constant airflow of 20 L/h at 120 °C (del P Sánchez-Camargo et al., 2019).

2.6. Color of soybean enriched with Soxhlet and SC-CO₂ extracts

After adding the extracts to the soybean oil, its color parameters were analyzed to verify color modifications according to Alvarado-López et al. (2024) protocol using a colorimeter (SPECORD 210 PLUS, Analytik Jena, Jena, Germany) with D65 illuminant and a standard 10° viewing angle, covering a spectral range from 380 to 780 nm. Values were expressed in the CIE Lab* color space, with L* representing lightness (L* = 0 for black and L* = 100 for white), a* indicating chroma from green (negative) to red (positive), and b* indicating chroma from blue (negative) to yellow (positive). Color difference (ΔE_{Lab}) was calculated with Eq. 2 to evaluate the effect of extract addition on oil color change. Color measurements were performed in duplicate (n = 2).

$$\Delta E_{Lab} = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2} \quad (2)$$

2.7. Characterization of extracts by gas chromatography-mass spectrometry

A tentative identification and quantification of volatile compounds extracted from tangerine leaves were performed by diluting the samples to a concentration of 2.5 mg/mL in EtOH. The extracts were filtered through a 0.45 µm nylon filter (Agilent Technologies, California, USA) and analyzed by gas chromatography-mass spectrometry (GC-MS) equipped with an electron impact (EI) ionization source. Helium served as the carrier gas at a linear velocity of 32.5 cm/s. Separation was achieved using an Agilent Zorbax DB5-MS + 10 m Duraguard capillary column (30 m, 0.25 mm, 0.25 µm). The oven temperature program

began at 45 °C, increased to 290 °C at 10 °C/min, and then rose to 325 °C at 5 °C/min, where it was held for 10 min. The injection volume was 1 µL in split mode, with an injector temperature of 250 °C. The mass spectrometer operated with an electron ionization (EI) source at 250 °C and an interface temperature of 335 °C. In SCAN mode, the mass analyzer used a scan rate of 1428 amu/s with an event interval of 0.40 s. Data were processed using Shimadzu GC Solution software, and terpenoids were identified with reference to a commercial mass spectral database (Wiley) and compared with literature data. Each analysis was performed on three independent extract samples to ensure accuracy and reproducibility.

2.8. Statistical analysis

Statgraphics Centurion version XVII (Statistical Graphics Corp, USA) was employed to compare the oxidative stability among tangerine leaves extracts obtained via Soxhlet and SC-CO₂. A one-way analysis of variance (ANOVA) using Fisher's exact test identified statistically significant differences (p-value ≤ 0.05) between the mean values of different extracts, with a 95% confidence interval. Each analysis was performed in triplicate for reliability. For the RCCD design, the effect of each experimental parameter on the response variables was studied at a 95% confidence level.

3. Results and discussion

3.1. Soxhlet extracts: Characterization and effects on oil oxidative stability and color

3.1.1. Soxhlet extraction yields and chemical profiling by GC-MS

Soxhlet extractions yielded 16.6 ± 0.8 g/100 g^{ab} (Hex-S), 18.0 ± 0.4 g/100 g^a (EtOAc-S), and 14.6 ± 0.6 g/100 g^b (EtOH-S). Extraction yield depended on solvent polarity, following the “like dissolves like” principle (Nielsen, 2019). EtOAc, with intermediate polarity, achieved the highest yield by extracting both polar and non-polar compounds (Kammoun Bejar, Boudhrioua Mihoubi, & Kechaou, 2012), while Hex, a nonpolar solvent, primarily extracted lipophilic compounds like waxes and lipids (Nielsen, 2019). Thus, EtOAc outperformed polar and nonpolar solvents by bridging both extraction capacities.

GC-MS analysis identified 21 terpenoids, 15 common across all extracts (Table 1). In Hex-S predominated triterpenes (42% of total peak areas) and flavonoids (34% of total peak areas), AcOEt-S presented tocopherols (50% of total peak areas), triterpenes (24% of total peak areas), and flavonoids (14% of total peak areas), while EtOH-S showed tocopherols (49% of total peak areas), flavonoids (27% of total peak areas), and triterpenes (14% of total peak areas). Overall, tocopherols were predominant in the AcOEt-S and EtOH-S extracts, while triterpenes dominated in the Hex-S extract. EtOAc-S and Hex-S extracts showed higher total peak areas than EtOH-S. In EtOAc-S extract, tangeritin (48 ± 1% of total peak area) and vitamin E (26 ± 3% of total peak area) were most abundant, while Hex-S extracts were rich in tangeritin (34 ± 3% of total peak area) and methyl comate 2 (22 ± 3% of total peak area). Tangeritin, a flavonoid frequent in citrus leaves (Leporini et al., 2020), interacts with both polar and nonpolar solvents due to its structure (Boye, Ahmad, Fakhri, Hussain, & Khan, 2021).

EtOH-S extracts predominantly contained methyl comate 2 (13.35 ± 0.05% of total peak area) and thymol (2.82 ± 0.68% of total peak area), a compound reported in *Citrus reticulata* leaves (Domínguez-Rodríguez et al., 2024; Fanciullino, Tomi, Luro, Desjobert, & Casanova, 2006). Triterpenes were the main group in Hex-S (41.4% of total peak area) and EtOH-S (14.2% of total peak area) extracts. Hex-S extract, known for isolating mono- and sesquiterpenoids (Siddiqui, Khan, Sharma, & Gupta, 2024), showed higher total terpenoid areas compared to EtOAc-S extracts. Additionally, EtOH extraction at 45 °C favored terpenoid solubilization and release by weakening cellular membranes (Rodrigues, de Melo, Portugal, & Silva, 2021; Yang et al., 2009). Our findings

Table 1Compounds identified in Soxhlet extracts and in optimal SC-CO₂ conditions by GC–MS and relative area percentage.

