Microchemical Journal 194 (2023) 109232

Contents lists available at ScienceDirect

Microchemical Journal

journal homepage: www.elsevier.com/locate/microc

Determination of oxidative stability of different vegetable oils by means of middle infrared spectroscopy and DFT calculations

Ayse Burcu Aktas [a,*,1], Taner Dastan [a,2], Konstantin P. Katin [b,3], Savas Kaya [c,*,4]

[a] Sivas Cumhuriyet University, Faculty of Science, Biochemistry Department, 58140 Sivas, Turkey
[b] Nanoengineering in Electronics, Spintronics and Photonics Institute, National Research Nuclear University "MEPhI", Kashirskoe Shosse 31, Moscow 115409, Russia
[c] Sivas Cumhuriyet University, Health Services Vocational School, Department of Pharmacy, 58140 Sivas, Turkey

ARTICLE INFO

Keywords:
Oxidative stability
Vegetable oils
Infrared spectroscopy
DFT calculations

ABSTRACT

Oxidative stability is one of the most important quality parameters of vegetable oils. This study aims to determine oxidative stability of five different vegetable oils by means of infrared spectroscopy combined with DFT calculations and to compare experimental and theoretical results. The oxidation induction times of hazelnut, corn, canola, safflower and sunflower oils were determined by the Rancimat method and fatty acid profile of the oils was analyzed by gas chromatography. Moreover, the middle infrared spectra of the samples was obtained by using Fourier transform infrared spectroscopy. The oxidative stability of the vegetable oils was analyzed by considering two mechanisms regarding to oxidation process in the theoretical parts of the study. The chemical hardness of fatty acids, a key characteristic of Conceptual Density Functional Theory, was calculated and discussed. It was evaluated that there was a remarkable correlation between oxidative stability and chemical hardness of fatty acids. The harder fatty acids had stronger oxidative stability. A new, accurate, cost-effective, and ecologically friendly technique was developed for determination of oxidative stability of vegetable oils.

1. Introduction

Oxidative stability (OS) is an important parameter for estimating the quality of edible oils. OS of vegetable oils also confirms the capability of their resistance to oxidative reactions throughout processing and storage periods [1]. Lipid oxidation is a major reaction for degradation of vegetable oils during processing and storage [2]. The lipid oxidation reactions mostly result in some alterations of different quality parameters including; degradation of essential fatty acids, production of toxic compounds, changes in color, flavour, aroma, and loss of nutrients. These alterations have remarkable effects on the shelf life and consumption of vegetable oils. Moreover, the end products of lipid oxidation reactions are highly reactive and could have undesirable effects on human health such as cancer, atherosclerosis, heart diseases and allergic responses [3].

The OS of vegetable oils is closely related to the their triacylglycerol content and fatty acid compositions, as well as some other minor antioxidant components and several external factors. The existence of unsaturated fatty acids in vegetable oils is the major intrinsic factor for oxidative reactions. The unsaturated fatty acids which have double bonds in their structure which react with oxygen through by free radical chain mechanism. The vegetable oils have contain higher amounts of monounsaturated (MUFA) and polyunsaturated (PUFA) fatty acids and are very prone to oxidative reactions due to the number double bonds present in the fatty acid structure [4]. Sunflower, safflower and corn oils are very rich in terms of PUFAs, particularly linoleic and linolenic acids [5]. However, the fatty acid profiles of canola, hazelnut and olive oils are mostly dominated by oleic acid which has a single double bond in their structure [6].Thus, it is highly essential to elucidate the fatty acid composition of vegetable oils in order to better understand their affinity to oxidative reactions.

There are many analytical and spectrophotometric methods to

* Corresponding authors.
E-mail addresses: burcuaktas@cumhuriyet.edu.tr (A.B. Aktas), tdastan@cumhuriyet.edu.tr (T. Dastan), KPKatin@yandex.ru (K.P. Katin), savaskaya@cumhuriyet.edu.tr (S. Kaya).
[1] Orcid ID: https://orcid.org/0000-0003-2520-0976.
[2] Orcid ID: https://orcid.org/0000-0003-0296-6979.
[3] Orcid ID: https://orcid.org/0000-0003-0225-5712.
[4] Orcid ID: https://orcid.org/0000-0002-0765-9751.

https://doi.org/10.1016/j.microc.2023.109232
Received 14 July 2023; Received in revised form 16 August 2023; Accepted 22 August 2023
Available online 25 August 2023

investigate the OS of edible oils [2]. The peroxide value (PV) is a parameter used for specifying the content of oxygen as peroxide, especially hydroperoxides in a oil sample. The PV of lipids is generally determined by a titrimetrical method. The conjugated diene value is often used to measure primary oxidation products and characterized by a spectrophotometrical technique. Malondialdehyde is one of the final products of peroxidation of PUFAs and detected by a spectrophotometric analysis. The p-anisidine value is recognized as a reagent of oxidation products such as aldehydes and ketones and determined by a spectrophotometric analysis as well [7]. However, more reliable, facile, and accurate methods were required to analyze the OS of edible oils. Therefore, the Rancimat method was developed to assess the OS index [8]. The Rancimat method is based on the conductometric determination of volatile degradation products generated by the thermally-induced oxidation of the oils. The induction time which is a numerical value is calculated as the end point of time before the rapid deterioration of lipids. Moreover, previous studies revealed that infrared spectroscopic (IR) techniques could also be used in the analyses of edible fats and oils. Since the IR spectra is intrinsically complex and has difficulty in direct interpretation, the IR spectra should be combined with different analytical and statistical techniques to investigate the properties of food lipids [9–11].

Although there are several chemical reactivity theories proposed in the current literature to explain reactivity, acidic and basic behavior, the most common one is Density Functional Theory (DFT). The electron density is the main parameter utilized by DFT to describe the reactivity of chemical systems. Conceptual DFT (CDFT) is a branch of DFT which deals with chemical reactivity. Global and local reactivities of chemical systems can be easily examined by CDFT using quantum chemical reactivity descriptors and electronic structure principles based on these descriptors [12,13].

According to the best of our knowledge of, no studies regarding the determination of OS of vegetable oils by means of middle infared spectroscopy combined with DFT calculations have been published. The hypothesis of this research is that IR spectroscopy, coupled to DFT calculations is able to analyze oxidative stability of vegetable oils. In present work, we aimed to analyze classic oxidation indices of five different vegetable oils including hazelnut, safflower, sunflower, canola, corn oils by rancimat method and fatty acid profile as well as to compare experimental results with the DFT calculations combined middle infrared spectral data in order to develop a new and simple method for determination of OS.

