Application of vibrational spectroscopic techniques for determination of thermal degradation of frying oils and fats: a review

Maninder Meenu, Eric A. Decker & Baojun Xu

Published online: 28 Feb 2021.

Submit your article to this journal

View related articles

View Crossmark data

Taylor & Francis
Taylor & Francis Group

REVIEW

Check for updates

Application of vibrational spectroscopic techniques for determination of thermal degradation of frying oils and fats: a review

Maninder Meenu[a], Eric A. Decker[b], and Baojun Xu[a]

[a]Food Science and Technology Program, BNU-HKBU United International College, Zhuhai, China; [b]Department of Food Science, University of Massachusetts Amherst, Amherst, MA, USA

ABSTRACT

Deep fried foods are popular among consumers due to their unique taste and texture. During the process of deep-frying, oil is subjected to a high temperature that results into the generation of harmful compounds. The repeated usage of frying oil is a common exercise and associated with various health hazards. Thus, determination of frying oil quality is a critical practice to follow. The chemical methods employed to determine the quality of frying oil are destructive and require large amount of harmful chemical, thus researchers are exploring the application of various vibrational spectroscopic techniques for this purpose. The first part of this review provides a detailed insight into fundamental theoretical aspects of two main vibrational spectroscopic techniques (infrared and Raman spectroscopy) and chemical alteration in frying oils under thermal stress. While in the following parts, the application of near-infrared (NIR) and Fourier transform infrared (FTIR) and Raman spectroscopy for evaluating the quality of various frying oils and fats under thermal stress has been discussed. It is anticipated that this review paper can serve as a reference source for impending research in this field.

KEYWORDS

FTIR spectroscopy; NIR spectroscopy; Raman spectroscopy; oil degradation; deep frying; PLS

Introduction

Deep frying is one of the oldest and prevalent food preparation methods globally (Pedreschi et al. 2005). The consumption of fried food is increasing gradually due to its pleasing and distinctive flavor, color, texture and appearance (Saguy and Dana 2003). During deep frying, food is submerged in hot oil at high temperatures (150–190 °C) and the simultaneous heat and mass transfer between food, oil and air result in the distinctive and desired quality of fried foods (Choe and Min 2007). The reuse of frying oils for repeated frying of various food products is a common practice in domestic and industrial cooking. This repetitive use of oil at high temperature possesses high impact on the shelf life and quality of frying oil as well as fried foods (Man and Jaswir 2000). The frying results in various chemical reactions e.g. hydrolysis, thermal reaction and oxidation that lead to the generation of various volatile and nonvolatile compounds (Ku et al. 2014). These three reactions are reported as superimposed and interrelated. The moisture content present in the food material leads to hydrolytic alterations in the frying oil and fat structure. Hydrolysis is a well-known reaction that involves the breakage of ester bond and results in the formation of free fatty acids (FFAs), monoacylglycerols, diacylglycerols and glycerol (Lalas 2009; Choe and Min 2007). Thermal reactions in frying oil occur at high temperature without the involvement of oxygen (Velasco, Marmesat, and Dobarganes 2009). These reactions result in

the formation of cyclic monomeric triglycerides, nonpolar dimeric and oligomeric triglycerides. The cyclic monomeric triglycerides are the cyclization product formed by intramolecular rearrangement catalyzed by free radical intermediate due to the alterations at $C=C$ present in the aliphatic chains. The stereomutation of $C=C$ results in the basic structure of these compounds and also lead to *cis* and *trans* configuration during deep frying. The unsaturation degree, configuration, and position of $C=C$ in the aliphatic chains has a great influence on composition, content, and degree of cyclization of cyclic monomeric triglycerides (Zhang et al. 2012). The dimer and polymers are formed by "Diels-Alder" reaction. This reaction involves a *trans-trans*-conjugated diene fatty acid, produced because of thermal or oxidation reaction, and olefin group of a fatty acid. The free radical reactions are also reported to be responsible for the polymer formation (deMan 1999). Dimers and polymers have –C-O-O-C- and –C-O-C- linkages, and epoxy, hydroxyl, hydroperoxyl, and carbonyl group (Choe and Min 2007).