Proposed compound	RT (min)	Molecular formula	Similarity (%)	Measured mass	Main fragments ions (m/z)	(Area % ± SD)			
						Hex	EtOAc	EtOH	Optimal extract
Linalool	8.244	C ₁₀ H ₁₈ O	97	154	121, 93, 71, 43	0.09 ± 0.01	4 ± 1	2.30 ± 0.40	35 ± 3
Hotrienol	9.484	C ₁₀ H ₁₆ O	85	152	119, 93, 71, 43	ND	0.5 ± 0.1	ND	1.8 ± 0.2
α-Terpineol	9.706	C ₁₀ H ₁₈ O	91	154	121, 93, 81, 59	ND	0.01 ± 0.01	0.10 ± 0.01	0.30 ± 0.01
2,6-Dimethyl-3,5,7-octatriene-2-ol	9.844	C ₁₀ H ₁₆ O	83	152	152, 119, 109, 81, 43	ND	ND	0.06 ± 0.01	0.10 ± 0.01
2,6-dimethyl, 1,7-Octadiene-3,6-diol	10.79	C ₁₀ H ₁₈ O ₂	92	170	137, 109, 67, 43	0.10 ± 0.01	0.24 ± 0.06	0.82 ± 0.05	0.42 ± 0.40
Carvacrol	10.954	C ₁₀ H ₁₄ O	94	150	150, 135, 91, 77, 39	0.01 ± 0.01	0.09 ± 0.06	0.14 ± 0.05	0.20 ± 0.09
Thymol	11.05	C ₁₀ H ₁₄ O	94	150	150, 135, 115, 91, 51	3.6 ± 0.2	15 ± 4	2.8 ± 0.7	27 ± 1
β-caryophyllene	13.02	C ₁₅ H ₂₄	92	204	204, 189, 147, 133, 93, 69, 41	0.10 ± 0.01	0.6 ± 0.2	0.26 ± 0.03	2.20 ± 0.05
A-Humulene	13.46	C ₁₀ H ₁₆ O	87	136	204, 147, 121, 93, 80, 41	ND	0.13 ± 0.01	0.05 ± 0.01	0.26 ± 0.01
α-Farnesene	13.927	C ₁₅ H ₂₄	92	204	204, 189, 161, 119, 93, 69, 41	0.09 ± 0.04	0.47 ± 0.11	0.16 ± 0.05	0.56 ± 0.05
Germacrene B	13.99	C ₁₅ H ₂₄	89	204	204, 161, 121, 93, 79, 41	ND	0.19 ± 0.03	0.12 ± 0.05	ND
Nerolidol	14.624	C ₁₅ H ₂₆ O	94	222	161, 121, 93, 69, 41	0.08 ± 0.01	0.29 ± 0.03	0.06 ± 0.05	0.26 ± 0.01
Spathulenol	15.00	C ₁₅ H ₂₄ O	90	220	205, 187, 159, 119, 91, 43	0.61 ± 0.01	0.9 ± 0.1	0.36 ± 0.04	2 ± 1
Caryophyllene oxide	15.095	C ₁₅ H ₂₄ O	91	220	177, 149, 121, 93, 79, 41	0.17 ± 0.01	0.36 ± 0.03	0.07 ± 0.06	0.30 ± 0.09
α-Sinensal	16.836	C ₁₅ H ₂₂ O	95	218	145, 134, 93, 91, 55	0.81 ± 0.02	1.4 ± 0.4	0.28 ± 0.08	1.05 ± 0.01
Phytol	20.369	C ₂₀ H ₄₀ O	96	296	123, 95, 71, 43	3.7 ± 0.1	4 ± 1	0.8 ± 0.1	5.50 ± 0.04
Squalene	26.128	C ₃₀ H ₅₀	95	410	341, 203, 175, 149, 137, 95, 69, 41	2.5 ± 0.7	2 ± 1	0.87 ± 0.01	3 ± 3
Vitamin E	28.289	C ₂₉ H ₅₀ O ₂	78	430	430, 205, 177, 165, 121, 97, 71, 43	14 ± 2	26 ± 3	48.95 ± 0.05	ND
Tangeritin	28.747	C ₂₀ H ₂₀ O ₇	64	372	357, 341, 313, 296, 271, 178, 167, 143, 93, 69, 53	34 ± 3	47.81 ± 0.01	26.72 ± 0.05	20.8 ± 0.4
Methyl Commate 1	30.387	C ₃₂ H ₅₂ O ₄	86	500	218, 189, 147, 119, 95, 81, 55	17 ± 3	ND	ND	ND
Methyl Commate 2	30.829	C ₃₁ H ₅₀ O ₄	85	486	231, 218, 189, 147, 119, 95, 69, 55	22 ± 3	19 ± 7	13.34 ± 0.05	ND

*ND: non-detect.

confirmed solvent-dependent differences in terpene compositions. Key compounds, such as methyl commate, tangeritin, and vitamin E, are listed in Table 1.