2. Materials and methods

2.1. Materials

Five different refined vegetable oils including hazelnut oil (Fiskobirlik, Turkey), sunflower oil (Orkide, Turkey), safflower oil (Orkide, Turkey), canola oil (Aysan, Turkey) and corn oil (Ulker, Turkey) were purchased from a local market. The oil samples were stored at + 4 °C before analyses. All other chemicals and solvents are of analytical or chromatographic grade and were obtained from Sigma (Sigma-Aldrich, Germany).

2.2. Determination of oxidative stability

The oxidation induction times of oil samples were determined by the Rancimat method and measured with the Rancimat apparatus[14] (873 Biodiesel, Metrohm, Switzerland). The Rancimat instrument has a temperature range of 50–220 °C and a temperature stability of less than 0.1 °C. For the measurement, 3 g of vegetable oil was placed inside the glass reaction vessel. Deionized water was chosen as the carrier medium. The reaction temperature was set to a constant of 120 °C for both columns of the Rancimat apparatus, with a constant air flow of 20 L/h. The measurements were replicated and the induction time estimated by second derivative method of conductivity versus time.

2.3. Determination of fatty acid content

The fatty acid composition of the oil samples was determined by converting them into their corresponding fatty acid methyl esters (FAME). Chromatographic analyses were performed with a gas chromatography (GC) instrument (Shimadzu GC QP2010 Ultra, Japan) equipped with an auto-sampler, a split/splittless (1:50) injector and an FID detector. An Rt 2560 capillary column (100 m × 0.25 mm ID × 0.2 μm) was used in the analyses. Conditions for GC analysis are described in a previous study [15]. A 37-component mixture of FAME (Sigma-Aldrich, Germany) was used as the standard. The analyses were carried out twice.

2.4. Infrared spectroscopy analyses

The infrared spectra (IR) of oil samples were acquired by a Fourier Transform Infrared Spectrometer (Bruker Tensor II, Bruker Inc., Billerica, MA, USA). The spectra were collected over the range of 4000–400 cm^{-1}, at 4 cm^{-1} resolution, by using a single reflection ZnSe ATR cell and 32 scans for both samples and background [16].

2.5. Details of Conceptual DFT based computations

Conceptual DFT developed by Parr and coworkers [17] effecting from the informations presented in the context of DFT presents some useful mathematical relations to compute the popular quantum chemical descriptors like chemical potential (μ), electronegativity (χ), hardness (η) and softness (σ). These relations mentioned are given as [18,19]:

$$\mu = -\chi = \left[\frac{\partial E}{\partial N}\right]_{\nu(r)} \tag{1}$$

$$\eta = \left[\frac{\partial \mu}{\partial N}\right]_{\nu(r)} = \left[\frac{\partial^2 E}{\partial N^2}\right]_{\nu(r)} \tag{2}$$

$$\sigma = 1/\eta \tag{3}$$

Note that the terms “hardness” and “softness” relate to any chemical compound, not specially to fatty acids.

In these mathematical relations, E, N and ν(r) represent the total electronic energy, total number of the electrons and constant external potential, respectively. It is clear after this explanation that chemical potential and chemical hardness are given as first and second derivative of total electronic energy with respect to the number of electrons, respectively. With the help of finite differences approach, one can present the relation with ionization energy (I) and electron affinity (A) of the a forementioned descriptors as [20,21]:

$$\mu = -\chi = -\left(\frac{I+A}{2}\right) \tag{4}$$

$$\eta = I - A \tag{5}$$

Here I and A are defined as:

$$I = E(N-1) - E(N) \tag{6}$$

$$A = E(N) - E(N+1) \tag{7}$$

According to the equation introduced by Parr, Szentpaly and Liu [22], first electrophilicity index (ω_1) is calculated as:

$$\omega_1 = \chi^2/2\eta = \mu^2/2\eta \tag{8}$$

Second electrophilicity index (ω_2), which its reliability was supported by especially Szentpaly and Kaya [23] is calculated as:

$$\omega_2 = \frac{I.A}{I - A} \tag{9}$$

One of the used alternative methods for the prediction of ionization energy and electron affinity of molecules is Koopmans Theorem [24]. In this paper, we used Koopmans Theorem presenting the relation with the energy of HOMO and LUMO orbitals of ionization energy and electron affiniry as:

$$I = -E_{HOMO} \tag{10}$$

$$A = -E_{LUMO} \tag{11}$$

In the theoretical part of the paper, the B3LYP/6–31 + G(d,p) level of density functional theory was applied [25–27]. This approach previously demonstrated high accuracy in describing of vibrational spectra of fatty acids [28].Grimme's D3 dispersion corrections were also introduced [29]. Geometry optimizing was performed with the advanced GeomeTRIC method [30] implemented in TeraChem software which provides using the power of graphical processor units for quantum chemistry [31–33]. The effect of media was taken into account with conductor-like solvent model COSMO [34]. We set the dielectric constant $\varepsilon = 3.1$ for all cases, since this value is typical for all the oils under consideration [35]. Vibrational modes and their infrared activities were determined at the same level of theory as optimal geometries.

3. Results and discussion

3.1. The fatty acid composition of the vegetable oils

The predominant fatty acids of vegetable oils were oleic, gondoic, linoleic, linolenic, stearic and palmitic acids (Table 1). While hazelnut oil has the most oleic acid content (75.74%), safflower oil has the highest amount of linoleic acid (75.16%). The higher percentages of linoleic acid in both sunflower (56.29%) and corn (54.73%) oils were also observed (Table 1). The most abundant unsaturated fatty acid of canola oil was oleic acid. All vegetable oil samples had relatively lower levels of saturated fatty acids including palmitic and stearic acids (Table 1). Generally, all the oil types are very rich in terms of oleic and linoleic acid which was expected and also observed in the previous studies [36–40].

