

Supplemental Material

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

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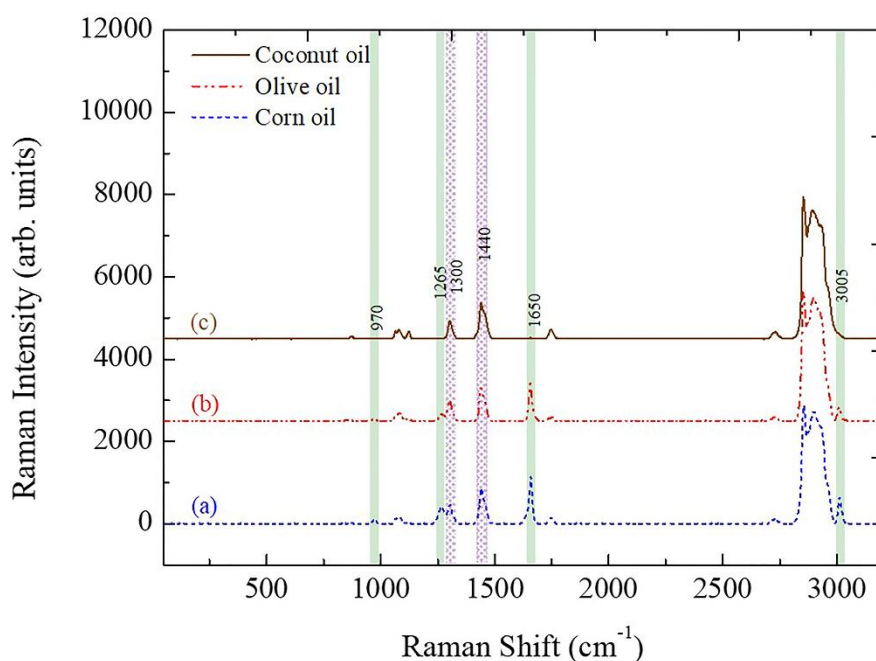


Figure S1. Representative Raman spectra of (a) corn, (b) extra virgin olive, and (c) coconut oil. The transparent coloured bars indicate the saturated (purple), and unsaturated (green) bonds in the oil.