3.1.2. Oxidative stability of soybean oil added to Soxhlet extracts

The stability of soybean oil containing tangerine leaves extracts obtained by Soxhlet extraction with different solvents (1000 ppm) was evaluated during an oven test at 60 °C (Fig. 1). The AV increased in all samples throughout storage, due to lipid oxidation (Fig. 1.A). After 20 days, the highest AV (0.30 ± 0.01 g/100 g oleic acid) was observed in oil with EtOAc-S extract, exceeding the control without antioxidant. Oils added with Hex-S and EtOH-S extracts, the control, and TBHQ reached lower AV values (0.21 ± 0.01 g/100 g oleic acid) after 20 days. These results suggest that the EtOAc-S extract composition contributed to higher AV, even exceeding that of the oil without antioxidant. This behavior may be associated with the presence of pro-oxidant compounds extracted from tangerine leaves. Several compounds can act as pro-oxidant agents in oils, particularly under thermal conditions. For example, Martin-Rubio, Sopelana, Ibargoitia, and Guillén (2018) demonstrated the pro-oxidant effect of α-tocopherol, the main compound group identified in the EtOAc-S extract, on soybean oil. Moreover, chlorophylls, which are readily extracted with ethanol, can act as photosensitizers upon exposure to light by absorbing energy, reaching an excited state, and transferring it to oxygen molecules, thereby

promoting lipid oxidation (Li et al., 2019). The resulting singlet oxygen can initiate lipid oxidation and lead to the formation of polar oxidation compounds, a phenomenon previously reported in soybean, coconut, and olive oils (Rigane, Bouaziz, Sayadi, & Ben Salem, 2013; Rukmini & Raharjo, 2010). Nevertheless, all oils maintained AV below the ICON-TEC limit (1.2 g/100 g oleic acid) and within the Codex Alimentarius threshold (0.3 g/100 g oleic acid) for refined oils.

During storage, the PV increased in all samples (Fig. 1.B). According to Nielsen (2019), PV in soybean oil is classified as low (1–5 meq O₂/kg), medium (5–10 meq O₂/kg), and high (>10 meq O₂/kg), with a Codex Alimentarius maximum of 10 meq/kg. By day 10, the control oil approached a high oxidation level (9.6 ± 0.3 meq O₂/kg), while other samples remained below the threshold. After day 10, oils with EtOAc-S and EtOH-S extracts exceeded 10 meq O₂/kg, reaching 38.1 ± 2.3 and 28.3 ± 1.0 meq O₂/kg by day 20, respectively, with no significant difference between them. From days 15 to 20, PV in the Hex extracted oil was stabilized, suggesting an equilibrium in primary oxidation (Kasimoglu, Tontul, Soyulu, Gulen, & Topuz, 2018). By day 20, TBHQ and Hex treated oils showed moderate PV (3.90 ± 0.02 and 5.2 ± 0.2 meq O₂/kg). In contrast, oils with EtOAc-S and EtOH-S extracts exceeded the Codex limit, indicating lower quality. Thus, Hex-S extracted compounds likely acted as primary oxidation inhibitors, similar to TBHQ, while EtOAc-S and EtOH-S extracts probably promoted lipid oxidation.

The pAV also increased in all samples during oven storage (Fig. 1.C),

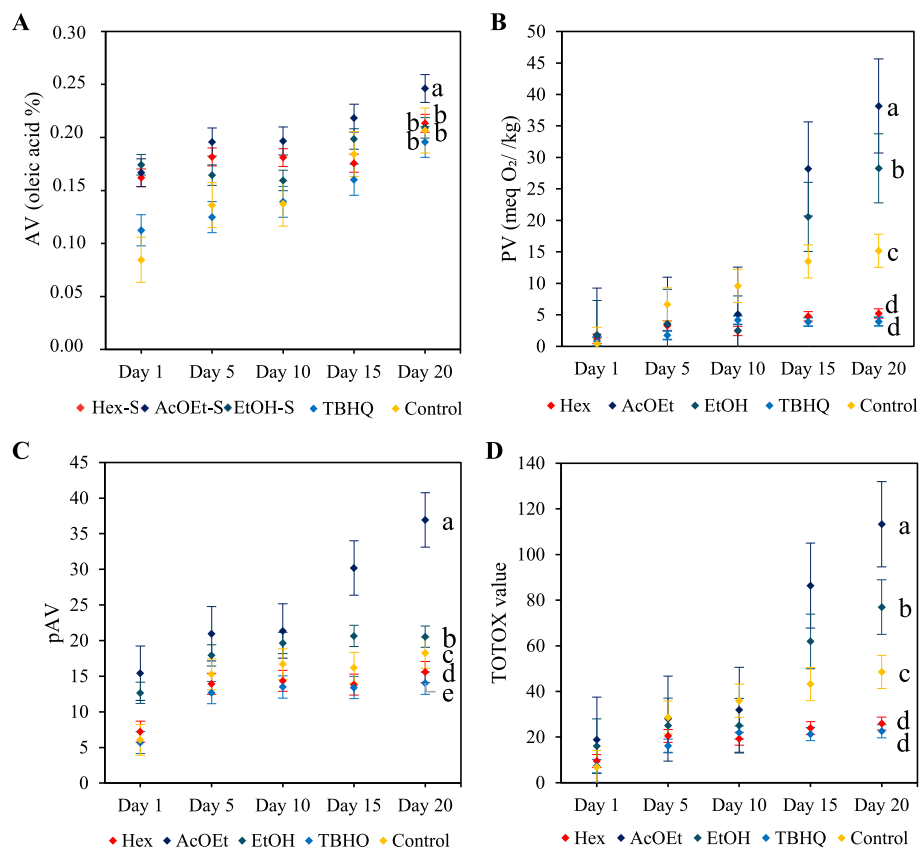


Fig. 1. Effect of the group of compounds extracted by Soxhlet using different solvents.