3.2. Oxidative stability (OS) of the vegetable oils

The oxidation induction times of oil samples were determined by Rancimat measurements and used as an index for the OS of vegetable oils. The oxidation induction times of the vegetable oils are provided in Table 1. The oxidation induction times of oil samples ranged from 2.13 to 5.07 h. Synthetic antioxidants are often employed in the food industry for preventing oxidative reactions, which could potentially improve the OS of the vegetable oils. Corn and sunflower oil samples had higher OS values compared to other oil types. Since these oil samples had a considerable percentage of palmitic acid, their OS values were relatively high (Table 1). The presence of of natural antioxidants as tocopherol and β-carotene may also have an effect on the improvement in the OS of corn and sunflower oils [40–41].Safflower oil is the least stable one against oxidation. The lower oxidation induction time of safflower oil could be attributed to its higher polyunsaturated acid and low tocopherol contents [38]. The higher tocopherol concentrations of vegetable oils, the better the OS. According to the literature, canola oil may have tocopherol contents up to in the range of 366 and 354 mg/kg and tocopherols in hazelnut oil range from 640 to 572 mg/kg [42,43]. Therefore, the OS values of canola and hazelnut oils may be related to their tocopherol contents. Moreover, canola and hazelnut oils, with higher oleic acid content (Table 1), could be assumed to be a relatively stable oil compared to other oil samples [15,42].

3.3. IR spectra of the vegetable oils

The vegetable oils were also characterized using FTIR spectroscopy. The absorbance region of IR spectra is between 3500 and 500 cm^{-1} and shown in Fig. 1. In general, similar spectral patterns with prominent absorbance bands were observed for all oil types. While the absorption around 3000–3500 cm^{-1} assigned to alkene (cis = C-H) stretching vibrations, the peaks at about 3000 cm^{-1} corresponding to asymmetric stretching of methylene ($–CH_2$) groups in all analyzed oil types (Fig. 1). The C-H stretching vibration bands for methyl ($–CH_3$) group were found around 2900 cm^{-1}. In general, more focus should be given on the fingerprint area of the IR spectra. The fingerprint area demonstrated the C-O-C vibration in esters, the C-H bending and stretching vibrations, and the second overtones of C = O and –OH in fatty acid structures. All oil types showed the highest absorbances around 1700 cm^{-1} assigned to C = O stretching vibrations and confirmed the presence of fatty acids particularly (Fig. 1). The presence of cis and trans fatty acids was associated with out-of-plane bending vibrations and stretching of -C-O- and $–CH_2$ between 1000 and 1500 cm^{-1} [44,45].

3.4. DFT calculations

We calculated the infrared spectrum for each fatty acid. The same scale factor of 0.95 was applied to all frequencies. Each frequency was broadened into a Gaussian curve with σ = 10 cm^{-1}. To obtain the spectrum of oils, we constructed a linear combination of the acids spectra with weights taken from Table 1. The result of comparing the measured and calculated infrared spectra is shown in Fig. 2. The right peak just below 3000 cm^{-1} corresponds to vibrations of the C—H bonds. The peak about 1750 cm^{-1} corresponds to fluctuations of the C═O double bonds in the carboxyl groups. The low-energy part of the spectrum is mainly due to rotation of atoms without significant changes in bonds lengths.

3.4.1. Oxidation mechanisms

There are many mechanisms of oxidation of fatty acids. The β-oxidation of fatty acids takes place in the mitochondria [46], while

Table 1
Fatty acid percentages and OS of vegetable oils.

Samples	Oleic acid % (C18:1)	Gondoic acid % (C20:1)	Linoleic acid % (C18:2)	Linolenic acid % (C18:3)	Palmitic acid % (C16:0)	Stearic acid% (C18:0)	OS (h)
Hazelnut oil	75.74 ± 0.05	0.16 ± 0.01	13.04 ± 0.03	0.09 ± 0.02	5.51 ± 0.02	2.39 ± 0.01	4.21 ± 0.03
Sunflower oil	29.73 ± 0.04	0.29 ± 0.01	56.29 ± 0.04	0.14 ± 0.01	6.55 ± 0.03	3.59 ± 0.01	5.03 ± 0.02
Safflower oil	14.06 ± 0.03	0.20 ± 0.02	75.16 ± 0.04	0.38 ± 0.02	6.16 ± 0.03	2.51 ± 0.01	2.13 ± 0.02
Corn oil	30.99 ± 0.04	0.96 ± 0.02	54.73 ± 0.03	0.41 ± 0.02	11.23 ± 0.04	2.06 ± 0.02	5.07 ± 0.05
Canola oil	57.82 ± 0.06	7.71 ± 0.04	24.22 ± 0.02	1.13 ± 0.03	4.94 ± 0.02	1.50 ± 0.01	4.48 ± 0.01

