

Calibrated Optical Markers to Study Thermal Degradation in Edible Oils Using Raman and Optical Transmission Spectroscopy

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Abstract

An "all optical" methodology, including Raman and optical transmission spectroscopy, is presented to study the thermal degradation in edible oils. Oils rich in monounsaturated (MU), polyunsaturated (PU), and saturated (S) fatty acids (FA) were heated above and below their smoke point ($\sim 230^\circ\text{C}$). While the intensity (I) of the identified saturated ($\text{C}-\text{C}$, @ 1440 cm^{-1}) FA Raman marker did not change appreciably, the identified unsaturated ($\text{C}=\text{C}$, @ 1265 cm^{-1}) FA marker decreased in these oils when heated above the smoke point. A Raman parameter, I_{1265}/I_{1440} , designating thermal degradation, is proposed that was found to decrease consistently for the PUFA-rich, and MUFA-rich oils when heated above the smoke point, while the SFA-rich oil did not degrade at all over the whole temperature range. An optical transmission marker at 2140 nm, was identified that decreased consistently with increased thermal stressing. These markers can be calibrated with the variations in the quantitative Iodine value, an industrial benchmark for the degree of unsaturation, for thermally stressed oils.

Keywords: Raman spectroscopy, edible oils, thermal degradation, optical transmission, iodine value, saturated fat, unsaturated fat

INTRODUCTION

Toxin screening to ensure food safety is currently a challenge. Frequent safety breaches,¹⁻³ driven mostly by economics, and to pass quality controls, involving unhealthy manipulation of food content, or application of banned preservatives, and pesticides, have led to the adoption of stringent measures by local authorities around the globe. Melamine contamination in baby food,³ maleic acid in rice and gluten-based products,⁴ are just few examples. The problem worsens when the cooking medium such as oil is adulterated, affecting public health in a much larger scale. It is well known now, how cheap gutter oil, is extracted from diverse kinds of used oil, from kitchen waste, sewers, and animal fat,^{5,6}

created a stir when it was found to contain carcinogenic toxins,⁷ affecting human health.⁸ One potential danger is presented in the form of re-used oils recklessly used in street food, chain stores, and restaurants. Such recycling of used oils is hard to detect and implicate legally as no contamination or harmful foreign substances have been added. However, free radicals, and species generated by re-cooking edible oils, particularly above their smoke point may be as harmful as contaminated oil.

Fatty acids (FAs),⁹ the building block for most oils, can be classified as unsaturated, those containing carbon–carbon (C=C) double bonds, or saturated, those containing C–C single bonds.⁹ Saturated FA (SFA), rich in C–C, are less reactive than polyunsaturated (PUFA), or monounsaturated (MUFA) FAs, containing C=C, which can undergo auto,¹⁰ photo,¹⁰ and thermal oxidation^{7,11} producing primary, secondary, and tertiary dissociation products unsuitable for consumption.⁸ Heating temperature, defined mostly by the smoke point, heating time, and the amount of oxygen or water present, will affect the thermal oxidation rate.^{10–12}

Quantitative analyses of edible oils have been done by gas chromatography,¹³ and liquid chromatography–mass spectroscopy. Qualitative analyses, such as oil classification, have been done using luminescence¹⁴ and absorption¹⁵ measurements as well. Fourier transform mid-infrared (FT-MIR),^{16–18} Fourier transform near-infrared (FT-NIR),¹⁹ and Fourier transform Raman (FT-Raman)^{18–21} spectroscopies have been used to distinguish and monitor adulteration in different edible oils. In comparison, Raman spectroscopy, a qualitative technique, has been used to study oils, but is limited by its low scattering cross-section.^{22–24} To promote it as an alternative and facile methodology to study thermally stressed edible oils, it has to be correlated vis-à-vis a quantifiable parameter and then calibrated. This can be done through "iodine value",^{25,26} or "bromine value",²⁷ which is defined as the mass of iodine/bromine, in grams, to react with 100 grams of a chemical and is a measure of the degree of unsaturation in FAs present in edible oils.

For this research, we have used Raman spectroscopy and ultraviolet–near infrared (UV–Vis–NIR) spectroscopy to study the degradation of different kinds of edible oils, when they are being heated for long time below, at, and above the respective smoke point, and then correlate the data independently with optical transmission, and Iodine value (I_v) measurements to have a new quantification platform to study thermal degradation of edible oils.

Experimental

Materials

The analytes used included different types of as-purchased refined edible oils (corn, sunflower, camellia, canola, peanut, extra virgin olive, and coconut oils), with and without thermal oxidation. For Raman study, aluminum plates were used as substrate and were locally purchased.

Methods

For Raman measurements, all edible oils were heated under 150, 250, and 300 °C for 1–5 hours, and 5 ml samples were decanted at hourly intervals. For Raman study, 0.5 µl of each oil was dropped on bare aluminum. The oil was uniformly distributed and spectra were collected from five different points on the same substrate. Spectra with the highest and lowest Raman intensities were ignored, and an average was calculated from the remaining three spectra. Baseline subtraction for all spectra were performed using Origin 9 software (OriginLab Corp.). First, a 100-points movable random baseline was created. These points were moved to overlap with the spectral background. The left and the right bases of each Raman band, assumed Lorentzian, were joined linearly with these movable points. Finally, the manually created baseline (for each spectrum) was subtracted from the raw data. Raman spectra were measured by using a commercial Jobin Yvon LabRAM HR800 (Horiba Ltd.) Raman spectrometer equipped with an Olympus BX-41 microscope, using 532 nm excitation. A 50X objective was used for focusing and data collection. A high-sensitivity liquid nitrogen cooled charge-coupled device (CCD) (UI-146Xle, IDS imaging Development Systems GmbH) was used as the detector. The exposure time was set at 20 s, with one accumulation for each spectrum. All experiments were carried out identically.

For optical transmission study, UV–Vis–NIR spectroscopy was used to analyze the changes in the transmission of the edible oils before, and after they had been heated (thermally oxidized). This study was carried out using the UV–Vis spectroscope (JASCO V-770, Jasco Corp.) in the range of 190–2700 nm.

For I_v determination,²⁵ approximately 0.2 g of oil was dissolved in 20 mL of anhydrous ethanol (ethanol, absolute; Fisher Chemical) in an Erlenmeyer flask and 0.5 g of pyridinium tribromide ($C_5H_6Br_3N^{-2}$, >95%, Acros, Belgium) was added. After about 30 s, 20 mL of distilled water, and 1.5 g of potassium iodide (KI, Fisher Chemical) was added successively. A few drops of starch (1%) were added to the flask as an indicator. Finally, the solution was titrated with 0.1 M sodium thiosulfate ($Na_2S_2O_3$, technical, SLR, Fisher Chemical) until the color changed to cloudy or clear.

Results and Discussion

Optical Images of Edible Oils

We will begin with a visual assessment of the edible oils, and what happens to them with heating at different temperatures. Figure 1 shows the digital photographs of seven selected edible oils heated under 150, 250, and 300 °C for one to five hours. The edible oils changed from pale (as-purchased), or white, to dark brown or black in color, and showed increasing viscosity with an increase in heating temperature and time. Thermal stressing will induce dissociation of double bonds ($C=C$) leading to a reduction in their degree of unsaturation, and increase in the viscosity.²⁸ Most of the oils, barring coconut and olive, became highly viscous or even solid after being heated at 300 °C for four to five hours after which optical transmission measurement became impossible. Hence, UV–Vis, along with Raman spectroscopy, was only conducted up to three hours of heating in the 300 °C case.