(Hex—S, EtOAc-S, EtOH-S) on the oil oxidative stability over storage test (20 days) at 60 °C measured by: (A) AV, (B) PV, (C) pAV, and (D) TOTOX value. TBHQ: Tert-butylhydroquinone. Results are presented as mean values $\pm$ standard deviation. Different letters represent significant differences ($p < 0.05$), according to ANOVA followed by Tukey's test.

consistent with previous studies (Asensio, Nepote, & Grosso, 2013; Kasimoglu et al., 2018; Keramat, Golmakani, Aminlari, & Shekarforoush, 2017), reflecting the decomposition of hydroperoxides into secondary oxidation products like 2-alkenals and 2,4-dienals (Nielsen, 2019). However, oils with leaf extracts maintained statistically similar pAV values ($p \geq 0.05$) at day 20, while the control showed a significantly higher pAV.

TOTOX values steadily rose during oxidation, reflecting AV and PV increases. EtOAc-S extracts exhibited a pro-oxidant effect (Fig. 1.D), reaching a TOTOX value of 113.3 ± 4.7 compared to 48.6 ± 2.3 in the control. TBHQ- and Hex-S treated oils showed the lowest TOTOX values (22.6 ± 0.1 and 26.0 ± 0.5 , respectively), with no significant difference between them. Since TOTOX values >30 indicate poor quality (Sun-Waterhouse, Thakorlal, & Zhou, 2011), Hex-S extracts effectively slowed oxidation, similar to TBHQ. These results emphasize the importance of solvent selection. Although EtOAc-S achieved a higher overall extraction yield than Hex-S (Section 3.2), it likely extracted additional compounds besides the antioxidants that catalyzed oil oxidation, as previously discussed regarding the extraction of α -tocopherol and chlorophyll and their prooxidant action.

3.1.3. Color of soybean enriched with Soxhlet and SC-CO₂ extracts

Fig. 2 presents the color modification caused in soybean oil after adding TBHQ (a synthetic antioxidant) and extracts from tangerine leaves by Hex-S, EtOAc-S, and EtOH-S. The color analysis, which is an indispensable quality parameter to evaluate the sensory quality of the oil (Gouveia et al., 2007), showed significant variations over time. The soybean oil supplemented with the EtOH-S extract exhibited the most significant color change ($\Delta E_{Lab} = 15.3 \pm 0.1$), followed by the Hex-S extract ($\Delta E_{Lab} = 13.3 \pm 0.1$) and the EtOAc-S extract ($\Delta E_{Lab} = 8.6$

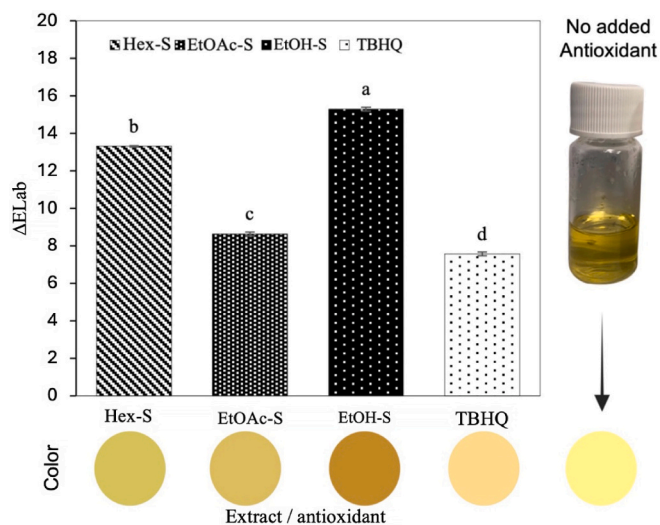


Fig. 2. Color difference (ΔE_{Lab}) between the control soybean oil added with TBHQ and soybean oil added with extracts obtained with Hex-S, EtOAc-S, and EtOH-S. Different letters represent significant differences ($p < 0.05$), according to ANOVA followed by Tukey's test.

± 0.0), when compared with the pure oil without added antioxidants or extracts. These differences can be attributed to the selective solubility and extraction capacity of each solvent. The chemical composition of the EtOH-S extract could contain more intensely colored compounds or

those with a greater capacity to interact with the oil. In fact, chlorophylls, the most common pigments in leaves, are readily soluble in lipophilic solvents such as Hex, as well as in polar solvents like EtOH and methanol (Kim, Bisson, Friesen, Pauli, & Simmler, 2020).

Results were presented as mean values $\pm$ standard deviation. Different letters represent significant differences ($p < 0.05$), according to

ANOVA followed by Tukey's test.