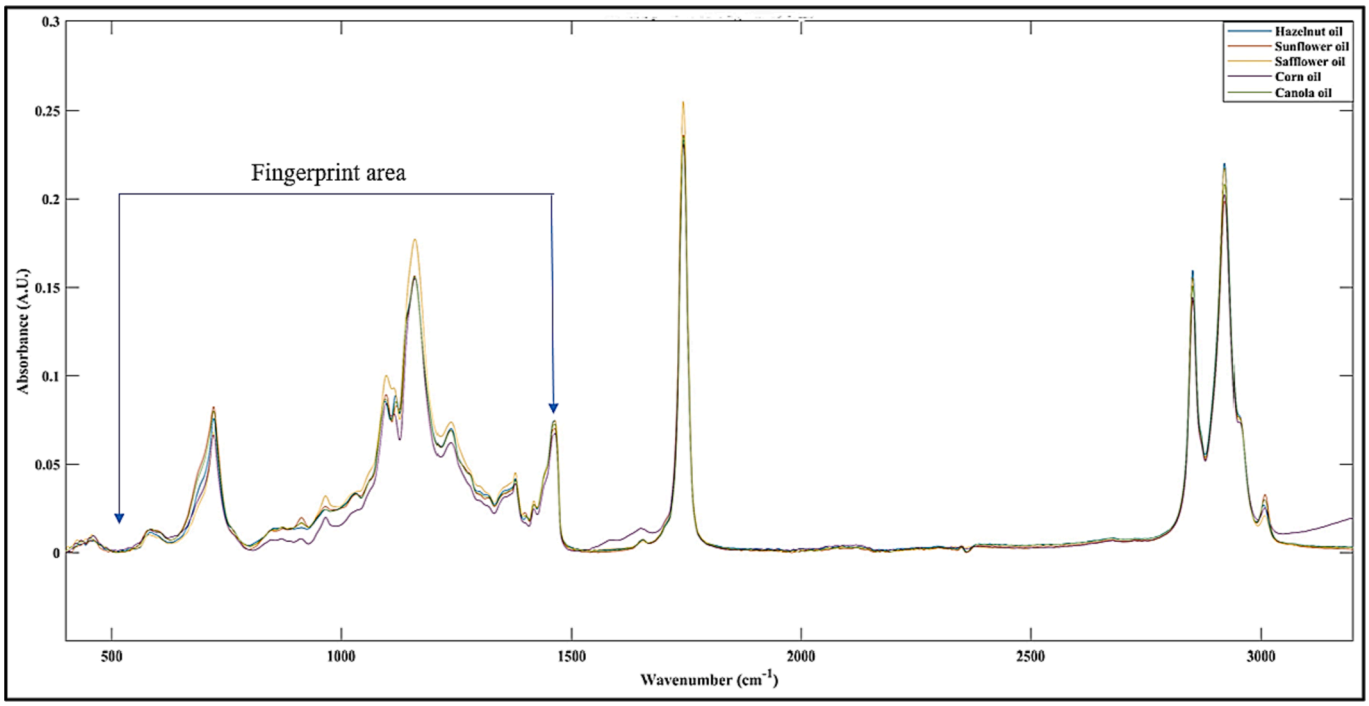

Fig. 1. The middle infrared spectra of vegetable oils.

their rancidity often follows the mechanism of auto-oxidation or photosensitized oxidation. In our simplified consideration, we regarded three model ways of interaction between fatty acids and oxygen molecule describe by the following reactions:

$$FA + 0.5O_2 \rightarrow FA\text{–}OH; \quad (12)$$

$$FA + 0.5O_2 \rightarrow FA = O + H_2. \quad (13)$$

Here FA–OH and FA = O are oxidized products, in which β carbon atom is functionalized with hydroxyl group or oxygen atom, respectively. For unsaturated acids, we also considered the third mechanism, in which two carbon atoms formed the double bond are oxidized:

$$FA + O_2 \rightarrow O = FA = O + H_2. \quad (14)$$

Here O = FA = O is the oxidized acid in which two carbon atoms formed double bond are functionalized with oxygen atoms. Corresponding three oxidized products of the oleic acid are shown in Fig. 3.

For reactions (12)–(14), the energy effects were calculated as the energy differences between products and reactants (Table 2). The negative energy effects indicate that all oxidation reactions are exothermic. It could be understand from Table 2 that the reaction (14) involving a double C=C bond is the most energetically feasible for all unsaturated acids as well as reaction (14) is much more energetically feasible compared to reaction (13).

We also calculated frontier orbitals energies and dipole moments of fatty acids and their oxidized products an the results are given in Table 3. Oxidation reactions let to slight changes in HOMO orbitals and some decreases in LUMO orbitals energies. Therefore, oxidized fatty acids (especially highly oxidized O = FA = O) possess lower HOMO-LUMO gaps.

Some parameters of Conceptual Density Functional Theory such as hardness, polarizability and electrophilicity provide useful hints in terms of the chemical reactivity of molecular system [47]. Especially, chemical hardness is good measure of the stability [48–50]. According to Hard and Soft Acid-Base Principle [51], hard acids bind powerfully to hard bases and soft acids bind powerfully to soft bases. It should be state that soft chemical systems exhibit high polarization while hard chemicals exhibit high resistance against the polarization. Maximum Hardness Principle [52] explain the relation between hardness and stability and it states that maximum hardness value corresponds to the most stable state of a chemical system. According to Minimum Polarizability Principle [53] introduced in the light of the inverse relation between hardness and polarizability, stable states correspond to the minimum value of the polarizability. One of the most important electronic structure rules is Minimum Electrophilicity Principle imparted to the literature by [54]. This rule argues that the electrophilicity index is minimized at stable states like polarizability. In a recent paper written by [23], second electrophilicity index given by Eq. (9) provides more compatible results compared to first electrophilicity index with Minimum Electrophilicity Principle. For that reason, it is more accurate to discuss the stability of the chemical systems in terms of the minimization of the second electrophilicity index. In Table 3, Frontier orbitals HOMO and LUMO (eV), energy gap (eV) and dipole moments (Debye), electronegativity, first electrophilicity index and second electrophilicity index of fatty acids (FA) and their oxidized products FA = O, FA–OH and O = FA = O are presented as detailed. Palmitic acid and stearic acid, both saturated fatty acids, were found to be the most resistant to oxidation in the calculations (Table 3). The findings were also correspond to the Maximum Hardness Principle, which has been described in previous studies [55]. On the other hand, unsaturated fatty acids including oleic, linoleic, and linolenic acids have lower chemical hardness values and are more prone to oxidation (Table 3). In this phase, we can compare the performances of various electrophilicity indexes in terms of electrophilicity minimization in stable states and conformers. It was observed that second electrophilicity index is minimized for the most stable fatty acid, namely palmitic acid (Table 3). Moreover, first electrophilicity index for same fatty acid had no minimum value among all the examined fatty acids. This finding also supports the usefulness of second electrophilicity index in chemical reactivity analysis. Furthermore, the variation in chemical hardness between palmitic acid (C16:0) and stearic acid (C18:0) could be attributed to differences in carbon chain length.

The computationally obtained data proposed that the most hard fatty acids are palmitic acid and stearic acid. Indeed, as these fatty acids are