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	–CH ₂	C–H	Combination

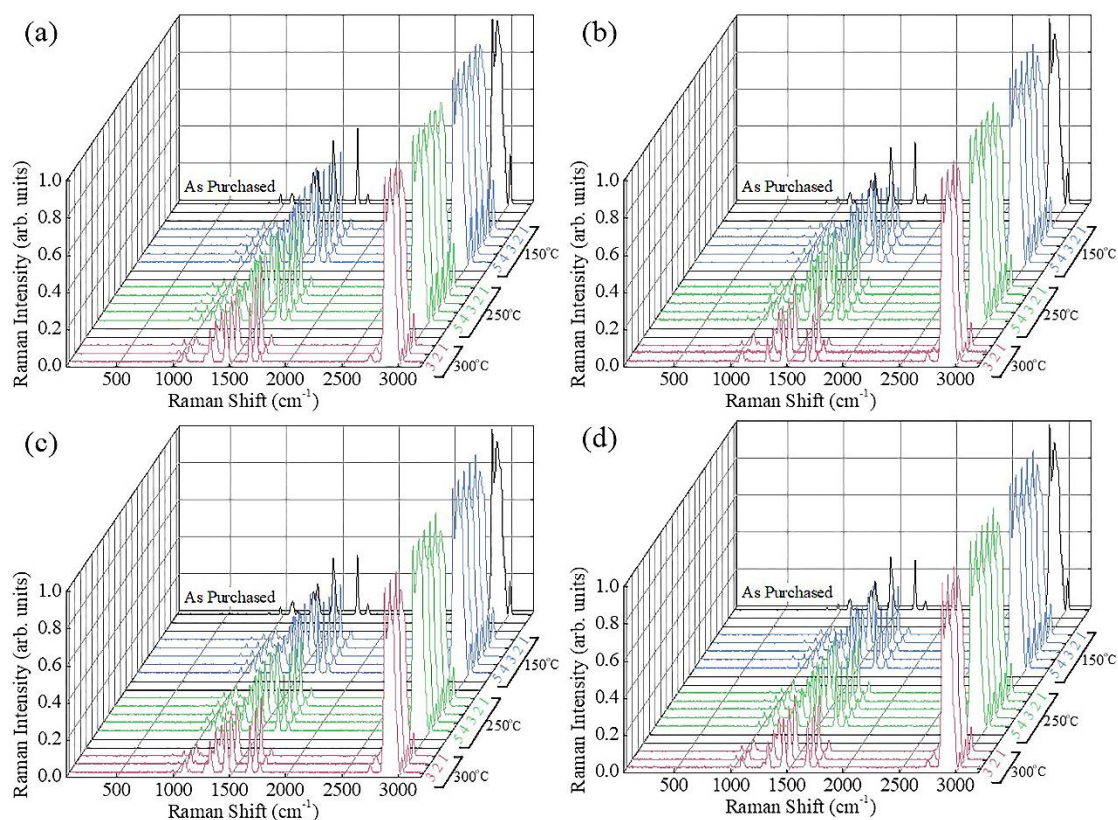


Figure S2. Normalized Raman spectra of (a) sunflower, (b) camellia, (c) canola, and (d) peanut oil under thermal oxidation at different temperature and time. The numbers 1–5 stand for the heating time from 1–5 h under each temperature of heating, namely 150 (blue set), 250 (green set), and 300 °C (red 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.

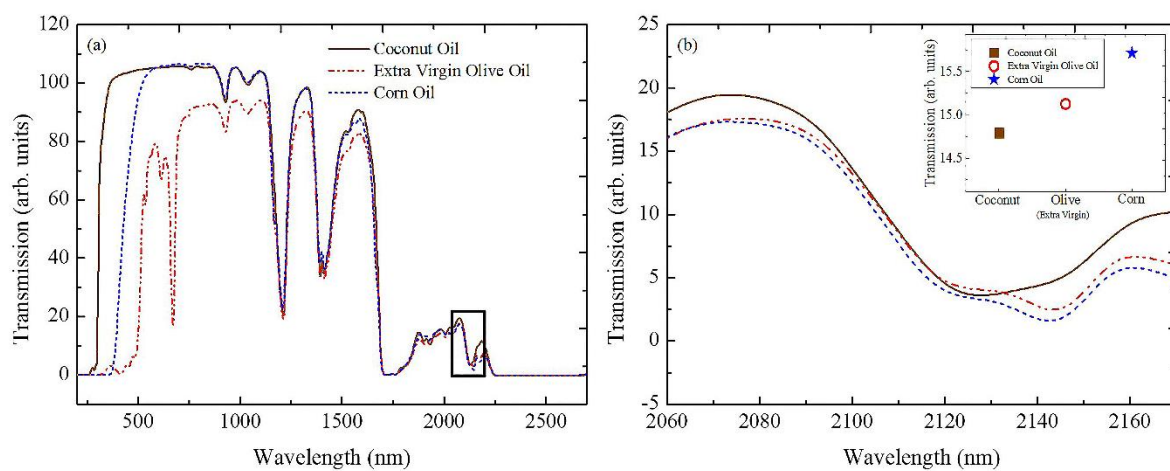


Figure S3. The UV–Vis transmission spectrum in the (a) 190–2700 nm and (b) 2060–2170 nm spectral range of the as-purchased corn, extra virgin olive, and coconut oils. Inset in (b) shows the transmission intensities of the dip near 2140–2150 nm, calculated from the transmission saturation near 2070 nm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