Therefore, although the Hex-S extract changed the oil's color, it provided greater oxidation protection. This behavior could be explained by Hex affinity towards nonpolar compounds, such as terpenes, (Table 1), which present antioxidant activity. Research has shown that certain terpenoids, like those identified in this extract (Section 3.2),

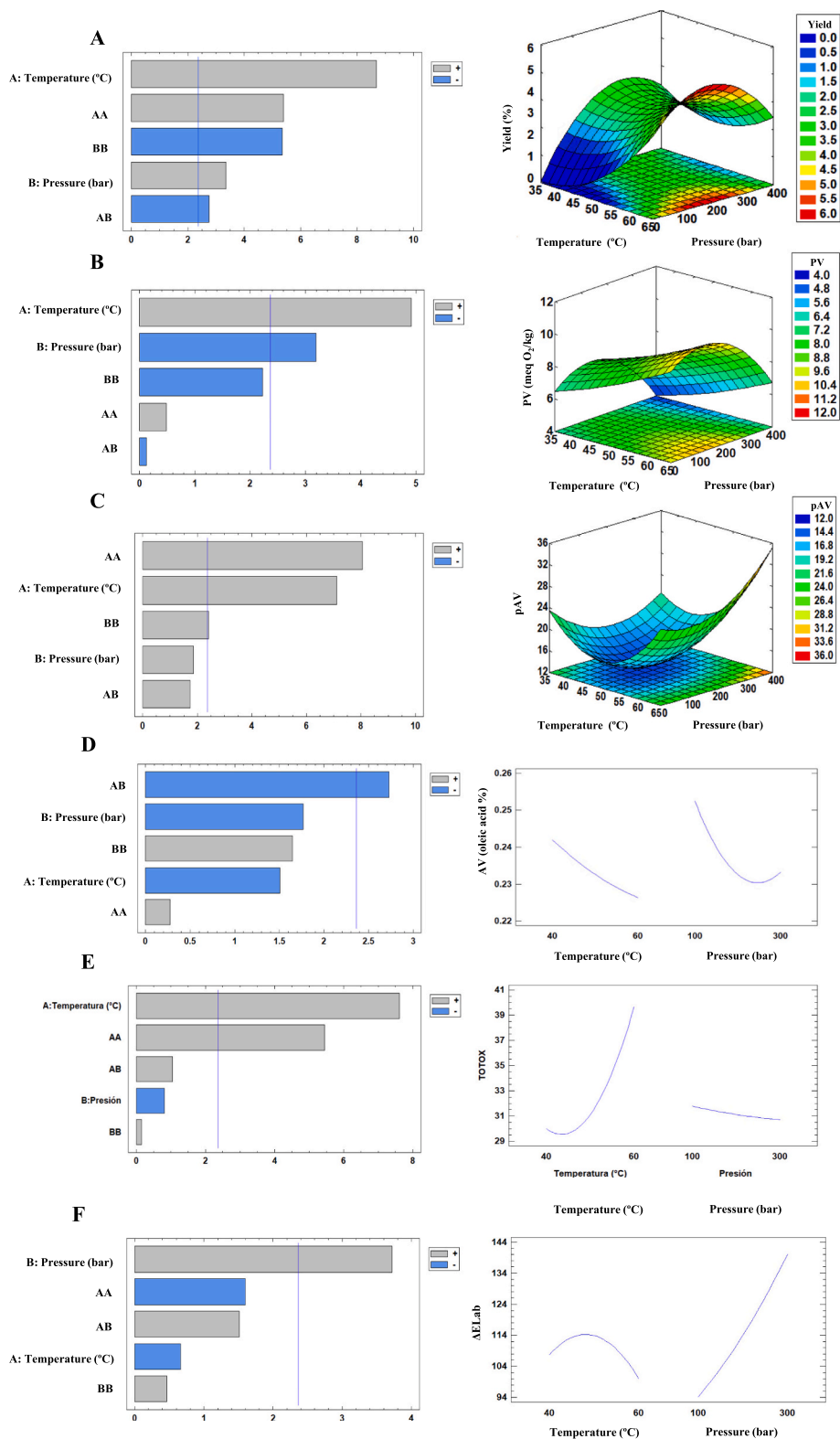


Fig. 3. Effects of extraction pressure and temperature on oxidative stability variables. (A) Pareto diagram and response surface Yield (%); (B) Pareto diagram and response surface PV; (C) Pareto diagram and surface response pAV.

possess notable antioxidant activity in food matrices (Gutiérrez-Del-Río et al., 2021). Among these, diterpenes such as vitamin E act as primary antioxidants, reacting with lipid and peroxy radicals ($\text{ROO}\cdot$, $\text{RO}\cdot$, $\text{R}\cdot$) to form more stable products (ROOH , ROH , RH) by donating hydrogen atoms and generating antioxidant radicals ($\text{A}\cdot$) in the process. Additionally, some terpenoids can serve as singlet oxygen scavengers, dissipating excess energy as heat (Gutiérrez-Del-Río et al., 2021).

3.2. Evaluation of SC-CO₂ to obtain oil preservatives

The kinetic study conducted at 50 °C and 200 bar (the central conditions of the experimental design) allowed the selection of the extraction time of 40 min, as no significant increase in yield was observed beyond this point (Fig. S1). Fig. 3 shows the effects of pressure and temperature on the extraction yield and characteristics of soybean oil added to extracts obtained by SC-CO₂. Linear and quadratic effects significantly influenced the extraction yield (Fig. 3A), with the highest temperature (64 °C) and an intermediate pressure of approximately 200 bar resulting in the highest yield.

The extraction temperature influences two opposing mechanisms during SC-CO₂. At a constant pressure, an increase in temperature reduces the density of the solvent, which decreases the solvation power of SC-CO₂. However, this increase can also enhance the vapor pressure of volatile compounds, potentially increasing the extraction yield and the solubility of analytes (Espinosa-Pardo, Nakajima, Macedo, Macedo, & Martínez, 2017; Natolino & Da Porto, 2019). Otherwise, increasing pressure typically allows for higher extraction yields because the CO₂ density increases at high pressure, which has been linked to higher lipid extraction yields (Dhara, Rani, & Chakrabarti, 2022; Leo, Rescio, Ciurlia, & Zacheo, 2005). However, at high pressures, the medium can also become compacted, creating preferential pathways and reducing extraction yield (Strieder et al., 2025).