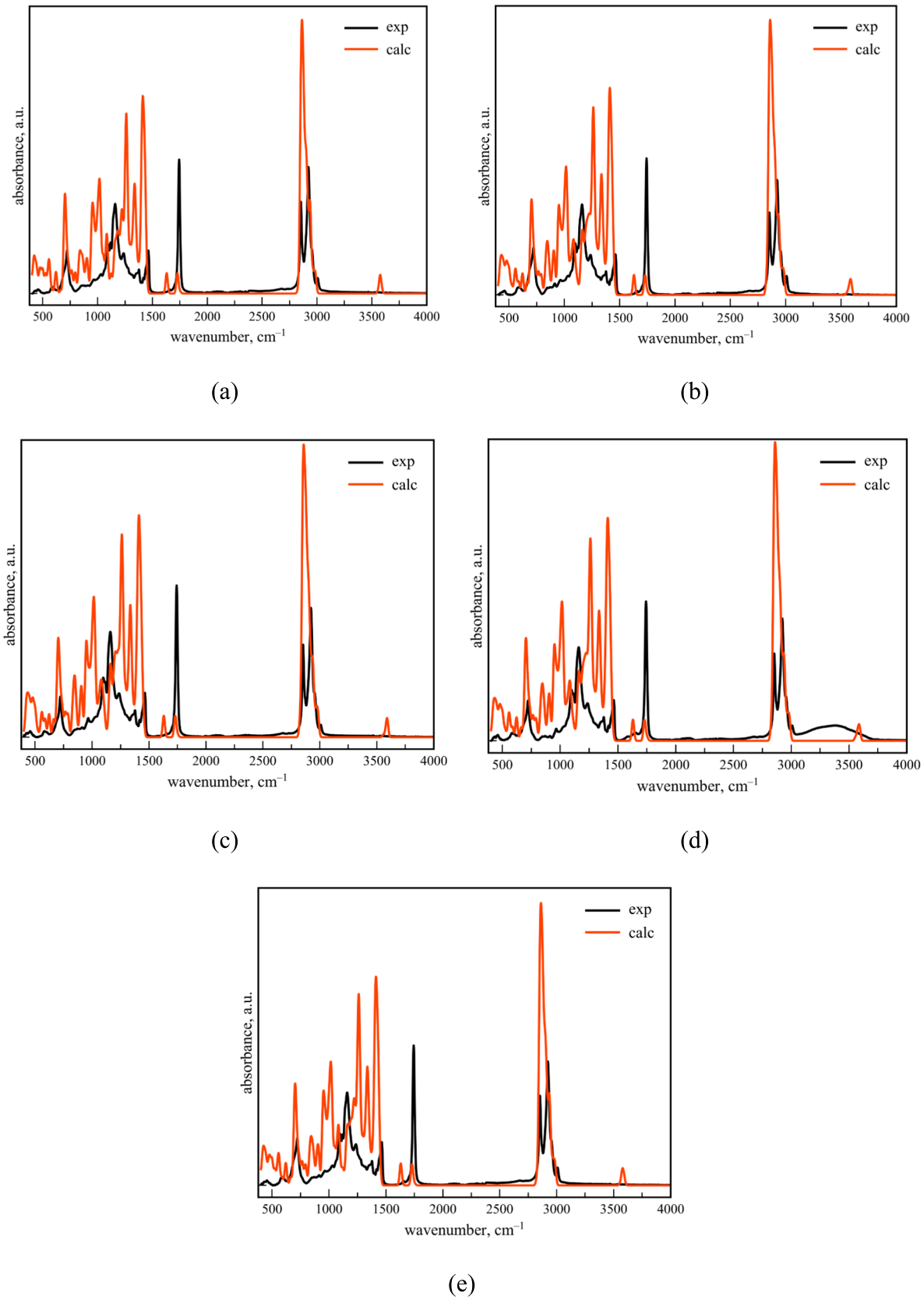

Fig. 2. Experimental (black lines) and calculated (red lines) infrared spectra of hazelnut oil (a), sunflower oil (b), safflower oil (c), corn oil (d) and canola oil (e). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

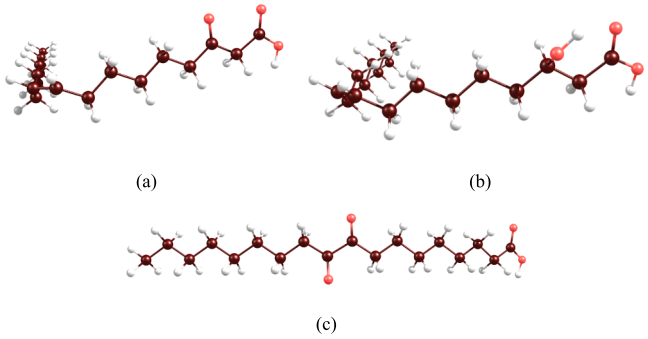

Fig. 3. Oxidized products FA = O (a), FA–OH (b) and O = FA = O (c) of oleic acid. Brown, red and write balls represent carbon, oxygen and hydrogen atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

saturated, their presence and concentrations improve the oxidative stability of vegetable oils. In the experimental part of the research, it was examined that the higher palmitic acid percentages of corn oil resulted in higher OS. According to the computational results, mono and polyunsaturated fatty acids have lesser chemical hardness, making vegetable oil more sensitive to oxidative processes. Moreover, the vegetable oils containing higher mono and polyunsaturated fatty acids ratios (especially safflower oil) had relatively lower OS as well (Table 1). The computational data and experimental results in our current work are in good agreement. As a result, combining DFT calculations with middle infrared spectra is an acceptable option for analyzing the oxidative stability of vegetable oils without the need for sample preparation, long-term instrumental analyses, solvent, or time waste.

4. Conclusion

In this work, oxidation induction times and fatty acid percentages of five different vegetable oils were determined. The chemical hardness of fatty acids was calculated by DFT calculations with middle infrared spectral data. The oxidative stability and oxidation process of fatty acids were firstly explained in the light of electronic structure principles such as Maximum Hardness and Minimum Electrophilicity Principles. One more time, it was proved that second electrophilicity index is more useful compare to first electrophilicity index in terms of electrophilicity minimization in stable states. Both computational and experimental results confirmed that the presence of saturated fatty acids particularly palmitic acid improve oxidative stability of vegetable oils. Mono- and polyunsatured fatty acids have lower chemical hardness which make

Table 2
Reaction energy effects (kcal/mol) calculated for the reactions (1)-(3).

	Oleic acid (C18:1)	Gondoic acid (C20:1)	Linoleic acid (C18:2)	Linolenic acid (C18:3)	Palmitic acid (C16:0)	Stearic acid (C18:0)
Reaction (12)	−42.2	−41.7	−42.2	−42.3	−42.3	−42.2
Reaction (13)	−99.6	−110.6	−104.0	−109.3	−109.4	−109.2
Reaction (14)	−158.7	−159.8	−155.7	−156.6	–	–

Table 3
Frontier orbitals HOMO and LUMO (eV), energy gap (eV) and dipole moments (Debye) of fatty acids (FA) and their oxidized products FA = O, FA–OH and O = FA = O.