Deep-frying of carbohydrate-rich food leads to the formation of 5-hydroxymethyl-2-furfural (HMF). The formation of HMF initiates with the hexoses or their sources such as cellulose, starch, oligosaccharides, and polysaccharides. The reaction starts with an important intermediate of glucose and fructose called as enediol followed by its dehydration to tetrahydroxy hex-2-enal. This compound is then isomerized to trihydroxy-2-oxohexanal and dehydration of this
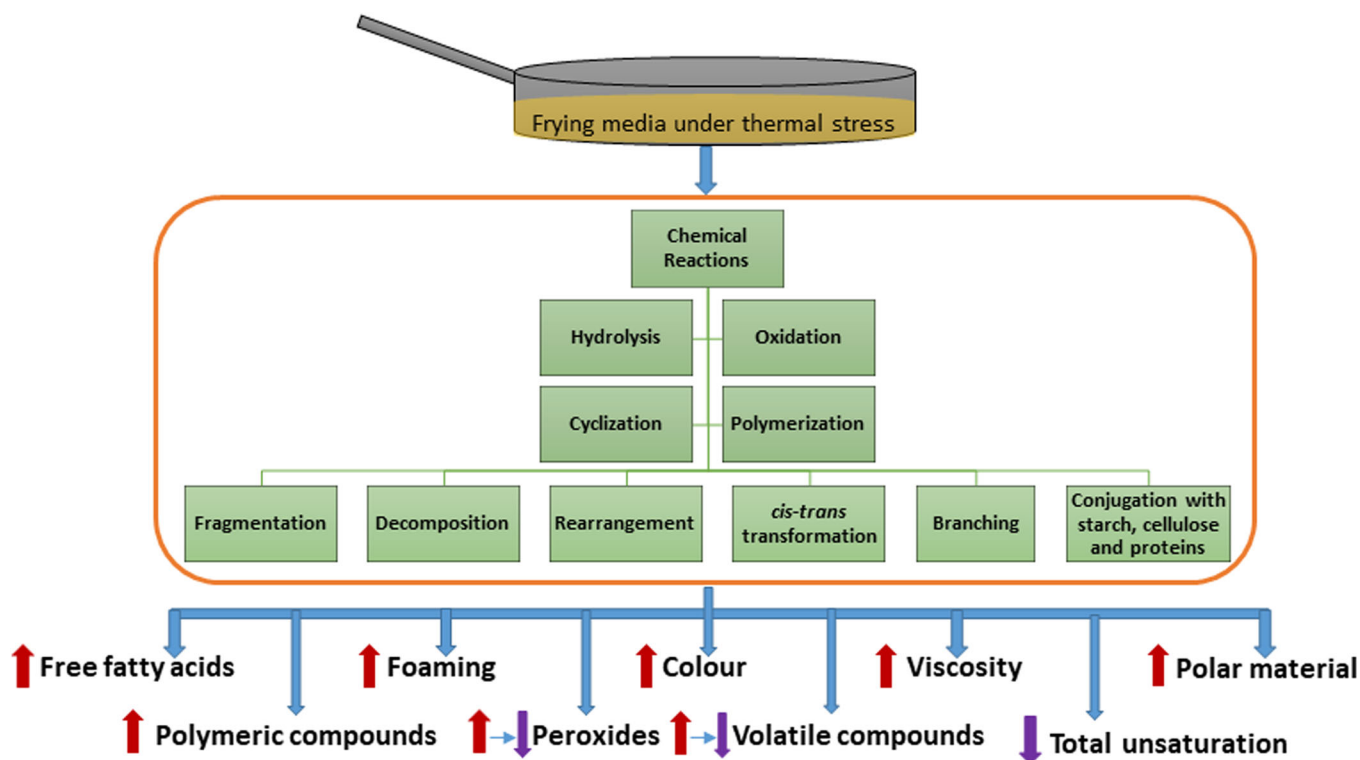
CONTACT Baojun Xu ✉ baojunxu@uic.edu.hk 📧 Food Science and Technology Program, BNU-HKBU United International College, 2000, Jintong Road, Tangjiawan, Zhuhai, Guangdong Province 519087, China