Extracts obtained under all SC-CO₂ conditions were added to soybean oil to evaluate their antioxidant effects and influence on color. PV was significantly affected by temperature ($p = 0.0017$) and pressure ($p = 0.0152$) (Fig. 3B). In contrast to the extraction yield results, the lowest temperature (35 °C) combined with the highest pressure (341 bar) led to the lowest PV in the oil. This outcome suggests that, although this condition resulted in a lower extraction yield, it may have offered greater selectivity for antioxidant compounds, which effectively protected the oil against primary oxidation. For pAV, significant factors were temperature ($p = 0.0002$), its quadratic effect ($p = 0.0001$), and the quadratic effect of pressure ($p = 0.0468$) (Fig. 3C), suggesting that intermediate pressure (~200 bar) and temperature (~40 °C) allowed extracts that better preserved oil against secondary oxidations.

The interaction between temperature and pressure (AB) significantly influenced the AV ($p = 0.0294$), the association of the higher temperature (60 °C) and intermediate to higher pressure allowed the lowest value of AV (Fig. 3D). Only temperature had a significant effect on the TOTOX values of the oils containing the extracts, with higher temperatures leading to increased TOTOX levels (Fig. 3E). This behavior suggests that SC-CO₂ extraction at lower temperatures favored the recovery of compounds with more antioxidant than pro-oxidant characteristics. This result was associated with the selective extraction of terpenoids like monoterpenes and sesquiterpenes, known for their antioxidant properties. Terpenoids protect lipids by scavenging free radicals and terminating chain reactions, offering a safer alternative to synthetic antioxidants (Foti et al., 2003; Gutiérrez-Del-Río et al., 2021). Moreover, diterpenes inhibit lipid peroxidation in unsaturated fatty acids, as Meenakshi (2023) reported, where 35 μM inhibited 60–90% of linoleic acid oxidation through chain-breaking mechanisms aided by electron-donating groups.

Only SC-CO₂ pressure (B) significantly affected oil color ($p = 0.0074$), with increased pressure (from 100 to 300 bar) enhancing the extraction of coloring compounds and causing higher ΔELab in the oil (Fig. 3F). This behavior was attributed to higher CO₂ density at elevated

pressures, reducing intermolecular distances and improving interactions with extracted molecules (Perva-Uzunalić, Škerget, Weinreich, & Knez, 2004).

3.2.1. Optimization of SC-CO₂ to obtain oil preservatives and its characteristics

In this study, optimal SC-CO₂ extraction conditions were identified to maximize yield and oil oxidative stability, aiming for an antioxidant extract with the best characteristics to maintain oil oxidative quality over time. The optimal conditions proposed by the model (37 °C and 273 bar) were evaluated for their effectiveness in maximizing extraction yield and minimizing oil oxidative stability indices (PV and pAV). The experimental results showed a yield of 3.36 g/100 g, with a 3.79% relative error compared to the predicted value of 3.24 g/100 g, indicating that the model accurately estimates extraction yield. For the PV the experimental value was 6.96 meq O₂/kg oil, with a 2.65% relative error to the predicted value of 6.78 meq O₂/kg oil, suggesting the model's suitability in predicting primary oxidative stability. However, the secondary oxidative stability (pAV) showed a greater discrepancy, with an experimental value of 13.36 mL/g and a relative error of 17.98% against the predicted value of 16.22 mL/g. This behavior indicates that the model may not fully capture the complex interactions that influence secondary oxidation. These findings demonstrate that the model is reliable for optimizing extraction yield and predicting primary oxidative stability (PV).

The extraction yield obtained under optimized SC-CO₂ conditions (3.3 ± 0.4 g/100 g) was intermediate, falling between the lowest yield (1.1 g/100 g at 40 °C and 100 bar) and the highest yield (5.5 g/100 g at 64 °C and 200 bar). Overall, SC-CO₂ extraction yielded lower yields than Soxhlet extraction, which produced yields above 14 g/100 g (Section 3.1). This difference may be attributed to the higher solvation power of liquid solvents at Soxhlet extraction conditions compared to the SC-CO₂ ones. Extractions performed by Soxhlet using hexane have resulted in higher global yields, associated with higher triglyceride content, such as stearic acid (Schoss & Glavač, 2024).

From the GC-MS analysis of the extract obtained with SC-CO₂ at 37 °C and 273 bar (Fig. S2) can be tentatively identified a total of 17 compounds: 6 monoterpenes, 7 sesquiterpenes, 1 diterpene, 2 flavonoids, and 1 triterpene. Table 1 lists the most abundant compounds, with linalool ($35 \pm 3\%$ of total peak area) being the most prevalent, followed by thymol ($27 \pm 1\%$ of total peak area) and tangeritin ($20.0 \pm 0.4\%$ of total peak area). Compared to Hex-S extraction, optimized SC-CO₂ extraction stands out for its ability to selectively obtain specific-polarity compounds. We notice that SC-CO₂ significantly favors the extraction of monoterpenes, with linalool being the most prominent ($34 \pm 3\%$ of total peak area) compared to its low concentration in the Soxhlet extract ($0.09 \pm 0.01\%$ of total peak areas). However, both methods manage to extract thymol, albeit with a significantly higher concentration in the SC-CO₂ extract ($27 \pm 1\%$ of total peak area) compared to the Soxhlet extract, where thymol has a lower relative area of $3.6 \pm 0.2\%$ of total peak area. On the other hand, tangeritin was detected in higher concentration in the Soxhlet extract ($34 \pm 3\%$ of total peak area) compared to SC-CO₂ ($19.6 \pm 0.4\%$ of total peak area), indicating a higher efficiency of the Soxhlet method in extracting this specific compound. Additionally, compounds such as vitamin E and methyl commate, present only in the Soxhlet extract, reinforce the ability of this method to extract a wider range of nonpolar compounds.