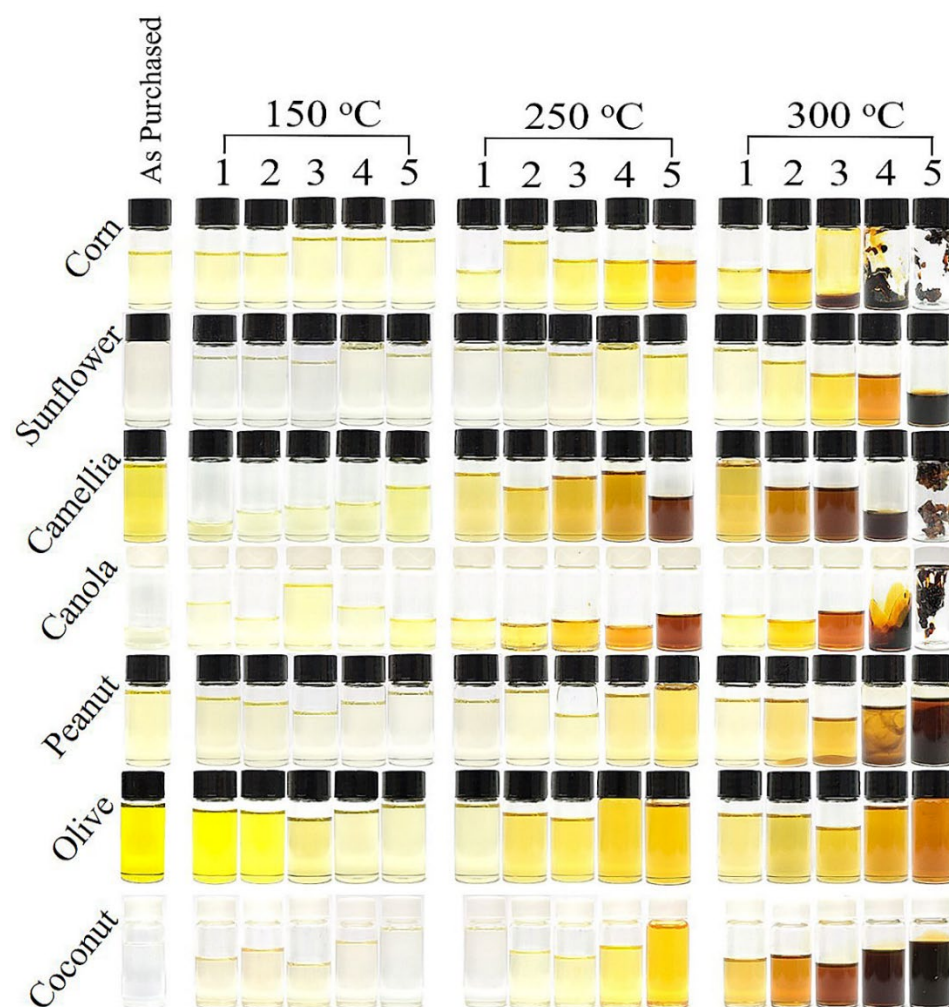


Figure 1. The digital photographs of corn, sunflower, camellia, canola, peanut, extra virgin olive, and coconut oils, heated under 150, 250, and 300 °C for 1–5 h.

Raman Spectra of Edible Oils

To accustom the readers with the Raman spectra of the edible oils, we present a comparison of the corn, extra virgin olive, and coconut oil in the Supplemental Material (Figure S1). corn, extra virgin olive, and coconut oils belong to the PUFA, MUFA, and SFA groups, respectively. The degree of unsaturation can be determined by comparing the C=C double bond (unsaturated fat) intensity with respect to the C–C single bond (saturated fat) intensity. For example, the peak at 1650 cm^{-1} is the strongest for the corn oil as it is a high PUFA (highest C=C content among these three) oil.^{9,11} For extra virgin olive oil, rich in oleic acid,^{9,11} all four C=C related peaks are relatively weaker than those of the PUFA rich corn oil. coconut oil, rich in SFA and lacking in C=C,^{9,11} depict only a weak 1265 cm^{-1} among all the C=C related peaks, others being at 970 , 1650 , and 3005 cm^{-1} . Hence, we will select only the 1265 cm^{-1} peak to represent the C=C or the signature for the degree of unsaturation in these oils.

Figure 2 shows the Raman spectra of three representative edible oils, viz, PUFA-rich corn (Figure 2a), MUFA-rich extra virgin olive (Figure 2b), and SFA-rich coconut (Figure 2c), under thermal stress to analyze their individual degradation. For the time being, representative spectrum from each heating group (150 , 250 , and $300\text{ }^{\circ}\text{C}$) may be compared. We observed that the C=C related 1265 cm^{-1} peak intensities, in the PUFA and MUFA group oils, decreased from very strong (sometime stronger than the C–C related 1440 cm^{-1} peak), in the as purchased case, to very weak, after the oils were heated to $300\text{ }^{\circ}\text{C}$, for longer durations. The other C=C related peaks, say at 3005 cm^{-1} , also showed consistent decrease in intensities after the oil was heated to 250 , and $300\text{ }^{\circ}\text{C}$ for long periods. In contrast, the peak intensities of C–C, at 1300 , and 1440 cm^{-1} , remained largely invariant with heating temperature. This is expected as C–C bonds are stable against thermal oxidation below the smoke point. Other than these specific peaks, other peaks did not show any consistent, valuable information for oil degradation analysis.^{29–31} coconut oil, low in C=C, and containing lauric acid,¹¹ showed a very weak 1265 cm^{-1} peak, while the other C=C related peaks were indistinguishable. In coconut oil, the C=C bond related peak intensities reached limit of detection levels only after heating for a short period of time indicating completion of thermal oxidation within the initial stages of heating. The Raman spectra of other edible oils, under thermal stress and belonging to these groups, are presented in Supplemental Material Figure S2. Few published articles have demonstrated thermal degradation of edible oils^{20,21,32} using Raman spectroscopy. However, the thermal stressing was limited to $205\text{ }^{\circ}\text{C}$ which is below the smoke point for

many edible oils.²¹ In our experiment, the range of thermal stressing cover values below and above smoke points for better understanding.

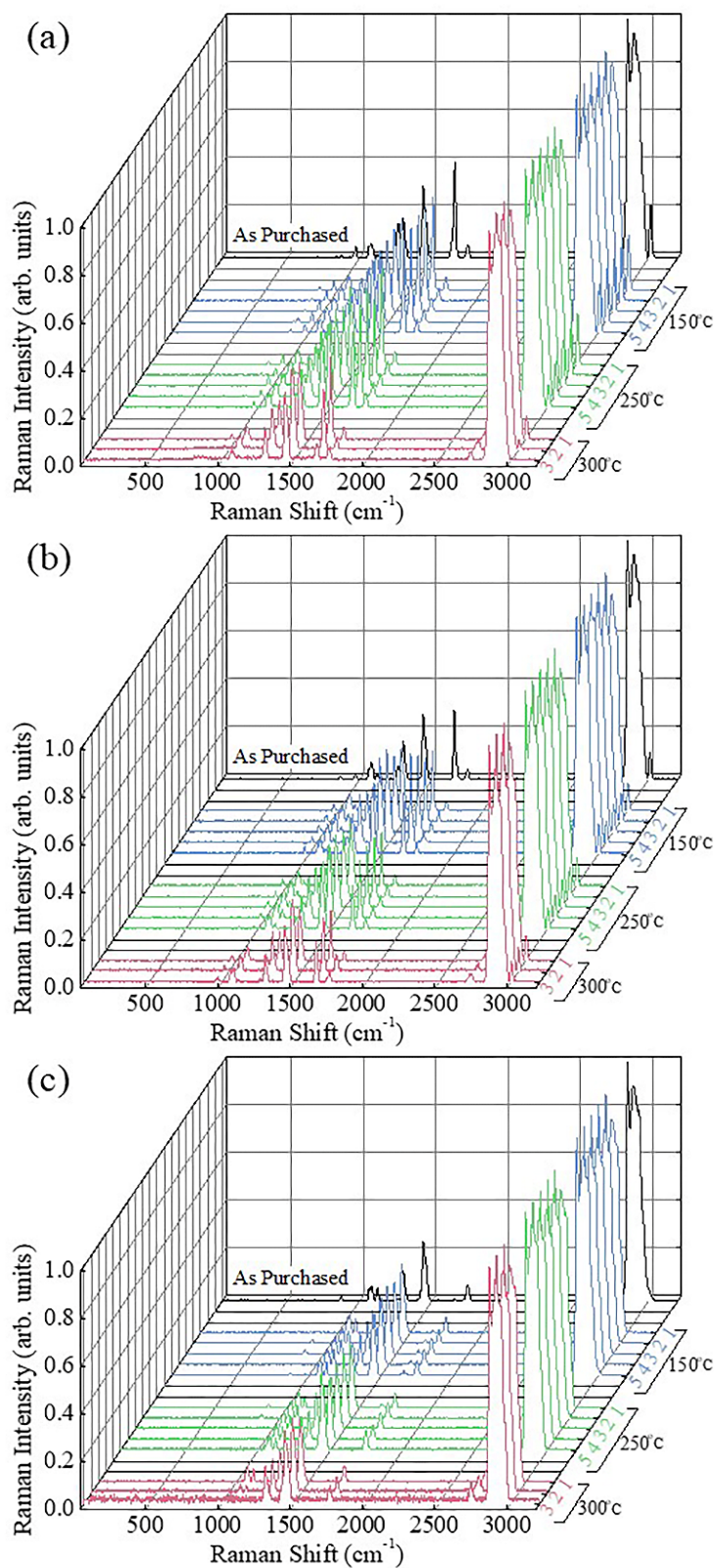


Figure 2. Normalized Raman spectra of (a) corn, (b) extra virgin olive, and (c) coconut oil under thermal oxidation at different heating temperature and time. The numbers 1–5 stand for the heating time from 1–5 hrs,

under each temperature of heating, namely, 150 (blue set), 250 (green set), and 300 °C (red set). The data for as-purchased oil (black) is also shown. The normalization is done with respect to the 2852 cm⁻¹ band for each spectrum.