Figure 1. Influence of thermal stress on physical and chemical properties of frying media.

compound produces an unstable compound dihydroxy-2-oxohex-3-enal. The cyclization of this compound leads to the formation of 2-hydroxy HMF and the last dehydration results in the formation of HMF (Zeb 2019). Acrylamide is another harmful compound formed during the deep-frying of carbohydrates through Millard reaction. Asparagine and reducing sugar with a free aldehyde group lead to the formation of N-glycoside. The cleavage at C-N bond of the later compound result into an intermediate that further produces acrylamide (Meulenaer, Medeiros, and Mestdagh 2016). Acrolein is also reported as a toxic compound produced during frying of protein-rich food. Acrolein is formed from threonine and methionine during frying via Strecker degradation. Methional and 2-hydroxypropanal are the Strecker aldehyde in case of methionine and threonine, respectively. Strecker aldehyde results in the formation of acrolein by the loss of a water molecule (Stevens and Maier 2008).

Most of the volatile compounds evaporate into the environment or can also be absorbed by the food undergoing the frying process. The nonvolatile compounds generated during the frying process are responsible for the alterations in the chemical and physical properties of oil and fried foods. Thus, reuse of frying oil for deep-frying process ultimately lead to an increase in foaming and viscosity (VISC), variations in FFAs, polar materials, polymeric compounds and unsaturated fatty acid concentrations in the oil (Figure 1) (Choe and Min 2007).

The consumption of chemically degraded oil is associated with deleterious health effects such as increased blood pressure, cardiovascular diseases, atherosclerosis, endothelial dysfunction, impaired vasorelaxation responses, hypertension,

elevated low-density lipoprotein and various cancers (Ganesan, Sukalingam, and Xu 2019; Ku et al. 2014). The decision for the prolonged usage or discarding the frying oils depends on various parameters such as conjugated diene (CD), conjugated triene (CT) and carbonyl value (CV), which are used as markers for the extent of primary and secondary oxidation (Talpur et al. 2015). To assess the deterioration of frying oil, total polar compounds (TPC) level is an important parameter as it is specifically associated with the development of high molecular weight compounds through the process of frying (Farhoosh and Moosavi 2008). The isomerization of unsaturated fatty acids from *cis* to *trans* configuration occurs during frying as does the generation of FFA (Mossoba et al. 1991). Various chemical methods are reported for the determination of these parameters (Engelsen 1997; Talpur et al. 2015), but these methods are costly, require extensive time for analysis, hazardous chemicals, complex sample preparation procedures and wastage of sample. To overcome the shortcomings associated with conventional chemical methods, over the past decade or more, vibrational spectroscopic techniques such as infrared (IR) and Raman spectroscopy along with chemometrics has drawn the attention and employed extensively for quality determination of various oils and fats under thermal stress.