3.2.2. Comparison of the extracts on the oil quality

IT represents the period before the onset of detectable rancidity or the point at which lipid oxidation accelerates rapidly (Nielsen, 2019). As shown in Fig. 4 while the IT achieved with natural extracts did not surpass the value obtained with TBHQ (7.9 ± 0.3 h), the sustainable advantages of SC-CO₂ extraction and the potential of natural extracts to enhance oxidative stability underscore their promise for industrial applications.

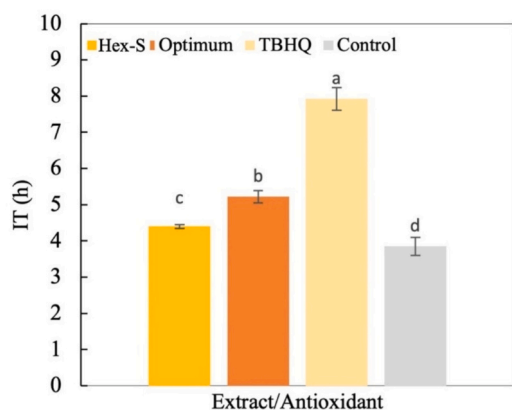


Fig. 4. Comparative analysis of IT. Different letters represent significant differences ($p < 0.05$), according to ANOVA followed by Tukey's test.

Over 20 days, the oxidative stability of soybean oil enriched with natural antioxidants and TBHQ was monitored, as shown in Fig. 5.

By day 20, oils with compounds extracted using Hex and SC- CO_2 exhibited slightly elevated AV levels (0.21 ± 0.01 g/100 g oleic acid and 0.22 ± 0.01 g/100 g oleic acid, respectively) (Fig. 5 A), yet both values remained well below the ICONTEC's limit of 1.2 g/100 g oleic acid, indicating excellent stability. Regarding PV (see Fig. 5 B), the oil with SC- CO_2 extract showed a value of 6.96 ± 0.03 meq O_2 /kg, higher than that obtained with the Hex extract (5.2 ± 0.2 meq O_2 /kg), but still represented a significant 54% reduction compared to the control oil

(15.2 ± 1.2 meq O_2 /kg). This outcome highlights the antioxidants' capability to significantly reduce peroxide formation and suggests a higher concentration of effective antioxidants in the SC- CO_2 extract.

Furthermore, the antioxidants in the oils maintained PV within moderate oxidation levels on day 20, suggesting a potential inhibitory effect on hydroperoxide formation and an improvement in the oil's oxidative stability under the tested conditions. Notably, the SC- CO_2 extract contained a dominant fraction of monoterpenes (62% of total peak areas), significantly contributing to its antioxidant potential. In line with these findings, the reduction in primary oxidation products contributed to lower levels of secondary oxidation products. By day 20, the pAV was statistically lower in the oil extracted with SC- CO_2 (13.4 ± 0.5 mL/g), closely followed by TBHQ (14.67 ± 0.18 mL/g), indicating that the optimal extract achieves better protection. The oil extracted with Hex reached a pAV of 15.55 ± 0.03 mL/g, with no significant difference compared to TBHQ (Fig. 5 C). These values are consistent with results from the Rancimat method, which also indicated a higher IT for oils containing antioxidant extracts. The TOTOX value, which combines both primary and secondary oxidation measures, was lowest in the oil with TBHQ (22.5 ± 0.1), followed by the oil with Hex extract (25.9 ± 0.5). The SC- CO_2 -extracted oil had a TOTOX value of 27.37 ± 0.7 , with no statistically significant difference from the Hex extract (Fig. 5 D). These results suggest that although TBHQ is more effective at inhibiting oxidation, natural extracts demonstrate strong antioxidant potential. This makes them a viable and sustainable alternative to synthetic antioxidants, enabling the production of solvent-free oils and supporting greener extraction methods.