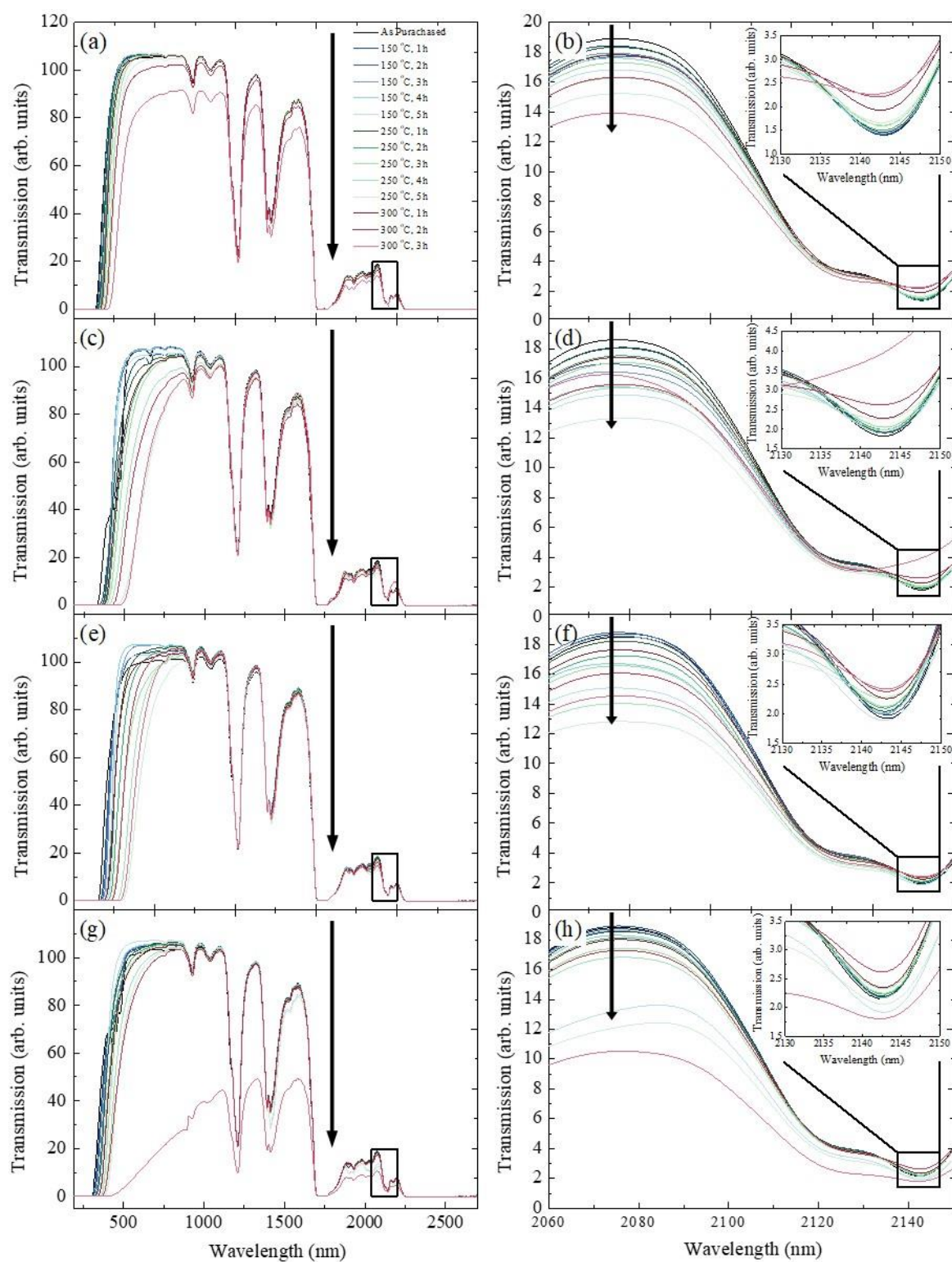


Figure S4. (a, c, e, g) The UV–Vis spectra for sunflower oil, camellia oil, canola oil, peanut oil in the 200–2700 nm range, and (b, d, e, h) in the 2060–2150 nm range. Inset in the 2060–2150 nm region shows an enlarged view of the 2130–2150 nm region for each oil.