Raman and Fourier transform infrared (FTIR) spectroscopic techniques are based on the enormously distinct physical phenomenon but frequently regarded as complementary techniques (Figure 2.) and commendably employed for the identification of the molecular structure of a sample under investigation (Craig, Franca, and Irudayaraj 2015, Meenu and Xu 2019). FTIR spectroscopy is focused on the detection of vibrations caused due to the changes in
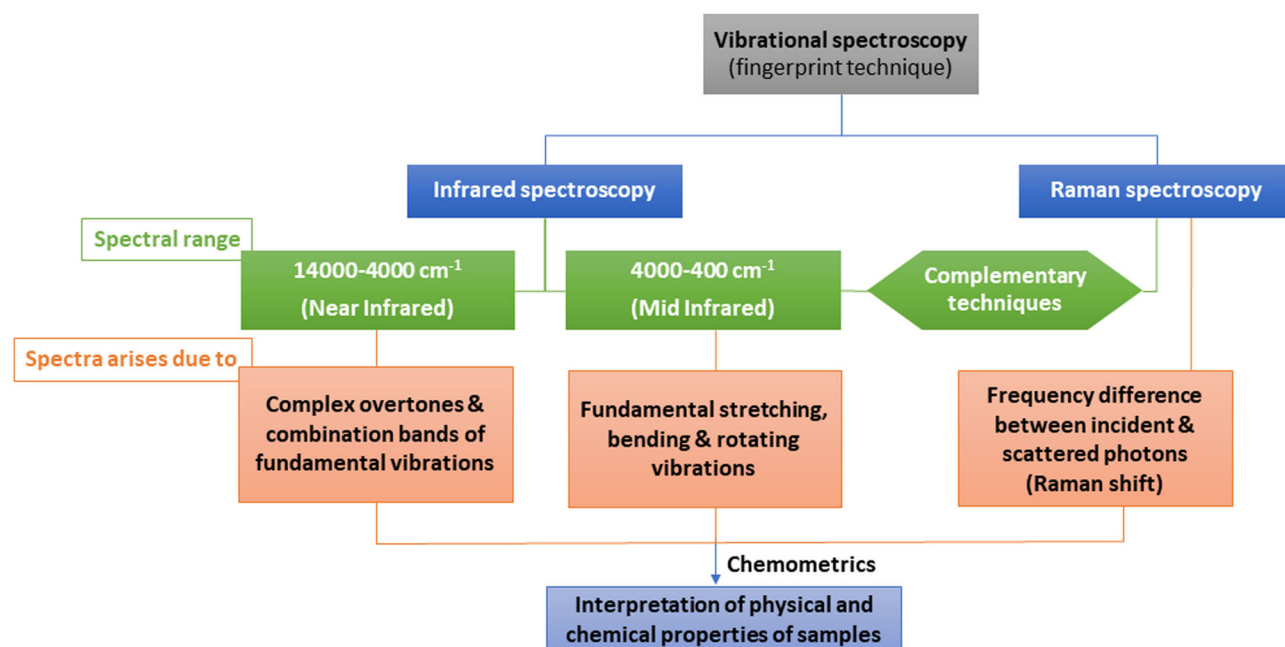
Figure 2. Basic concepts of vibrational spectroscopy.

electrical dipole moment (Rodriguez-Saona and Allendorf 2011, Meenu, Cai, and Xu 2019). Whereas Raman spectroscopy is based on the detection of vibrations triggered due to the changes in the electrical polarizability. On the other hand, near-infrared spectroscopy (NIRS) determines the broad overtone and combination bands of certain fundamental vibrations. This overlapping of numerous overtone and combination bands lead to broad peaks and very low structural selectivity compared to the fundamental peaks observed in isolated positions in the case of FTIR or Raman spectroscopy (Craig, Franca, and Irudayaraj 2015, Meenu et al. 2016).

As mentioned previously, deep-frying is a complex physiochemical process influenced simultaneously by various factors such as type of frying oil, frying material, temperature, frying time, fryer model and intermittent or continuous heating. Together all these factors and complex substrates, several reaction products will be generated. In addition, deep-frying with food and without food reported to generate significantly different chemicals in reaction pathways (Zhang et al. 2012). Thus, to elucidate the impact of complexity and different reaction products generated during deep-frying with food and without food on the prediction of certain chemical parameters using a particular vibrational spectroscopic technique, following sections have reviewed the prediction of thermal degradation of oils with and without food by employing infrared and Raman spectroscopic techniques.

Application of FTIR spectroscopy for determination of thermal degradation of frying oils and fats without food material

FTIR spectroscopy in conjunction with chemometrics has been extensively employed to determine the thermal degradation of frying oils and fats. The detail of thermal treatment, oil samples, parameters studied, mathematical treatment and instrumentation used in previous studies are mentioned in Table 1. Previously, FTIR spectroscopy together with partial least square (PLS) regression was reported to predict both anisidine value (AnV) and individual aldehydes (hexanal, hexenal, decadienal) formed in canola oil in response to thermal stress (120, 155, and 200 °C). AnV was used to express the formation of aldehydic compounds in canola oil. The calibration model for AnV showed standard error (SE) $= 0.99$ and coefficients of determination $(R^2) = 0.998$ and for individual aldehydes, SE ranges from 0.06-1.76 and R^2 was 0.890-0.996 (Dubois et al. 1996). Another study reported that mid-band FTIR spectroscopy along with a PLS as a proficient and precise technique for the prediction of AnV of thermally oxidized palm olein with a standard error of prediction (SEP) $= 0.51$ and $R^2 = 0.99$ (Man and Setiowaty 1999).