		Oleic acid (C18:1)	Gondoic acid (C20:1)	Linoleic acid (C18:2)	Linolenic acid (C18:3)	Palmitic acid (C16:0)	Stearic acid (C18:0)
FA	**HOMO**	−6.49	−6.46	−6.41	−6.42	−7.72	−7.68
	LUMO	−1.06	−0.11	−0.11	−0.12	−0.10	−0.11
	Gap	5.43	6.35	6.30	6.30	7.62	7.57
	DM	5.59	5.90	5.37	5.71	5.44	5.45
	χ	3.775	3.285	3.260	3.270	3.910	3.895
	η	5.430	6.350	6.300	6.300	7.620	7.570
	σ	0.184	0.157	0.159	0.159	0.131	0.132
	ω_1	1.312	0.850	0.843	0.849	1.003	1.002
	ω_2	1.267	0.112	0.112	0.122	0.101	0.112
FA = O	**HOMO**	−6.51	−6.51	−6.36	−6.48	−7.64	−7.63
	LUMO	−0.85	−1.40	−1.01	−1.41	−1.40	−1.40
	Gap	5.66	5.12	5.35	5.08	6.24	6.23
	DM	8.69	7.27	6.56	6.95	7.22	7.15
	χ	3.680	3.955	3.685	3.945	4.520	4.515
	η	5.660	5.110	5.350	5.070	6.240	6.230
	σ	0.177	0.196	0.187	0.197	0.160	0.161
	ω_1	1.196	1.531	1.269	1.535	1.637	1.636
	ω_2	0.978	1.784	1.201	1.802	1.714	1.715
FA–OH	**HOMO**	−6.48	−6.47	−6.37	−6.42	−7.53	−7.54
	LUMO	−0.39	−0.38	−0.40	−0.41	−0.40	−0.39
	Gap	6.09	6.09	5.97	6.01	7.13	7.15
	DM	5.78	5.84	5.55	5.74	5.49	5.50
	χ	3.435	3.425	3.385	3.415	3.965	3.965
	η	6.090	6.090	5.970	6.010	7.130	7.150
	σ	0.164	0.164	0.168	0.166	0.140	0.140
	ω_1	0.969	0.963	0.960	0.970	1.102	1.099
	ω_2	0.415	0.404	0.427	0.438	0.422	0.411
O = FA = O	**HOMO**	−6.78	−6.76	−6.59	−6.57	–	–
	LUMO	−2.52	−2.50	−2.56	−2.34	–	–
	Gap	4.25	4.26	4.03	4.23	–	–
	DM	5.48	5.40	5.23	5.39	–	–
	χ	4.650	4.630	4.575	4.455		
	η	4.260	4.260	4.030	4.230		
	σ	0.235	0.235	0.248	0.236		
	ω_1	2.538	2.516	2.597	2.346		
	ω_2	4.011	3.967	4.186	3.634		

vegetable oils more susceptible to oxidative reactions. It was also demonstrated that safflower oil, which has a higher percentage of unsaturated fatty acid ratios, has the lowest oxidative stability. As a result, bringing together DFT computations with middle infrared spectral data to evaluate the oxidative stability of vegetable oils is a potential approach. The determination of oxidative stability of vegetable oils using DFT computations with middle infrared spectra is a novel, rapid, cost-effective, and ecologically friendly technique. The changes in OS and fatty acid profile of vegetable oils stored under different conditions could be examined by infrared spectroscopy and DFT calculations as a further study.

CRediT authorship contribution statement

Ayse Burcu Aktas: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Data curation, Writing – original draft, Writing – review & editing, Visualization, Supervision, Project administration. **Taner Dastan:** Formal analysis, Investigation, Resources, Data curation, Writing – original draft, Visualization, Supervision. **Konstantin P. Katin:** Software, Formal analysis, Investigation, Resources, Data curation, Writing – original draft, Visualization, Supervision. **Savas Kaya:** Conceptualization, Methodology, Software, Validation, Formal analysis, Investigation, Resources, Data curation, Writing – original draft, Writing – review & editing, Visualization, Supervision, Project administration.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: [Ayse Burcu Aktas reports was provided by Cumhuriyet University. Ayse Burcu Aktas reports a relationship with Cumhuriyet University that includes: employment. nothing].

Data availability

The data that has been used is confidential.

References

[1] X. Yang, R.A. Boyle, Sensory evaluation of oils/fats and oil/fat–based foods, in: M. Hu, C. Jacobsen (Eds.), Oxidative Stability and Shelf Life of Foods Containing Oils and Fats, The Netherlands, Elsevier, Amsterdam, 2016, pp. 157–185.

[2] A. Syed, in: Oxidative Stability and Shelf Life of Foods Containing Oils and Fats, Elsevier, 2016, pp. 187–207.

[3] L. Redondo-Cuevas, G. Castellano, F. Torrens, V. Raikos, Revealing the relationship between vegetable oil composition and oxidative stability: a multifactorial approach, J. Food Comp. Anal. 66 (2018) 221–229, https://doi.org/10.1016/j.jfca.2017.12.027.

[4] J. Li, J. Liu, X. Sun, Y. Liu, The mathematical prediction model for the oxidative stability of vegetable oils by the main fatty acids composition and thermogravimetric analysis, Lwt 96 (2018) 51–57, https://doi.org/10.1016/j.lwt.2018.05.003.

[5] C. Dorni, P. Sharma, G. Saikia, T. Longvah, Fatty acid profile of edible oils and fats consumed in India, Food Chem. 238 (2018) 9–15, https://doi.org/10.1016/j.foodchem.2017.05.072.

[6] M. Shen, S. Zhao, F. Zhang, M. Huang, J. Xie, Characterization and authentication of olive, camellia and other vegetable oils by combination of chromatographic and chemometric techniques: Role of fatty acids, tocopherols, sterols and squalene, Euro. Food Res. Technol. 247 (2) (2021) 411–426, https://doi.org/10.1007/s00217-020-03635-4.

[7] S. Martín-Torres, L. Ruiz-Castro, A.M. Jiménez-Carvelo, L. Cuadros-Rodríguez, Applications of multivariate data analysis in shelf life studies of edible vegetal oils–a review of the few past years, Food Pack. Shelf Life. 31 (2022), 100790, https://doi.org/10.1016/j.fpsl.2021.100790.