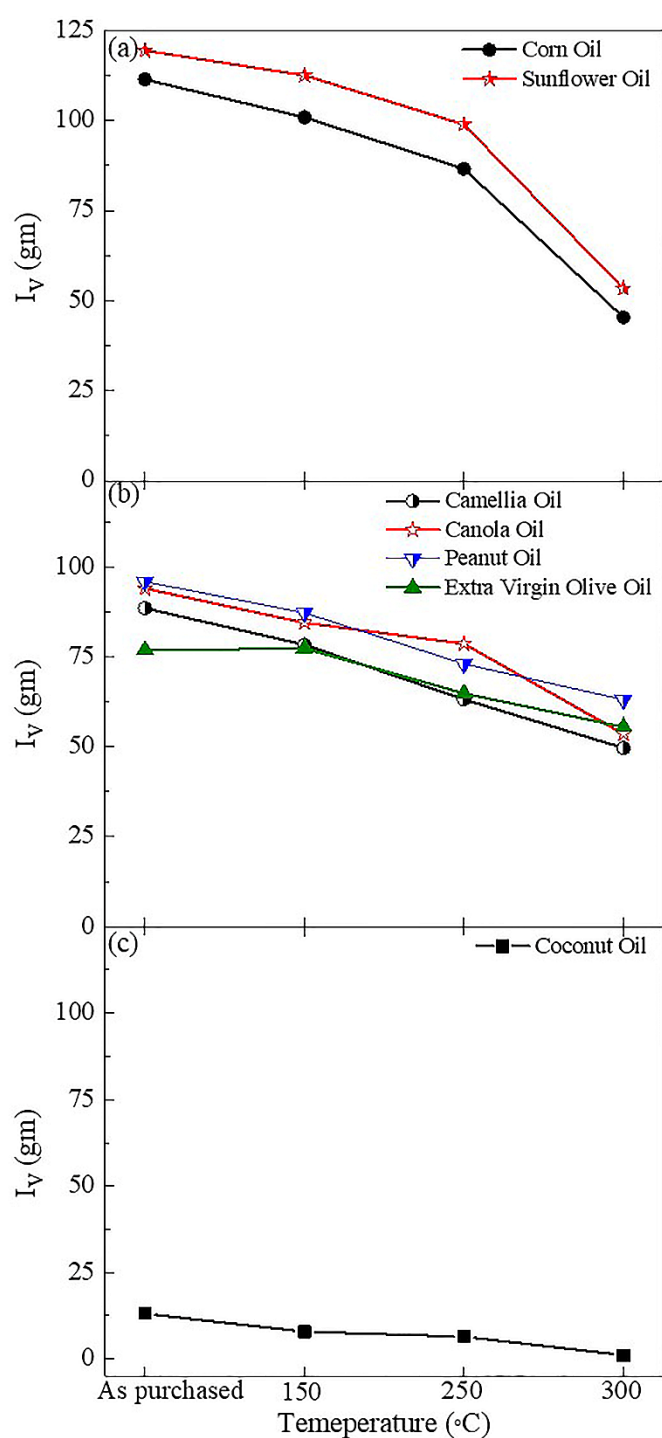


Figure S5. The variation of the iodine value as a function of different heating conditions in (a) PUFA, (b) MUFA, and (c) SFA. The heating conditions incorporate heating temperatures (150, 250, 300 °C). The as-purchased values of these parameters are also mentioned. The line joining the data points is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