A method was also reported to estimate the alteration in the composition of olive oil, corn oil, sunflower oil and seeds oil (sunflower, canola and safflower seed) subjected to thermal treatment at 80 °C to 300 °C for 20-40 min using FTIR spectroscopy and absorbance correction method. The formation of *trans*-isomers was determined by calculating absorbance quotient ($970 \, cm^{-1}/2246 \, cm^{-1}$), whereas unsaturation percentage was determined by absorbance quotient ($3008 \, cm^{-1}/2246 \, cm^{-1}$). An increase in *trans*-fatty acid isomers and a decrease in the fatty acid unsaturation was observed at 150 °C and a significant variation was perceived at about 250 °C (Moreno et al. 1999a). The decrease in the unsaturation percentage of frying oil samples was as following: olive oil (19-6%), corn oil (28-18%), sunflower oil (29-12%), and seeds oil (23-11%) (Moreno et al. 1999b). These two methods were comparatively simple and rapid compared to the previous studies as no chemical analysis was involved in the calibration procedure. However, the whole

Table 1. Summary of application of FTIR spectroscopy for determination of thermal degradation of oils and fats.

Sample (n)	Treatment	Spectrometer, Spectral range, resolution	Attributes	Preprocessing	Multivariate analysis	Remarks	Reference
Canola oil (32)	120, 155, and 200 °C	Nicolet Impact 400 FTIR spectrometer, 4 cm^{-1}	AnV and Aldehydes	–	PLS (Nicolet QuantIR software package)	Efficient method to detect oxidative state of frying oils or biodegradable lubricants	Dubois et al. (1996)
Palm olein (30)	120 °C for 6 d	Perkin-Elmer 1600 series FTIR spectrometer, 4000-400 cm^{-1}, 8 cm^{-1}	AnV	–	PLS (Nicolet Turbo Quant IR-Calibration and Prediction Package ver. 1.1)	Precision of method was comparable with American Oil Chemists' Society method (R^2=0.99)	Man and Setiowaty (1999)
Sunflower, corn, olive, seed oil and lard	80 °C-300 °C for 20-40 min	Perkin-Elmer 1600, Model 1605 FTIR Spectrometer, 4000-450 cm^{-1}, 4 cm^{-1}	Unsaturation grade and trans isomers generation	Absorbance correction method	–	Intense frying changes oil composition; increases trans isomers and decrease in unsaturated components	Moreno et al. (1999a)
Virgin olive, corn, sunflower, safflower and canola oil (11)	80-300 °C, 20-40 min	Perkin Elmer 1600 FTIR spectrometer, 4000-400 cm^{-1}, 4 cm^{-1}	PUFA	–	–	FTIR revealed decrease in unsaturation level of oils in response to thermal treatment	Moreno et al. (1999b)
Soybean oil used for frying potato chips	180 °C for 600 min	Mattson 1000 FTIR spectrometer	PV, IV and FFAs	–	–	Major changes in oil with frying time was successfully determined by FTIR	Goburdhun, Jhaumeer-Laulloo, and Musruck (2001)
Frying oil samples	Collected from cafeterias during each frying cycle for 4 wk	Nexus 870 FTIR spectrometer, 4000-850 cm^{-1}, 4 cm^{-1}	Density, dielectric properties, FFAs and PV	–	General Linear Model and LSD (SAS ver. 8 ed.), PCA (WIN-DAS software)	PCA discriminate between acceptable, borderline and degraded frying oils	Innawong et al. (2004)
Olive oil, sunflower oil, its mixture and waste oil sample (5)	150 °C and 225 °C for 1-15 days	Nicolet Magna IR-560 Spectrometer, 4000-400 cm^{-1}, 4 cm^{-1}	Density, VISC, structure of oils and oil/water interfacial tension	–	–	Remarkable decrease in the degree of unsaturation with increasing heating time of oils	Valdés and Garcia (2006)
Corn oil with/without the addition of oregano	130-275 °C for 30 min and UV treatment	Perkin-Elmer Spectrum RXI FT-IR spectrophotometer, 4000-400 cm^{-1}, 4 cm^{-1}	PV and carbonyl compounds	–	–	Change in 3050-2800 and 1745 cm^{-1} represented thermal degradation	Vlachos et al. (2006)
Sunflower-refined oil and seeds-refined oil (639)	147, 171 and 189 °C for 1920min (32 h)	FTIR spectrometer model Tensor 27, 4000-400 cm^{-1}, 4 cm^{-1}	cis-unsaturation, trans-fatty acids content and FFAs	Baseline correction	HCA, PLS1 and PLS2 (TurboQuant Analyst 6.0 software)	PLS1 models were recommended for prediction of oil heating conditions	Moros et al. (2009)
Oils from four almond cultivars (31)	75 °C until the secondary oxidation products appeared	Vector 22 FTIR spectrometer, 4000-400 cm^{-1}, 4 cm^{-1}	FAME content	–	LDA (SPSS ver. 15.0)	Butte cultivar had higher linoleic acid and more prone to oxidative deterioration	Sanahuja et al. (2009)
Virgin olive, soybean and			TPC, FA Composition	–	Stepwise MLR (Statistica ver. 6.0)	Area under the band 978-960 cm^{-1} was	