UV–Visible Spectra of Edible Oils

Figure S3a shows the UV–Vis transmission spectrum (200–2700 nm) of the as purchased corn, extra virgin olive, and coconut oil, depicting dips related to different molecular absorption.^{14,30} The spectral features of most of the edible oils are located in the near-infrared (1000–2500 nm) spectral region.³⁰ Extra virgin olive oil has a strong dip located near 670 nm, which is due to absorption of the chlorophyllic fraction³¹ responsible for the green pigments in olive drupe.^{31,32} However, most of the dips in the visible region are not useful for the thermal degradation analysis. The one which holds key information is located near 2140–2150 nm (Figure S3b), corresponding to the *cis*- FAs denoting degree of unsaturation in these edible oils.¹⁵ The dip intensities were calculated from the transmission saturation near 2070 nm, and plotted for the three oils (inset, Figure S3b). The transmission intensities were the highest for high PUFA containing corn oil,¹⁶ followed by the high MUFA containing extra virgin olive oil,¹⁶ and smallest for the high SFA containing coconut oil.^{15,30}

Broad, and narrowband UV–Vis transmission spectra of the high PUFA rich corn (Figure 3a,b), MUFA-rich olive (Figure 3c,d), and SFA-rich coconut oil (Figure 3e, f) under thermal stressing is shown in Figure 3. UV–Vis spectra of the other four oils, under thermal stress, are shown in Supplemental Material Figure S4. We observed consistent decrease of the 2140 nm transmission dip with increased thermal stressing (Inset, Figure 3b) in corn oil. The observation is true for the MUFA-rich olive oil too (Inset, Figure 3d). However, unlike the PUFA and MUFA group oils, the SFA-rich coconut dips near 2145 nm and does not even appear in the spectrum of even the as-purchased coconut oil (inset, Figure 3f) and reached the limit of detectability in the UV–Vis machine. **The sentence beginning "However, unlike the PUFA and MUFA group oils,..." was rewritten for clarity. Please confirm the Editor maintained your meaning here.** This data is corroborated by Hourant and colleagues¹⁶ who showed that oils containing less C=C double bond, such as coconut, and palm oils have very weak 2145 nm transmission dip, while those with high C=C double bonds, including corn, sunflower, grapeseed, and soybean oil, have strong transmission dips.¹⁵ We concluded that the 2140 nm band is a good indicator to observe the thermal degradation.

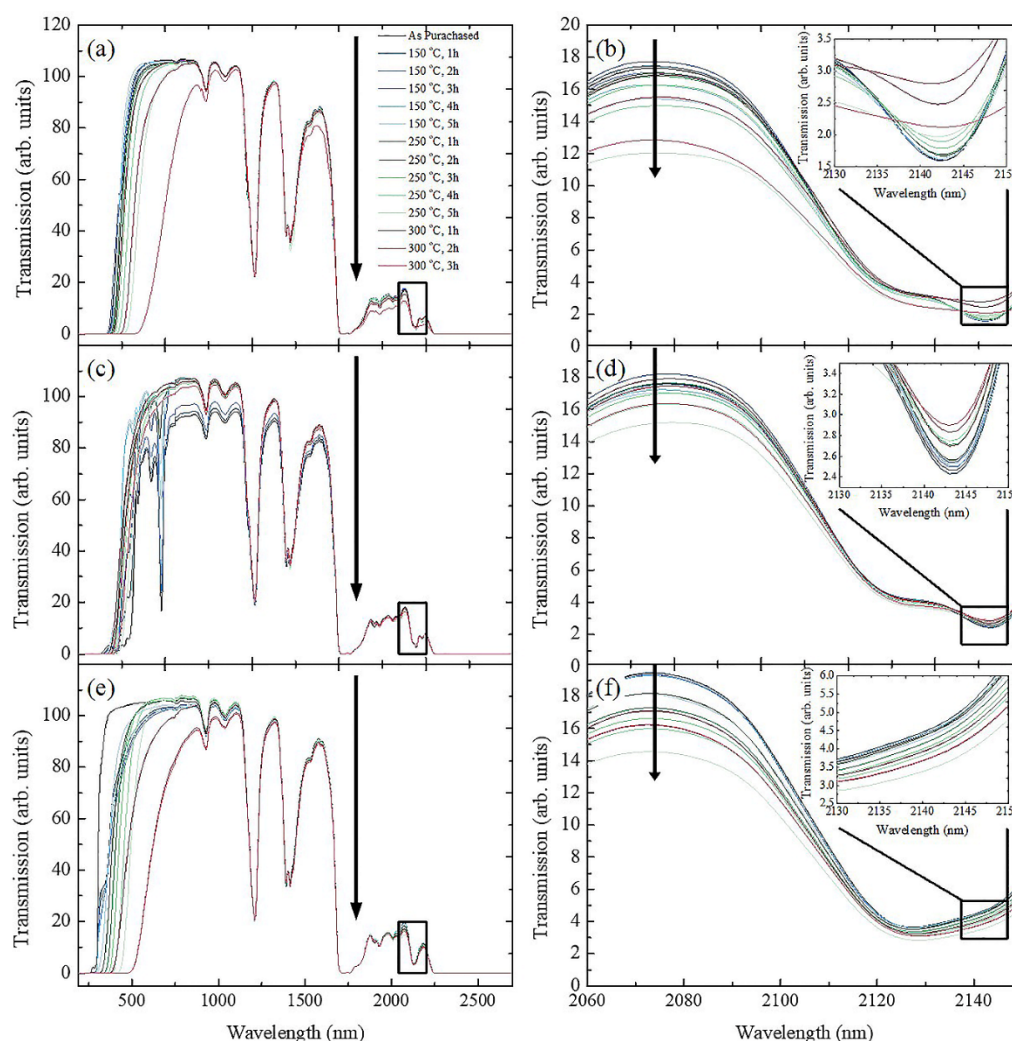


Figure 3. Wide (200–2700 nm) and selected region (2060–2150 nm) scans of UV–Vis spectra for (a, b) corn oil, (c, d) extra virgin olive oil, and (e, f) coconut oil. The selected boxes in (a, c, e) are enlarged and shown in (b, d, f), respectively. Insets in (b, d, e) are zoomed (2130–2150 nm) depictions of the boxed regions in them. The direction of the arrow indicates increased heating temperature and heating period.

Edible Oils Degradation Analysis

The Raman and optical transmission (2140 nm) data of the oils under thermal stress were analyzed. The C=C vibrations of the edible oils occurred at 970, 1265, 1650, and 3005 cm^{-1} , whereas the C–C bond-related peaks were located at 1300 and 1440 cm^{-1} (Supplemental Material Table S1).^{19,22} Theoretically, C–C single bonds are very stable during thermal stressing as marginal oxidation can occur below the smoke point^{19,22} Hence, we did not expect changes in the saturated fat (C–C) signal during the heating process. The C=C bonds are prone to dissociation resulting in harmful free radicals, ultimately degrading the edible oils.^{11,24} However, each individual oil has different contents of C–C, and C=C bonds. Hence, in our analysis, we would normalize the changes in the Raman peak intensities that change

with respect to the ones that are fairly stable, with thermal oxidation. In other words, we may use a ratio of any one of the four C=C peaks (at 970, 1265, 1650, and 3005 cm^{-1}) to that of the C–C peaks (at 1300 or 1440 cm^{-1}) as a marker to estimate the thermal degradation. We have used the C=C peak at 1265 cm^{-1} , and normalized with the C–C peak intensity at 1440 cm^{-1} , the I_{1265}/I_{1440} ratio, to study the thermal degradation. Although, all the other peaks also provided identical, and consistent information on their variation under thermal stressing.

Figure 4 shows the variation of the I_{1265}/I_{1440} ratio, and optical transmission at 2140 nm, as a function of different heating conditions for the PUFA-rich corn and sunflower oils. Interestingly, both the parameters showed a decrease at the initial stages of heating (below the smoke point), and then degraded (decreased) rapidly when heated above the smoke point. At 250 or 300 °C, both parameters showed sharp decreases, indicating that a significant number of C=C double bonds underwent accelerated thermal oxidation during heating. The decreasing transmission data matches with the visual observation that the oils turn darker at higher heating conditions or thermal oxidation. The trends are very similar for most of the oils studied, with differences only in the degree of degradation. However, the degree of decrease in the parameters studied is the highest in corn oil (19–50 % of oleic, and 34–62 % of linoleic acids) compared to sunflower oil (14–19.4 % of oleic, and 48.3–74 % of linoleic acids).^{11,33}