[8] H. Hadorn, K. Zurcher, Zur bestimmung der oxydationsstabilitat von olen und fetten, Dtsch. Lebensm.-Rundsch. (1974).

[9] M. Allendorf, A. Subramanian, L. Rodriguez-Saona, Application of a Handheld Portable Mid-Infrared Sensor for Monitoring Oil Oxidative Stability, J. Am. Oil Chem. Soc. 89 (1) (2012) 79–88.

[10] A. Kaur, B. Singh, A. Kaur, N. Singh, Changes in chemical properties and oxidative stability of refined vegetable oils during short-term deep-frying cycles, J. Food Pro. Pre. 44 (6) (2020) e14445.

[11] L. Xu, X. Yu, L. Liu, M. Li, R. Zhang, A rapid method for evaluating the edible oil oxidative stability during ambient storage by FTIR spectroscopy using a mesh cell, Anal. Methods 8 (25) (2016) 5117–5122, https://doi.org/10.1039/C6AY01511E.

[12] N. Islam, S. Kaya, Conceptual density functional theory and its application in the chemical domain, CRC Press, 2018.

[13] L. Guo, Z.S. Safi, S. Kaya, W. Shi, B. Tüzün, N. Altunay, C. Kaya, Anticorrosive effects of some thiophene derivatives against the corrosion of iron: a computational study, Fron. chem. 6 (2018) 155, https://doi.org/10.3389/fchem.2018.00155.

[14] O. Uncu, B. Ozen, Prediction of various chemical parameters of olive oils with Fourier transform infrared spectroscopy, Lwt 63 (2) (2015) 978–984, https://doi.org/10.1016/j.lwt.2015.05.002.

[15] A.B. Aktas, B. Ozen, C. Alamprese, Effects of processing parameters on chemical and physical properties of enzymatically interesterified beef tallow–corn oil blends, J. Food Pro. Pre. 45 (8) (2021) e14587.

[16] A.B. Aktas, G.N. Temur, B.N. Okcu, Fourier transform infrared spectroscopy and chemometrics for chemical property prediction of chemically interesterified lipids with butterfat and vegetable oils during storage, J. Mol. Struc. 1274 (2023), 134503, https://doi.org/10.1016/j.molstruc.2022.134503.

[17] R.G. Parr, W. Yang, Density-functional theory of the electronic structure of molecules, Ann. rev. phys. chem. 46 (1) (1995) 701–728, https://doi.org/10.1146/annurev.pc.46.100195.003413.

[18] S. Kaya, A. Robles-Navarro, E. Mejía, T. Gómez, C. Cardenas, On the prediction of lattice energy with the fukui potential: some supports on hardness maximization in inorganic solids, J. of Phys. Chem. A 126 (27) (2022) 4507–4516, https://doi.org/10.1021/acs.jpca.1c09898.

[19] S. Kaya, M.V. Putz, Atoms-in-molecules' faces of chemical hardness by conceptual density functional theory, Molecules 27 (24) (2022) 8825, https://doi.org/10.1021/acs.jpca.1c09898.

[20] S. Şimşek, Y. Derin, S. Kaya, Z.M. Şenol, K.P. Katin, A. Özer, A. Tutar, High-performance material for the effective removal of uranyl ion from solution: computationally supported experimental studies, Langmuir 38 (33) (2022) 10098–10113, https://doi.org/10.1021/acs.langmuir.2c00978.

[21] S. Kaya, C. Kaya, A simple method for the calculation of lattice energies of inorganic ionic crystals based on the chemical hardness, In. chem. 54 (17) (2015) 8207–8213, https://doi.org/10.1021/acs.inorgchem.5b00383.

[22] R.G. Parr, L.V. Szentpály, S. Liu, Electrophilicity index, J. Am. Chem. Soc. 121 (9) (1999) 1922–1924, https://doi.org/10.1021/ja983494x.

[23] L. von Szentpály, S. Kaya, N. Karakuş, Why and when is electrophilicity minimized? new theorems and guiding rules, Chem. A Eur. J. 124 (51) (2020) 10897–10908, https://doi.org/10.1021/acs.jpca.0c08196.

[24] T. Koopmans, Über die zuordnung von wellenfunktionen un9d eigenwerten zu den einzelnen elektronen eines atoms, Physica 1 (1–6) (1945) 104–113, https://doi.org/10.1016/S0031-8914(34)90011-2.

[25] A. D. Becke, Density-functional thermochemistry. IV. A new dynamical correlation functional and implications for exact-exchange mixing, J. chem.phys. 104(3) 1996 1040-1046. https://doi.org/10.1063/1.464913.

[26] C. Lee, W. Yang, R.G. Parr, Development of the colle-salvetti correlation-energy formula into a functional of the electron density, Phys. Rev. B 37 (2) (1988) 785, https://doi.org/10.1103/PhysRevB.37.785.

[27] M. Tanaka, M. Katouda, S. Nagase, Optimization of RI-MP2 auxiliary basis functions for 6–31G** and 6–311G** basis sets for first-, second-, and third-row elements, J. Comp. Chem. 34 (29) (2013) 2568–2575, https://doi.org/10.1002/jcc.23430.

[28] J. Grabska, K.B. Beć, M. Ishigaki, C.W. Huck, Y. Ozaki, NIR spectra simulations by anharmonic DFT-saturated and unsaturated long-chain fatty acids, J. Phys. Chem. B 122 (27) (2018) 6931–6944.

[29] S. Grimme, S. Ehrlich, L. Goerigk, Effect of the damping function in dispersion corrected density functional theory, J. comp. chem. 32 (7) (2011) 1456–1465, https://doi.org/10.1002/jcc.21759.

[30] L.-P. Wang, C. Song, Geometry optimization made simple with translation and rotation coordinates, J. Chem. Phys.. 144 (21) (2016), 214108, https://doi.org/10.1063/1.4952956.

[31] I.S. Ufimtsev, T.J. Martinez, Quantum chemistry on graphical processing units. 3. analytical energy gradients, geometry optimization, and first principles molecular dynamics, J. Chem. Theory Comput. 5 (10) (2009) 2619–2628.

[32] A.V. Titov, I.S. Ufimtsev, N. Luehr, T.J. Martinez, Generating efficient quantum chemistry codes for novel architectures, J. Chem. Theo. Comp. 9 (1) (2013) 213–221, https://doi.org/10.1021/ct300321a.