Sample	Heating/treatment condition	Instrument	Parameter	Chemometric method	Findings	Reference
sunflower oil (114 + 105)	190 °C for 0-94 h and samples were collected after 2-5 h	Bruker 55 Equinox S FTIR spectrometer, 4000-600 cm⁻¹, 4 cm⁻¹	PTG	First derivative	used to establish a model for estimating TPC	Tena, Aparicio, and García-González (2009)
Olive oil (118)	Continuous heating at 190 °C and foodstuff exchanged every 45 min	IFS 66 v/S FTIR spectrometer with ATR, 4000-950 cm⁻¹, 4 cm⁻¹	PTG	iPLS, UVE-PLS, expert knowledge (Matlab 7.7.0)	All of the variable selection methods offered an efficient PLS models for the prediction of PTGs	Kuligowski et al. (2010a)
Olive, cotton, corn and sunflower oil (11)	Microwave heating for 2 – 28 min at 450 and 630 W	FTIR spectrometer Jasco 430, 4000-400 cm⁻¹	–	–	Heating at 630 W for any given time led to initial decrease in ratios RI, RII and RIII due to reduction in 18:2 and 18:3 fatty acids	Moharam and Abbas (2010)
Sunflower, olive and canola oil	130, 150 and 170 °C for 60 min	Vector 33 spectrophotometer, 4000-600 cm⁻¹, 4 cm⁻¹	Monitoring the thermal stability of oils	Spline baseline correction (Matlab 7.6.0.324)	Peaks at 3008, 985, 970 and 710 cm⁻¹ assigned to cis/trans isomerization; 3539 cm⁻¹: hydroperoxides formation, 1732 and 1699 cm⁻¹: secondary oxidation products	Pinto et al. (2010)
Deep-fried corn, sunflower, and olive oil (281)	Heating at 190 °C, simulated frying process of cafeterias and foodstuff exchanged every 45 min	IFS 66 v/S FTIR spectrometer, 4000-950 cm⁻¹, 4 cm⁻¹	PTG	PLS-DA (Matlab 7.7.0)	Efficient PLS models developed based on particular calibration sets compare to the calibration set comprising samples from all classes	Kuligowski et al. (2011)
Palm (23) and soybean oil (16)	Sample collected after total time of 48 h for frying Falafel at150-160 °C	IR Prestige-21 FTIR spectrophotometer, 4000-400 cm⁻¹, 1.9 cm⁻¹	FA composition, FFAs, VISC, and TPC	MLR, PCR, PLS1, and PLS2 (Matlab7.0)	Oil samples were efficiently grouped into two clusters even following the 48 h of frying process	Al-Degs, Al-Ghouti, and Salem (2011)
Almond oil from different cultivar of almonds	100 °C for 1, 3, 5, 7, 10, 15 and 20 days	Vector 22 FTIR spectrometer, 4000-400 cm⁻¹, 4 cm⁻¹	Volatile compounds	LDA (SPSS 15.0)	Volatile compounds determined by reference method and variations in ATR-FTIR spectra reflected the progress of oxidation process	Beltrán et al. (2011)
Extra-virgin olive oil (3)	30, 60 and 90 °C up to 35 days	Bruker Vertex 70 spectrophotometer, 4000-400 cm⁻¹, 2 cm⁻¹	Mechanisms of oil degradation	–	Initial increase in hydroperoxides and subsequent formation of alcohols and secondary oxidation products	Navarra et al. (2011)
Methyl oleate and methyl linoleate	180 °C for 15 h	Bio-Rad Digilab FTS 60A spectrometer interfaced to gas chromatograph,	Short-chain esterified compounds	–	Oxidation compounds formed during thermal treatment	Berdeaux et al. (2012)