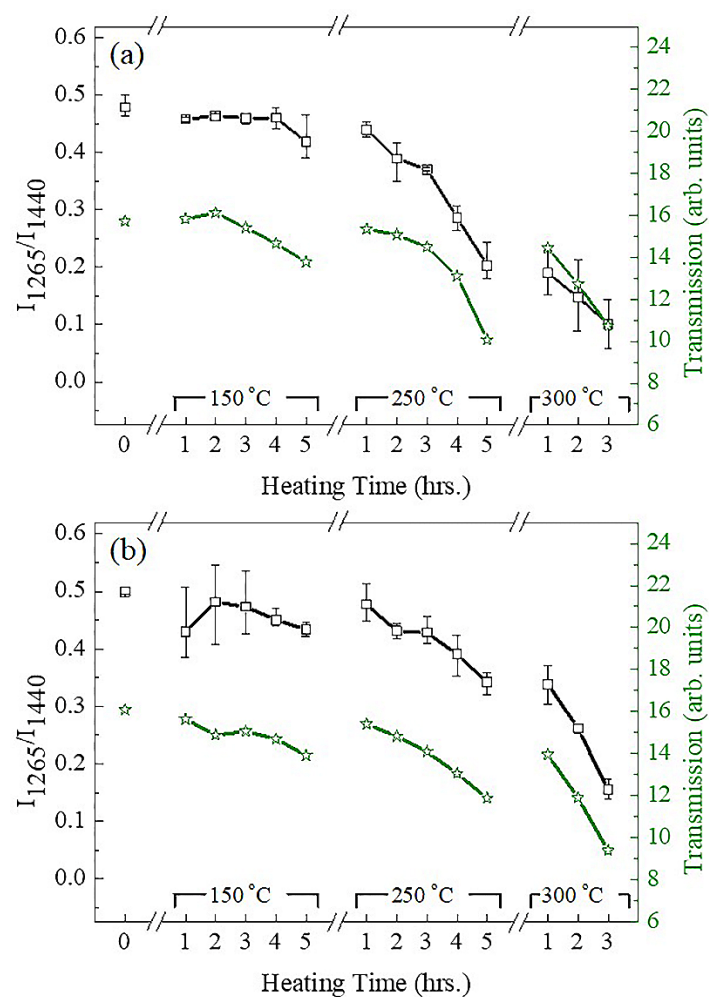


Figure 4. The variation of the (□) Raman I_{1265}/I_{1440} ratios, optical transmission at 2140 nm (☆) as a function of different heating conditions in (a) corn and (b) sunflower oil, which are the high in PUFA. The heating conditions incorporated heating temperatures (150, 250, and 300 °C) and time (1–5 hrs). For the heating condition of 300 °C, the duration was limited to 3 h, after which the samples solidified, making the studies erroneous. The as-purchased (heating time = 0) values of these parameters are also mentioned. The line joining the data points is only a guide.

Figure 5 shows the variation of the I_{1265}/I_{1440} ratios, and the optical transmission value at 2140 nm, for the MUFA-rich oils, (a) camellia, (b) canola, (c) peanut, and (d) extra virgin olive oil, demonstrating similar changes as discussed for the PUFA-rich group of oils.

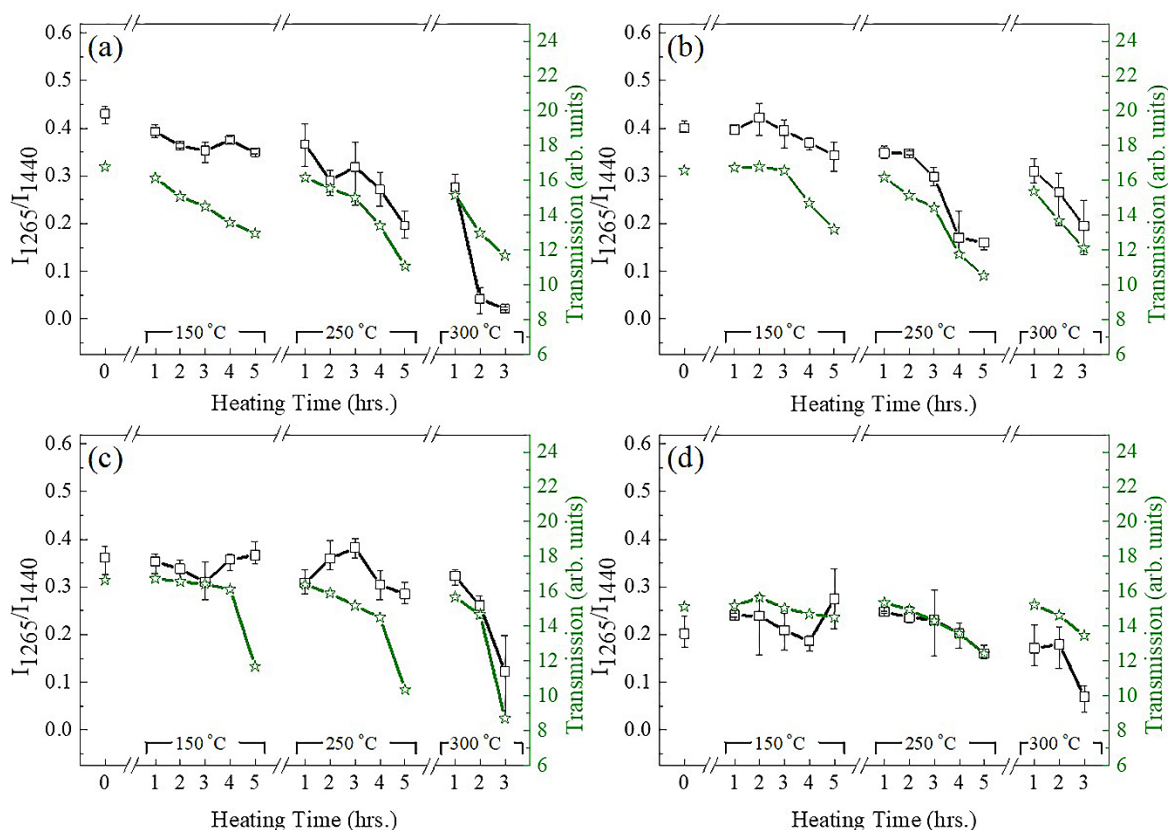


Figure 5. The variation of the ($\square$) Raman I_{1265}/I_{1440} ratio, optical transmission at 2140 nm ($\star$) as a function of different heating conditions in (a) camellia oil, (b) canola oil, (c) peanut oil, and (d) extra virgin olive oil, which is considered an MUFA. The heating conditions incorporate heating temperatures (150, 250, and 300 °C), and time (1–5 hrs). For the 300 °C heating conditions, the duration is limited to 3 h, after which the samples solidify, making the studies erroneous. The as-purchased (heating time = 0) values of these parameters are also mentioned. The line joining the data points is only a guide.

Figure 6 shows the variation of the I_{1265}/I_{1440} ratio, and the optical transmission at 2140 nm, as a function of different heating conditions of SFA-rich coconut oil. Compared to the PUFA, and MUFA-rich oils, both the measured parameters remain nearly stable under the applied thermal stress. This is expected as the activation energy for the degradation of the C–C is higher than C=C. Therefore, although this oil has higher saturated fat, its thermal degradation is the least compared to all the oils studied here.

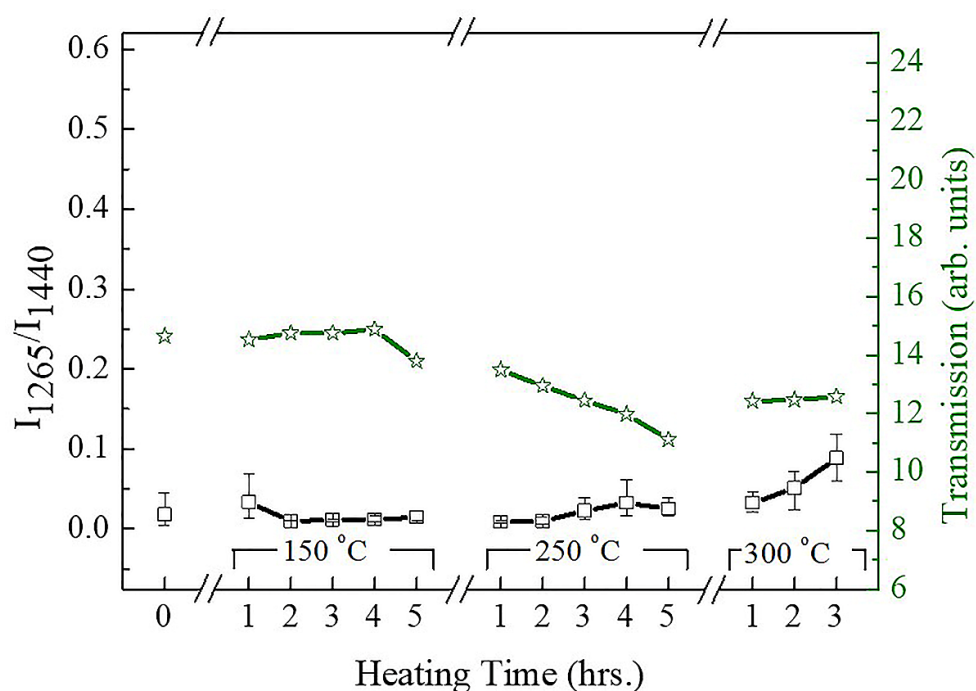


Figure 6. The variation of the (□) Raman I_{1265}/I_{1440} ratios, optical transmission at 2140 nm (☆) as a function of different heating conditions in coconut oil, which is considered an SFA. The heating conditions incorporate heating temperatures (150, 250, 300 °C), and time (1–5 hrs). For the heating condition of 300 °C the duration is limited to 3 h, after which the samples solidify, making the studies erroneous. The as-purchased (heating time = 0) values of these parameters are also mentioned. The line joining the data points is only a guide.