[33] J. Kästner, J.M. Carr, T.W. Keal, W. Thiel, A. Wander, P. Sherwood, DL-FIND: an open-source geometry optimizer for atomistic simulations, Chem. A Eur. J. 113 (43) (2009) 11856–11865, https://doi.org/10.1021/jp9028968.

[34] F. Liu, N. Luehr, H.J. Kulik, T.J. Martínez, Quantum chemistry for solvated molecules on graphical processing units using polarizable continuum models, J. Chem. Theory Comput. 11 (7) (2015) 3131–3144.

[35] H. Lizhi, K. Toyoda, I. Ihara, Dielectric properties of edible oils and fatty acids as a function of frequency, temperature, moisture and composition, J. food engin. 88 (2) (2008) 151–158, https://doi.org/10.1016/j.jfoodeng.2007.12.035.

[36] D. Barrera-Arellano, A.P. Badan-Ribeiro, S.O. Serna-Saldivar, Corn oil: composition, processing, and utilization, In Corn, AACC International Press, 2019. https://doi.org/10.1016/B978-0-12-811971-6.00021-8.

[37] E. Duman, M.M. Ozcan, The influence of industrial refining stages on the physico-chemical properties, fatty acid composition and sterol contents in hazelnut oil, J. Food Sci. Technol. 57 (7) (2020) 2501–2506, https://doi.org/10.1007/s13197-020-04285-w.

[38] A. Fernández-Cuesta, L. Velasco, M.V. Ruiz-Méndez, Novel safflower oil with high γ-tocopherol content has a high oxidative stability, Euro. J. lipid sci. technol. 116 (7) (2014) 832–836, https://doi.org/10.1002/ejlt.201300208.
[39] A. Lewinska, J. Zebrowski, M. Duda, A. Gorka, M. Wnuk, Fatty acid profile and biological activities of linseed and rapeseed oils, Molecules 20 (12) (2015) 22872–22880, https://doi.org/10.3390/molecules201219887.
[40] D. Wang, W. Fan, Y. Guan, H. Huang, T. Yi, J. Ji, Oxidative stability of sunflower oil flavored by essential oil from Coriandrum sativum L. during accelerated storage, Lwt 98 (2018) 268–275, https://doi.org/10.1016/j.lwt.2018.08.055.
[41] A. Bastürk, M.M. Ceylan, M. Çavus, G. Boran, I. Javidipour, Effects of some herbal extracts on oxidative stability of corn oil under accelerated oxidation conditions in comparison with some commonly used antioxidants, Lwt 89 (2018) 358–364, https://doi.org/10.1016/j.lwt.2017.11.005.
[42] G. Durmaz, V. Gokmen, Effect of refining on bioactive composition and oxidative stability of hazelnut oil, Food Res. Int. 116 (2019) 586–591, https://doi.org/10.1016/j.foodres.2018.08.077.
[43] S.M. Ghazani, G. García-Llatas, A.G. Marangoni, Minor constituents in canola oil processed by traditional and minimal refining methods, J. Am. Oil Chem. Soc. 90 (5) (2013) 743–756, https://doi.org/10.1007/s11746-013-2215-2.
[44] R. Jamwal, Amit, S. Kumari, S. Sharma, S. Kelly, A. Cannavan, D.K. Singh, Recent trends in the use of FTIR spectroscopy integrated with chemometrics for the detection of edible oil adulteration, Vib. Spectros. 113 (2021), 103222, https://doi.org/10.1016/j.vibspec.2021.103222.
[45] Q. Li, J. Chen, Z. Huyan, Y. Kou, L. Xu, X. Yu, J.M. Gao, Application of Fourier transform infrared spectroscopy for the quality and safety analysis of fats and oils: a review, Cri. Rev. food sci. nut. 59 (22) (2019) 3597–3611, https://doi.org/10.1080/10408398.2018.1500441.
[46] M.M. Adeva-Andany, N. Carneiro-Freire, M. Seco-Filgueira, C. Fernández-Fernández, D. Mouriño-Bayolo, Mitochondrial β-oxidation of saturated fatty acids in humans, Mitochondrion 46 (2020) 73–90, https://doi.org/10.1016/j.mito.2018.02.009.
[47] Ş. Erdoğan, Z.S. Safi, S. Kaya, D.Ö. Işın, L. Guo, C. Kaya, A computational study on corrosion inhibition performances of novel quinoline derivatives against the corrosion of iron, J. Mol. Struc. 1134 (2017) 751–761, https://doi.org/10.1016/j.molstruc.2017.01.037.
[48] S. Kaya, C. Kaya, A new method for calculation of molecular hardness: a theoretical study, Comp. theo. Chem. 1060 (2015) 66–70, https://doi.org/10.1016/j.comptc.2015.03.004.
[49] S. Kaya, C. Kaya, A new equation for calculation of chemical hardness of groups and molecules, Mol. Phys. 113 (11) (2015) 1311–1319, https://doi.org/10.1080/00268976.2014.991771.
[50] S. Kaya, C. Kaya, N. Islam, Maximum hardness and minimum polarizability principles through lattice energies of ionic compounds, Phys. B Condens. Matter 485 (2016) 60–66, https://doi.org/10.1016/j.physb.2016.01.010.
[51] R.G. Pearson, Hard and soft acids and bases, J. Am. Chem. Soc. 85 (22) (1963) 3533–3539, https://doi.org/10.1021/ja00905a001.
[52] R.G. Parr, P.K. Chattaraj, Principle of maximum hardness, J. Am. Chem. Soc. 113 (5) (1991) 1854–1855.
[53] P.K. Chattaraj, S. Sengupta, Popular electronic structure principles in a dynamical context, J. Phys. Chem. 100 (40) (1996) 16126–16130, https://doi.org/10.1021/jp961096f.
[54] E. Chamorro, P.K. Chattaraj, P. Fuentealba, Variation of the electrophilicity index along the reaction path, Chem. A Eur. J. 107 (36) (2003) 7068–7072, https://doi.org/10.1021/jp035435y.
[55] S. Pan, M. Sola, P.K. Chattaraj, On the validity of the maximum hardness principle and the minimum electrophilicity principle during chemical reactions, Chem. A Eur. J. 117 (8) (2013) 1843–1852, https://doi.org/10.1021/jp312750n.