(continued)

Table 1. Continued.

Sample (n)	Treatment	Spectrometer, Spectral range, resolution	Attributes	Preprocessing	Multivariate analysis	Remarks	Reference
Extra virgin olive oils (24)	100 °C until the sample polymerization started	4000–700 cm⁻¹, 8 cm⁻¹; FTIR spectrometer, Vector 22, 4000 to 650 cm⁻¹, 4 cm⁻¹	FAs, SFA, MUFA, PUFA, C18:1/C18:2	Rutherford baseline correction	PCA and LDA (IBM SPSS statistics ver.19)	were identified using GC-MS and GC–FTIR; Kinetic parameters of *cis/trans* isomerization represented an important tool for cultivar classification	Falcó et al. (2012)
Waste frying oils: palm oil, soybean oil and hydrogenated vegetable fat (48)	–	Perkin-Elmer Spectrum One spectrometer, 3000–600 cm⁻¹, 4 cm⁻¹	–	First derivative, second order polynomial, SG	PCA and PLS (Unscrambler ver. 9.1)	PLS models based on MIR spectra found to be a suitable method for determination of waste frying oil composition	Hocevar et al. (2012)
Extra virgin olive oil, sunflower oil and their mixture	200 °C for 8 and 16 h.	FTIR-8400S FTIR spectrophotometer, 4000–600 cm⁻¹, 4 cm⁻¹	Monitoring the quality changes in response to thermal treatment	–	LDA (Origin 6.0 software)	Spectral changes at 3050–2800 and 1745 cm⁻¹ represents thermal degradation; 3011, 3006 and 912 cm⁻¹ represents adulteration of oil	Poiana et al. (2013)
Virgin olive oil (47)	190 °C for 94h for 8h cycles per day	Bruker 55 Equinox S FTIR spectrometer, 4000-400 cm⁻¹, 4 cm⁻¹	TPC, FA Composition and phenol content	–	–	Individual FTIR analysis of polar and nonpolar fractions of thermoxidized virgin olive oil allowed better interpretation of neat oil spectra	Tena, Aparicio-Ruiz, and García-González (2013)
Deep frying oil samples (109)	Oil samples were used for deep frying of various foods by street vendors	Nicolet 6700 Spectrometer from Thermo Fisher Scientific with ATR, 4000–400 cm⁻¹, 4 cm⁻¹	FFA, TPC, and VISC	Smooth, bin, first & second derivative, SNV	PLS (DeLight 3.2 software package)	Less satisfying prediction of FFA but good predictability for VISC and TPC	Shen et al. (2014)
Rapeseed oil (156)	Frozen par-fried French fries fried at f 180, 200, or 220 °C for 3 min at 22 min interval for 7h a day for 4 days	Nicolet 6700FT-IR spectrometer, 4000–650 cm⁻¹, 4 cm⁻¹	AV and TPC	First and second derivative	PLS (Unscrambler)	Best calibration model was developed using second derivative spectra compared to models based on raw and first derivative spectral data	Chen et al. (2015a)
Two types of rapeseed oil (156)	Frozen par-fried French fries fried for 3 min at 180, 200 and 220 °C at 22min interval for 7 h each day for 4 successive days	Nicolet 6700FT-IR Spectrometer, 4000–650cm⁻¹, 4 cm⁻¹	CV	First and second derivative	PLS (Unscrambler software ver. 7.6)	PLS in combination of second derivation spectra resulted in good calibration model for prediction of CV	Zhang et al. (2015)
Frying canola oil (7)	Potato chips fried at 180 °C for 5 min/		TPC, CV, conjugated diene and triene		PLS (Turbo Quant analyst 7.2 software)	FTIR-PLS were resulted in development of	Talpur et al. (2015)