Iodine Values of Edible Oils

The degree of unsaturation of edible oils can be obtained by measuring the I_v which has been adopted by the oil industry. Figure S5 shows the I_v (averaging three measurements) of different as-purchased edible oils, and the values after they were heated to 150, 250, and 300 °C for 3 h. The as-purchased PUFA-rich corn, and sunflower oils (Figure S5a), shows higher I_v between 111–120. The I_v of MUFA-rich camellia, canola, peanut, and extra virgin olive oil (Figure S5b), ranged from 77–95. SFA-rich coconut oil (Figure S5c), shows I_v of 13, which is the lowest. From the I_v vs. thermal stress plot (Figure S5), a sharp decreasing trend is observed in corn, and a gradual decrease for extra virgin olive oil. However, the coconut oil demonstrate only a marginal decrease in the I_v .

If a decreasing I_v is a measure of the thermal degradation, then calibrating the I_{1265}/I_{1440} ratio, and the optical transmission at 2140 nm could give us a measure of degradation from the optical studies. This is shown for MUFA-rich (Figure S6), PUFA-rich (Figure S7), and SFA-rich oil (Figure S8). Through this correlation we hope to see the response of the oils in their initial stage (as purchased), and when heated below, and above

their smoke points. From Figure S6a, b (corn oil, and sunflower oil), it can be observed that the ratio I_{1265}/I_{1440} , and the optical transmission at 2140 cm^{-1} , decreases sharply above the smoke point denoted by the scale break in the I_v axis. The variation of the parameters with I_v is similar for the MUFA oils, i.e., camellia (Figure S7a), canola (Figure S7b), peanut oils (Figure S7c), and extra virgin olive oil (Figure S7d), albeit with a smaller degree in the variation. Interestingly, for coconut oil (Figure S8), the variation or degradation is minimal. Somewhat random data points were obtained which indicates that the variation of the parameters with I_v is rather insignificant for coconut oil.

To establish an all-optical methodology to study thermal degradation in edible oils, it becomes imperative to graphically correlate the optically derived signatures with the industrially approved parameter I_v . Similar correlation studies between I_v and Raman spectral intensities in edible oils has been done before.^{34,35} However, those studies did not involve thermal stressing as an experimental variable.^{34,35} Here, we correlated the changes in Raman signals and I_v of the oils under thermal stress (Figure 7). The oils were classified according to their I_v and the corresponding I_{1265}/I_{1440} ratio is plotted for all the oils under as purchased (Figure 7a), and heated conditions (Figure 7 b–d). The data could be linearly fitted whose slope decreased consistently with increasing heating temperatures. The decrease in the slope is marked at $300\text{ }^{\circ}\text{C}$ which is above the smoke point for all of these oils studied. This indicates, that the Raman signal ratio, presented here, could be a verifiable, and quantifiable signature to study thermal degradation in edible oils.

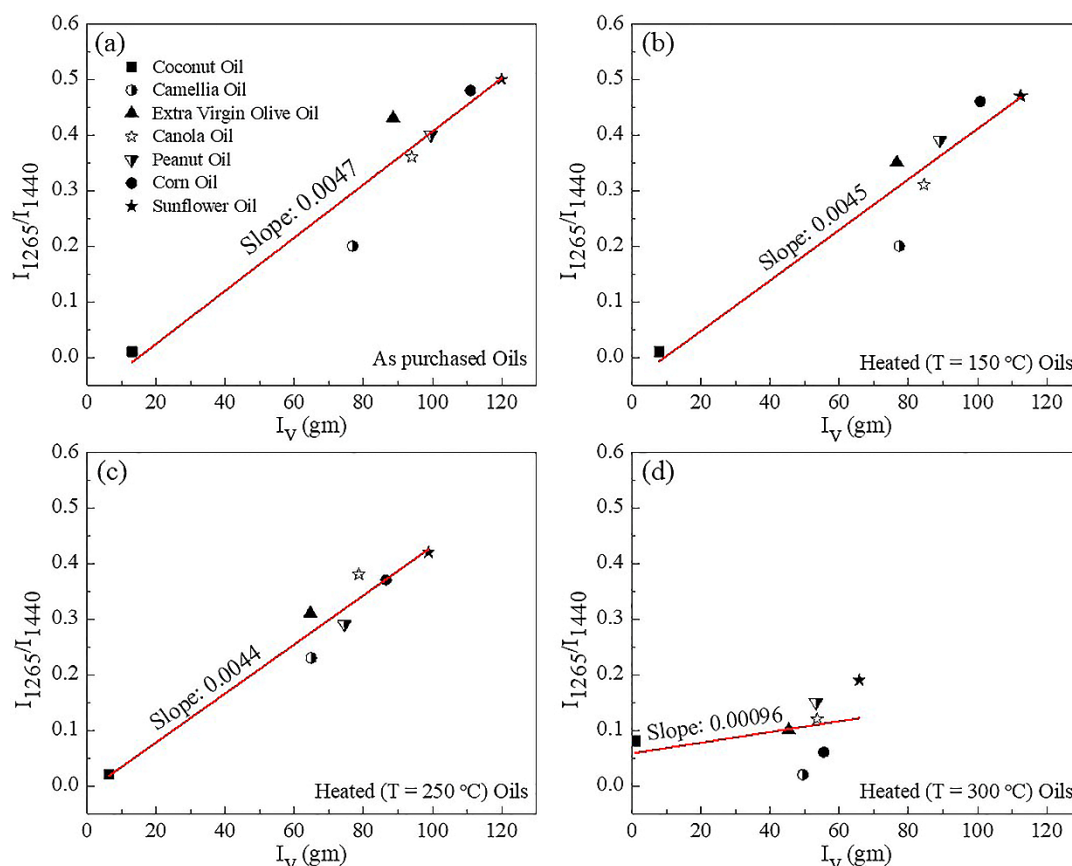


Figure 7. The variation of the Raman spectroscopy derived I_{1250}/I_{1440} ratios as a function of Iodine values for edible oils under different heating conditions: (a) as purchased and heated at (b) 150, (c) 250, and (d) 300 °C for 3 h. The line joining the data points is a linear fit with slopes mentioned alongside each line.

Conclusion

In summary, this research presents the use of Raman, and UV–Vis spectroscopy for the study of the thermal degradation of edible oils. The ratio of vibrational signal intensities of C=C (at 1265 cm^{-1}) to C–C (at 1440 cm^{-1}) is identified to be a thermal degradation marker in edible oils via Raman spectroscopy. From optical transmission, the band at 2140 nm is identified for the purpose. The decrease of these two parameters or markers with thermal stress was significant above the smoke point ($\sim 230^\circ\text{C}$), and was repeatable and consistent. The degradation was the most in PUFA, and MUFA rich oils, barring olive which showed a mild degradation. The degradation of the parameters was the least for the SFA rich coconut oil. These parameters, individually, follow the degradation of Iodine values, which is an accepted industrial benchmark for the degree of unsaturation in edible oils, and their decrease with thermal stressing. A fully optical technique has been adopted for measuring oil degradation, that has the potential to replace commonly performed viscosity based Rheological tests to study thermal degradation.

Conflict of Interest

The authors declare no conflict of interest.

Acknowledgment

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Supplemental Material

All Supplemental Material mentioned in the text is available in the online version of the journal.