The addition of extracts obtained via Hex-S and SC- CO_2 extraction

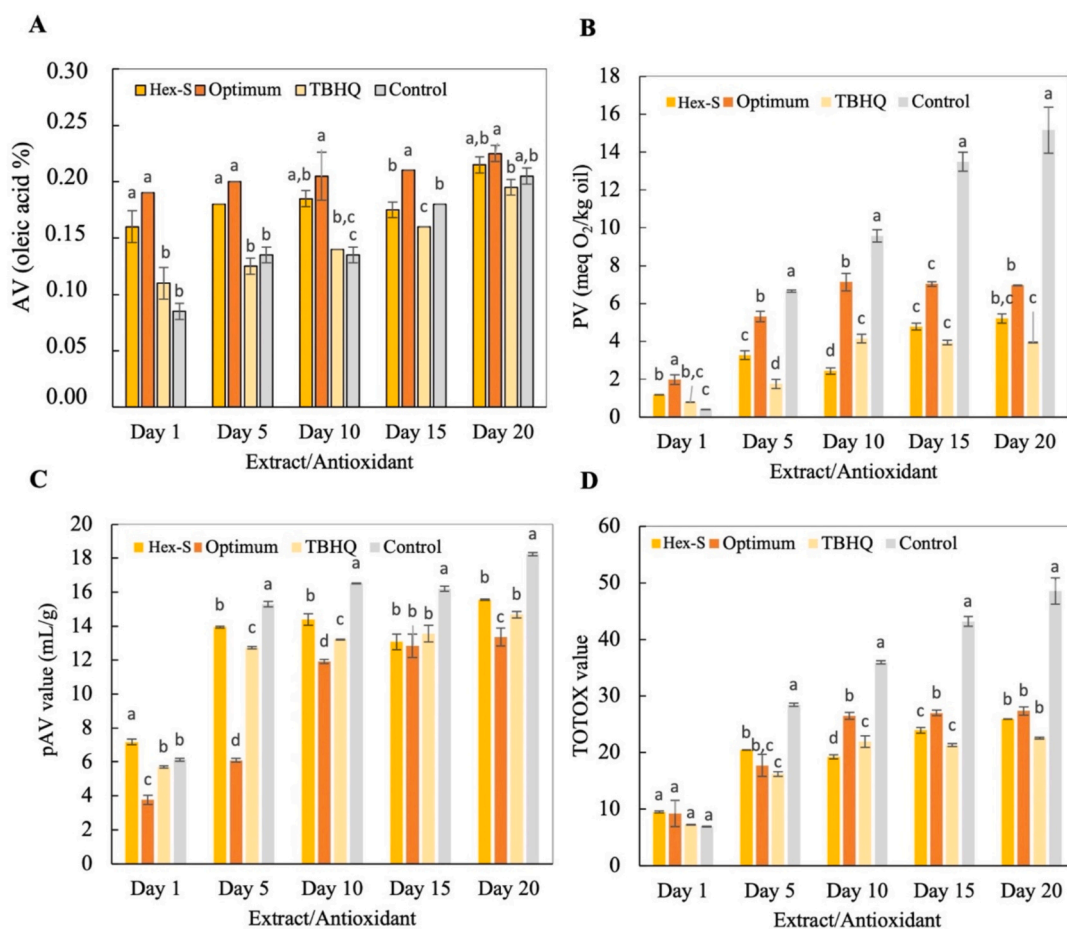


Fig. 5. Comparison of oxidative stability of soybean oil with the addition of tangerine leaves extracts. (A) AV; (B) PV; (C) pAV; (D) TOTOX value. Different letters represent significant differences ($p < 0.05$), according to ANOVA followed by Tukey's test.

increased the chroma value in soybean oil, resulting in significantly higher color saturation and a more intense perceived color. **Fig. S3** presents the color results for oils with 1000 ppm of added extract. The smallest color change (ΔE) was observed with the optimized SC-CO₂ extract, showing a value of 11.36 ± 0.4 , which is significantly lower than the ΔE of 13.3 ± 0.08 recorded for the Hex-S extract. Furthermore, the optimized extract exhibited significant differences from the control in terms of lightness, a^* , chroma, and hue coordinates, suggesting a color shift less perceptible to the human eye compared to that caused by the Hex-S extract. This indicates that both extracts impact the oil's color, likely due to the presence of pigmented compounds, such as terpenoids, which influence the oil's chromatic properties. The optimized SC-CO₂ extract produces a subtler color alteration (**Fig. S3**), potentially indicating a better integration within the oil matrix, enhancing the sensory appeal of the color for consumers.

4. Conclusion

Nonpolar compounds such as linalool, thymol, tangeretin, and phytol extracted via SC-CO₂ from tangerine leaves (*Citrus reticulata*) var. Arrayana demonstrated enhanced activity in preserving soybean oil, surpassing extracts obtained through Soxhlet methodology with Hex—S, EtOAc-S, and EtOH-S as solvents. Notably, the SC-CO₂ extraction method developed only lasts 40 min, in stark contrast to the Soxhlet extraction which takes 10 h, highlighting the efficiency of the developed process. Our results demonstrated that lower supercritical CO₂ temperatures (37 °C) combined with intermediate pressures (273 bar) enabled the extraction of compounds with enhanced protective activity against heat-promoted oil oxidation. This extract resulted in significantly reduced PV (6.96 meq O₂/kg compared to 15.16 meq O₂/kg in the control) and lower pAV (13.36 mL/g compared to 18.24 mL/g in the control) in the soybean. Moreover, it achieved a longer IT (5.2 h compared to 4.4 h for Hex-S extraction and 3.8 h for the control) and demonstrated a superior TOTOX value, allowing a oil with better resistance to both primary and secondary oxidation. In conclusion, supercritical CO₂ extraction emerges as a sustainable and viable method for valorizing tangerine agricultural waste, producing extracts that enhance the oxidative stability of soybean oil. This approach not only provides an environmentally friendly alternative to synthetic antioxidants but also delivers a rich diversity of phytochemicals, particularly terpenoids, which could have extensive industrial applications.

CRediT authorship contribution statement

Camilo Rodríguez-García: Writing – original draft, Investigation, Data curation. **Monique Martins Strieder:** Writing – review & editing, Supervision, Methodology, Conceptualization. **Gloria Domínguez-Rodríguez:** Writing – review & editing, Supervision, Methodology, Conceptualization. **Michael Ernesto Moreno Caballero:** Writing – review & editing, Supervision. **Liliam Palomeque:** Writing – review & editing, Supervision. **Alejandro Cifuentes:** Writing – review & editing, Supervision, Resources, Funding acquisition. **Fabián Parada-Alfonso:** Writing – review & editing, Supervision. **Elena Ibáñez:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ifset.2026.104449>.

Data availability

Data will be made available on request.

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