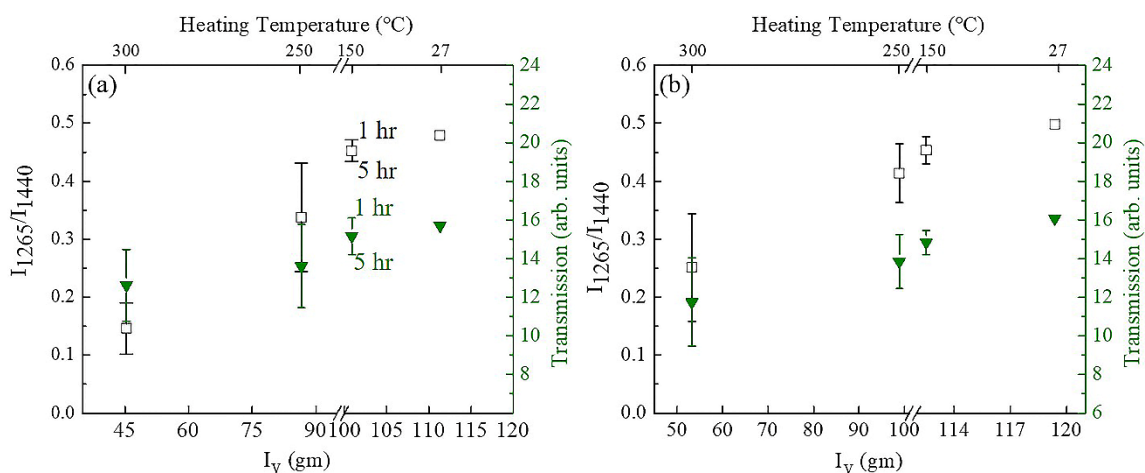


Figure S6. The correlation of the (□) Raman, and (▼) optical transmission at 2140 nm, with Iodine value and different heating conditions in (a) corn oil and (b) sunflower oil. The heating conditions incorporate heating temperatures 150, 250, and 300 °C. The room temperature values of these parameters 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.