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Supplemental Material

Calibrated Optical Markers to Study Thermal Degradation in Edible Oils Using Raman and Optical Transmission Spectroscopy

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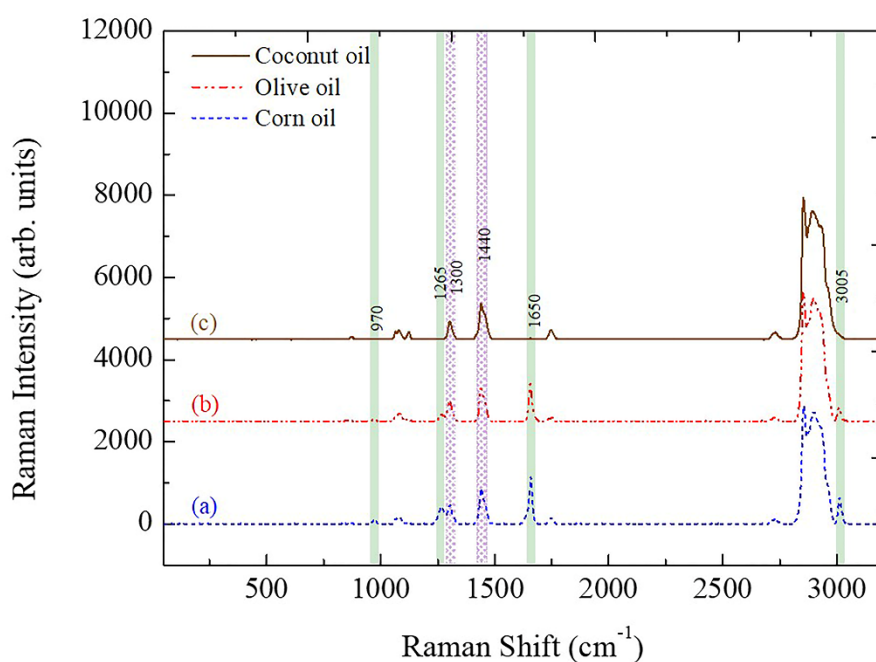


Figure S1. Representative Raman spectra of (a) corn, (b) extra virgin olive, and (c) coconut oil. The transparent coloured bars indicate the saturated (purple), and unsaturated (green) bonds in the oil.

Figure S1 shows the (a) Raman, spectra of the as-purchased coconut oil, extra virgin olive oil, and corn oil. There are 12 peaks in the spectra, related to different molecular vibrations in the

oil, that can be observed in the Raman spectrum (Table S1).^{1,2} Among them, the peaks at 1300 and 1440 cm^{-1} are related to the C–C (saturated) vibrations (marked with purple bars), and the peaks at 970, 1265, 1650, and 3005 cm^{-1} are related to the C=C (unsaturated) vibrations (marked with green bars). Among these four C=C vibration peaks, the one at 970 cm^{-1} related to the trans C=C groups is relatively weak in intensity, and the other three are related to the cis C=C groups, are relatively stronger in intensities. This can be explained by the low content of trans unsaturated fatty acids, and high content of cis unsaturated fatty acids in the natural edible oils.^{3,4} The peaks located at 868, 1078, 1750, 2850, 2897, and 2924 cm^{-1} do not have any significant, or consistent variation in different oils, so they will not be used in this oil degradation analysis.

The marked (transparent coloured bars) peaks noted in the Raman spectra can be assigned to different molecular vibration mode presents in oils and shown in Table S1 and Table S2.

Table S1. Assignment of major Raman peaks in edible oils.¹

Wavenumber (cm^{-1})	Molecule/group	Vibrational mode
3005	cis RHC=CHR	=C–H Symmetric stretching
2924	–CH ₂	C–H Asymmetric stretching
2897	–CH ₃	C–H Symmetric stretching
2850	–CH ₂	C–H Symmetric stretching
1750	RC=OOR	C=O stretching
1650	cis RHC=CHR	C=C stretching
1440	–CH ₂	C–H bending (scissoring)
1300	–CH ₂	C–H bending (twisting)
1265	cis RHC=CHR	=C–H bending (scissoring)
1078	–(CH ₂) _n –	C–C stretching
968	trans RHC=CHR	C=C bending
868	–(CH ₂) _n –	C–C stretching

Table S2. Assignment of major optical transmission dips in edible oils.⁵

Wavenumber (nm)	Molecule	Group	Vibrational mode
850–950	–CH ₂ –CH ₃	C–H	3rd overtone
1090–1180	–CH ₂	C–H	2nd overtone
1100–1200	–CH ₃	C–H	2nd overtone
1150–1260	–CH=HC–	C–H	2nd overtone
1350–1430	–CH ₂	C–H	Combination
1360–1420	–CH ₃	C–H	Combination
1390–1450	H ₂ O	O–H	1st overtone
1650–1780	–CH ₂ –CH ₃ –CH=HC–	C–H	1st overtone
1880–1930	H ₂ O	O–H	Combination
2100–2200	–CH=HC–	C–H	Combination
2240–2360	–CH ₃	C–H	Combination

2290–2470

–CH₂

C–H

Combination

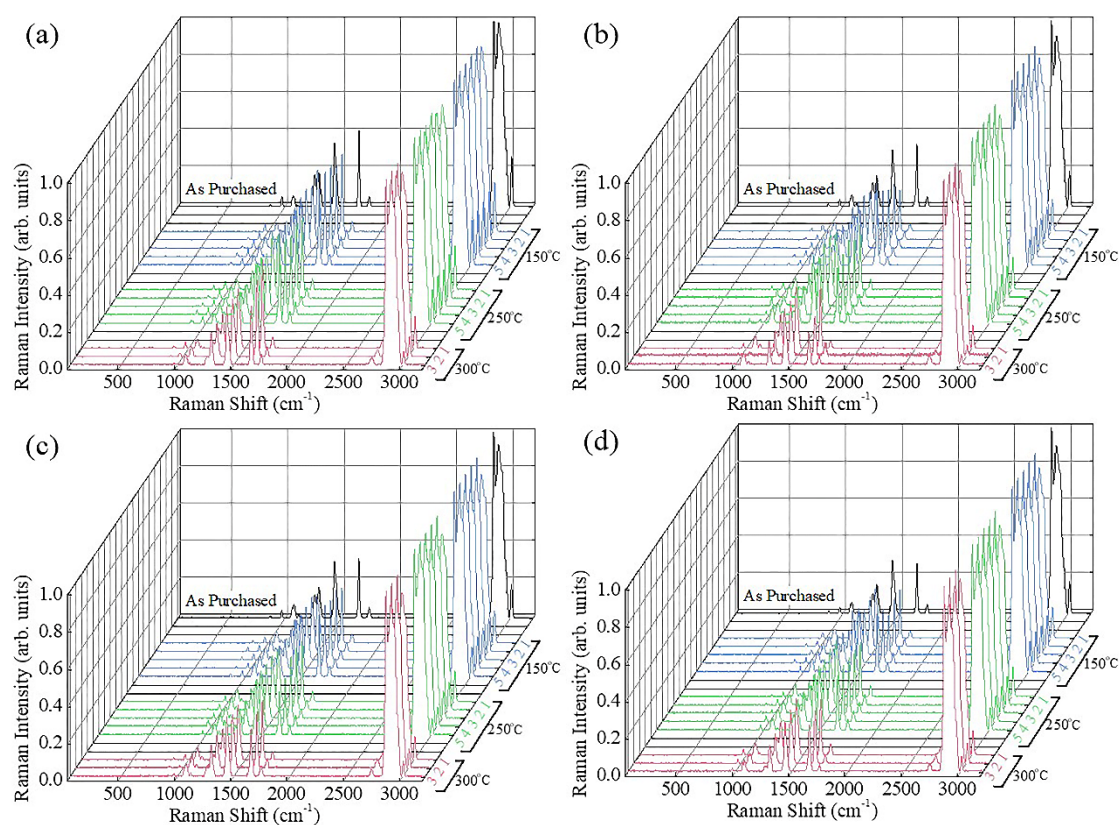


Figure S2. Normalized Raman spectra of (a) sunflower, (b) camellia, (c) canola, and (d) peanut oil under thermal oxidation at different temperature and time. The numbers 1–5 stand for the heating time from 1–5 h under each temperature of heating, namely 150 (blue set), 250 (green set), and 300 °C (red set). The data for as-purchased oil (black) is also shown. The normalization is done with respect to the 2852 cm⁻¹ band for each spectrum.

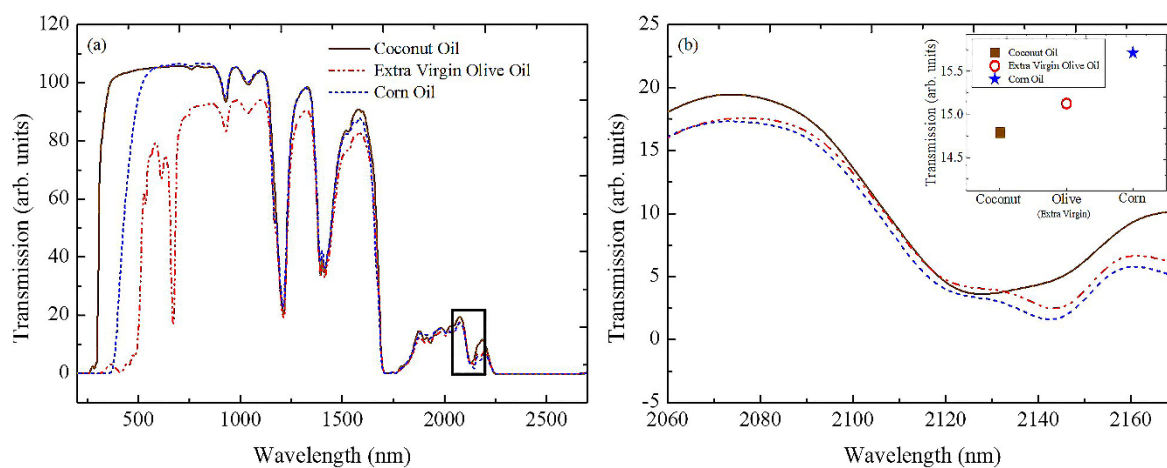


Figure S3. The UV–Vis transmission spectrum in the (a) 190–2700 nm and (b) 2060–2170 nm spectral range of the as-purchased corn, extra virgin olive, and coconut oils. Inset in (b) shows the transmission intensities of the dip near 2140–2150 nm, calculated from the transmission saturation near 2070 nm for the three oils, corn, extra virgin olive, and coconut.

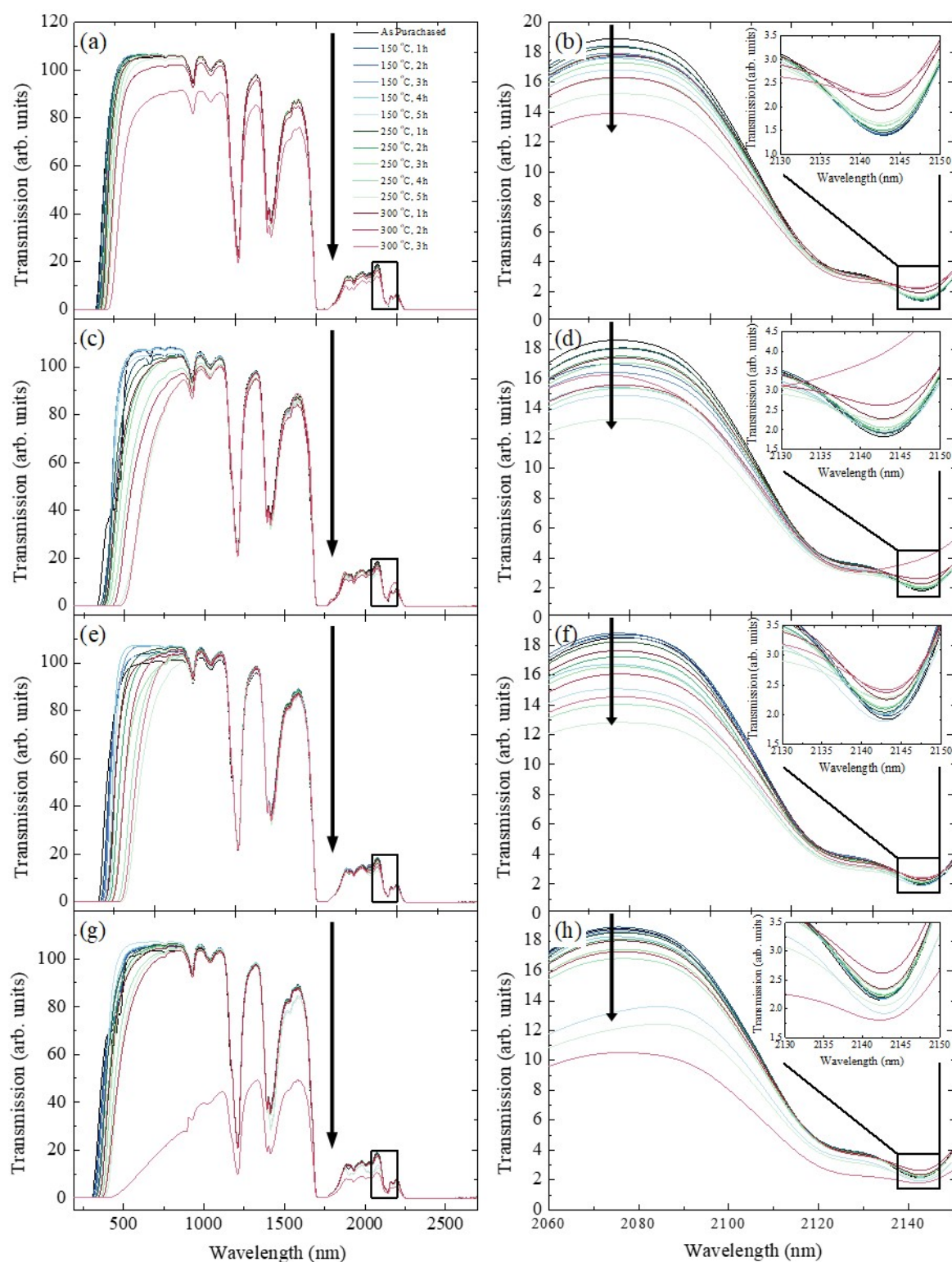


Figure S4. (a, c, e, g) The UV–Vis spectra for sunflower oil, camellia oil, canola oil, peanut oil in the 200–2700 nm range, and (b, d, e, h) in the 2060–2150 nm range. Inset in the 2060–2150 nm region shows an enlarged view of the 2130–2150 nm region for each oil.

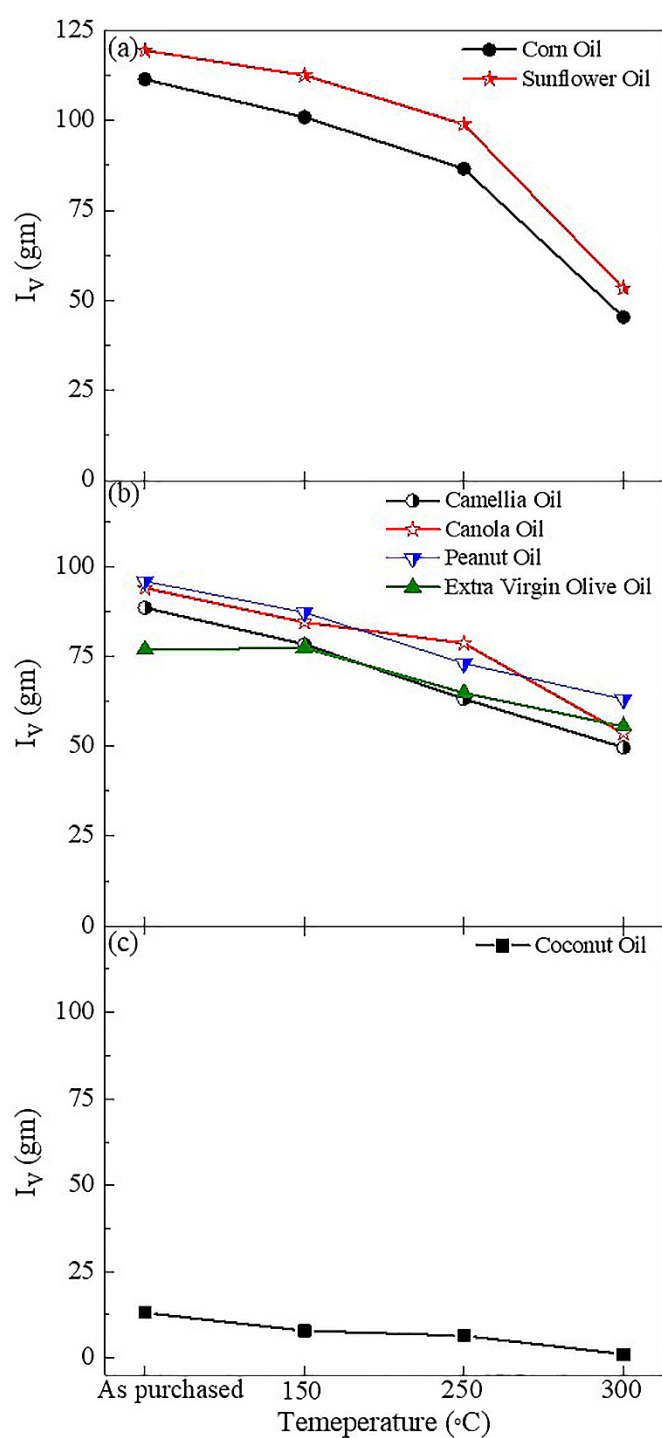


Figure S5. The variation of the iodine value as a function of different heating conditions in (a) PUFA, (b) MUFA, and (c) SFA. The heating conditions incorporate heating temperatures (150, 250, 300 °C). The as-purchased values of these parameters are also mentioned. The line joining the data points is a guide to the eye only.