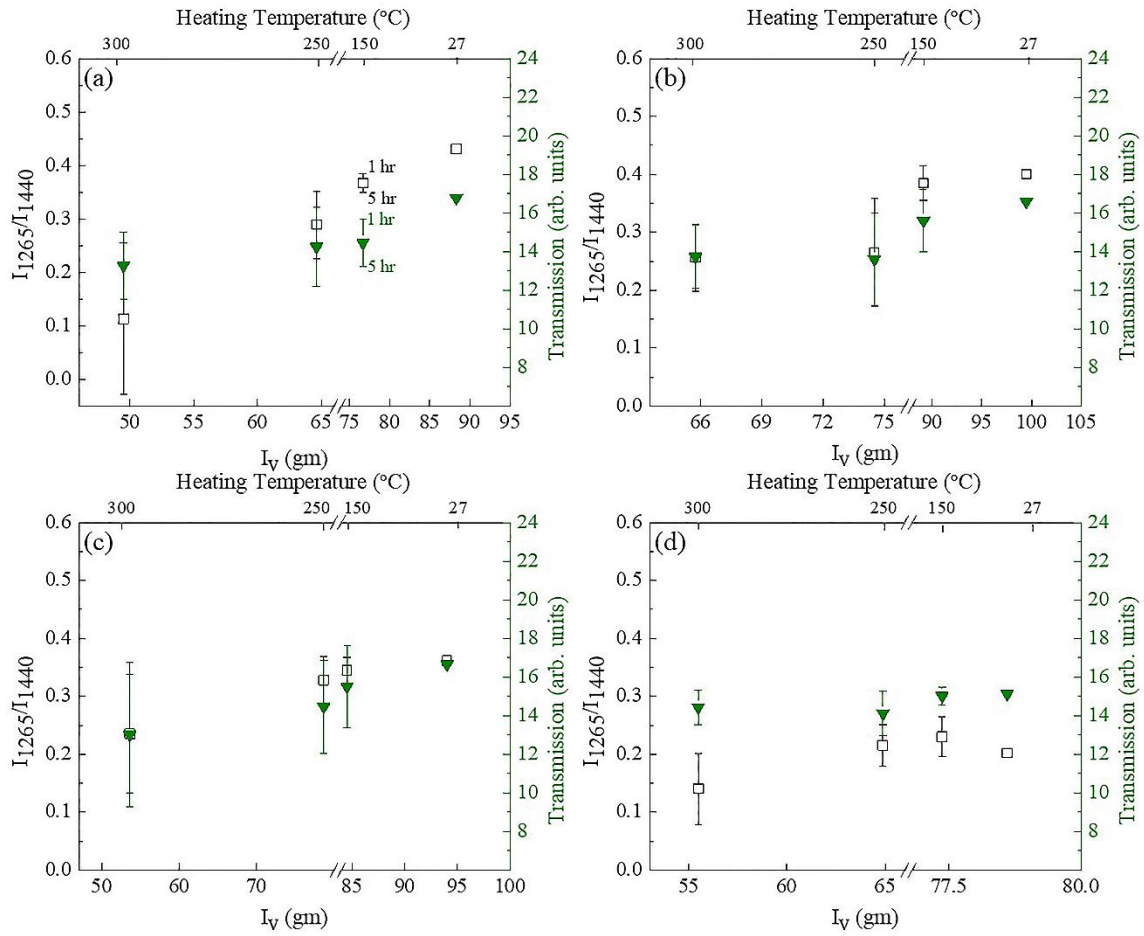


Figure S7. The correlation of the (\square) Raman, (\blacktriangledown) optical transmission at 2140 nm, with Iodine value and different heating conditions in (a) camellia, (b) canola, (c) peanut, and (d) extra virgin olive oil. the heating conditions incorporate heating temperatures of 150, 250, 300 °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.

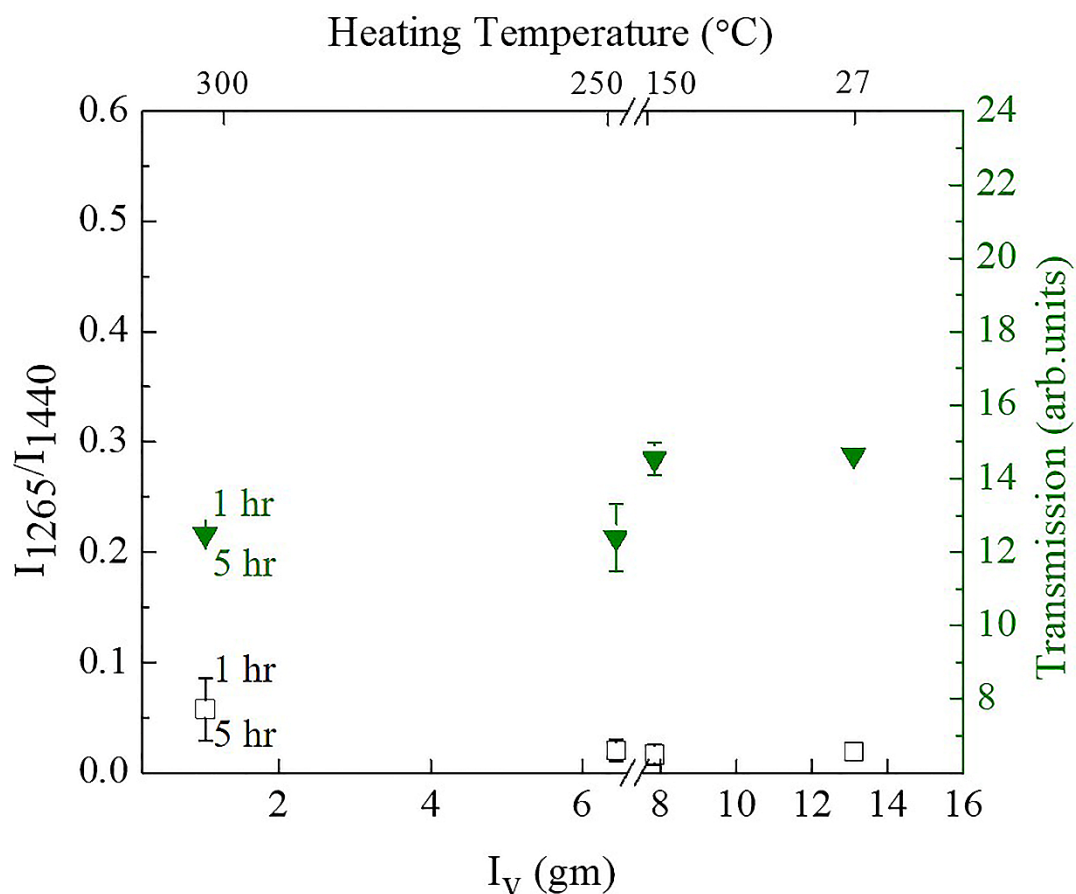


Figure S8. The correlation of the (□) Raman, (▼) optical transmission at 2140 nm with the iodine value and different heating conditions of coconut oil. The heating conditions incorporate heating temperatures at 150, 250, and 300 °C. The room temperature values of these parameters are also mentioned. 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.

References

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