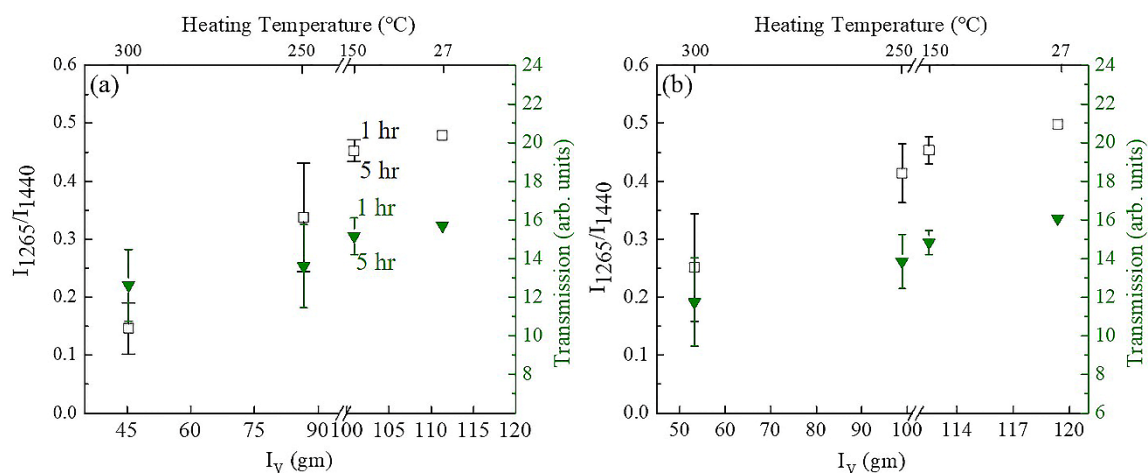


Figure S6. The correlation of the ($\square$) Raman, and ($\blacktriangledown$) optical transmission at 2140 nm, with Iodine value and different heating conditions in (a) corn oil and (b) sunflower oil. The heating conditions incorporate heating temperatures 150, 250, and 300 °C. The room temperature values of these parameters are also mentioned. The error bars indicate the heating time. The top, and the bottom of the error bars indicates the 1 h and 5 h of heating, respectively. The scale breaks are to show the smoke point for each oil.

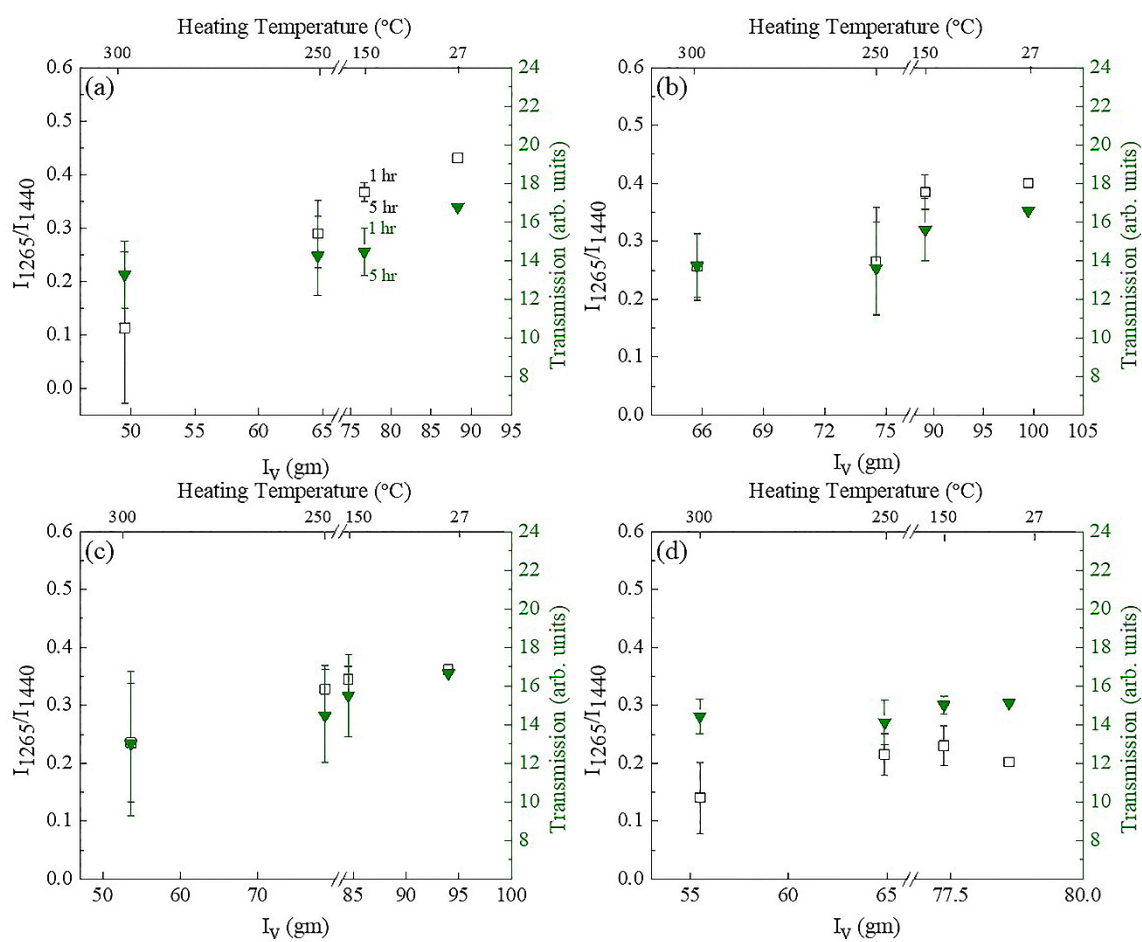


Figure S7. The correlation of the (□) Raman, (▼) optical transmission at 2140 nm, with Iodine value and different heating conditions in (a) camellia, (b) canola, (c) peanut, and (d) extra virgin olive oil. the heating conditions incorporate heating temperatures of 150, 250, 300 °C. The room temperature values of these parameters are also mentioned. The error bars indicate the heating time. The top, and the bottom of the error bars indicates the 1 h and 5 hours of heating, respectively. The scale breaks are to show the smoke point for each oil.

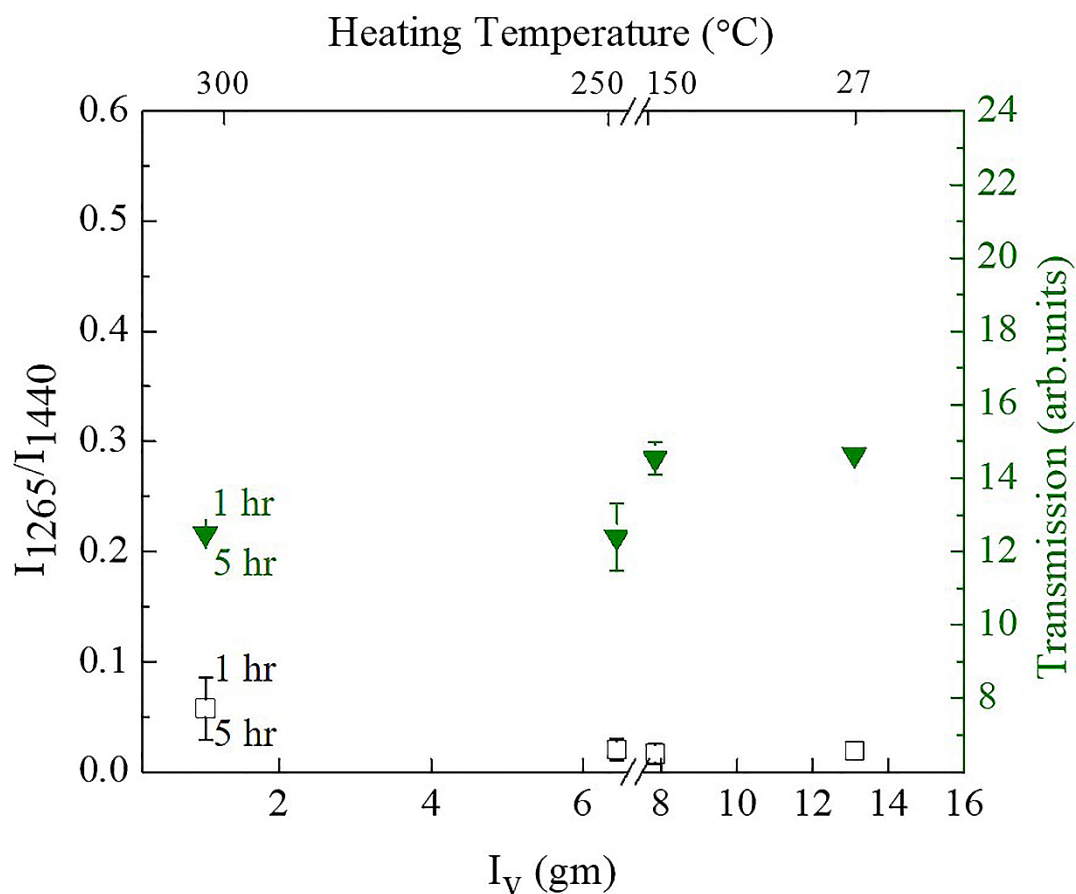


Figure S8. The correlation of the ($\square$) Raman, ($\blacktriangledown$) optical transmission at 2140 nm with the iodine value and different heating conditions of coconut oil. The heating conditions incorporate heating temperatures at 150, 250, and 300 °C. The room temperature values of these parameters are also mentioned. The error bars indicates the heating time. The top, and the bottom of the error bars indicates the 1 h and 5 h of heating, respectively. The scale breaks are to show the smoke point for each oil.

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