Sample	Sample treatment	Instrument	Preprocessing	Parameters studied	Chemometrics/Software	Key findings	References
	cycle. Sample collected after 2 h (24 batch frying cycles)	Nicolet 5700 FTIR spectrometer, 4,000–400 cm⁻¹, 4 cm⁻¹	Baseline correction, Savitsky-Golay smoothening			satisfactory calibration models for all parameters	
Extra virgin olive oil adulterated with soybean oil	185 °C for 4 and 8 h	FTIR-8400S from Shimadzu, 4000–400 cm⁻¹, 4 cm⁻¹	–	Structural changes in thermally treated virgin olive oil	LDA (Origin 6.0 software)	Changes at 722, 885, 987, 967, 1743 cm⁻¹ represented thermal degradation of oil	Poiana et al. (2015)
Corn and mustard oils	Potatoes fried at constant temperature for three frying times	FTIR Spectrometer Model I-R Prestige 21 Shimadzu, 4000–400 cm⁻¹	–	Density, VISC, IV and PV	–	Significant change was observed in band 2852.7–2926.0 cm⁻¹ at boiling point while mustard oil present a supplementary peak at 3633.8 cm⁻¹	Zahir et al. (2017)
Different vegetable oils (30)	180 °C for 8 h	MIR data: Bomem-Hartmann & Braun 102 spectrometer, 4000–650 cm⁻¹, 4 cm⁻¹	Baseline correction	IV and transesterification of FAs	Common components and specific weights analysis (Matlab R2008b)	High intensity of band at 3008 cm⁻¹ in case of oils with high degree of unsaturation and decrease in this band intensity was reported after thermal treatment	Rampazzo et al. (2018)
Soybean, rapeseed, sunflower and peanut oil	50 °C to 260 °C heated twice for 30–35 min	ThermoNicolet 5700 ATR-FTIR, 670–1900 cm⁻¹, 4 cm⁻¹ inVia Qontor confocal Raman microscope, 670–1900 cm⁻¹	SNV, SG, second derivative	PV, AV	UVE and SPA used for feature variables extraction, PLS	Data fusion along with SPA results in best prediction; for PV, $R_c^2 = 0.964$ and $R_p^2 = 0.939$; RMSEC $= 0.060$ and RMSEP $= 0.080$; For AV, $R_c^2 = 0.955$ and $R_p^2 = 0.919$; RMSEC $= 0.025$ and RMSEP $= 0.027$	Liu et al. (2020)
Mustard oil (182)	Fried oil sample were collected after 7 days of frying potato pieces at 220 °C till preset texture and color achieved	Thermo Scientific NICOLET iS50 ATR-FTIR spectrophotometer, 4000–400 cm⁻¹, 4 cm⁻¹	SG, first and second derivative	Detection of fried mustard oil in pure mustard oil	PCA, LDA, PCR and PLS (Unscrambler®X 10.5.1)	Proposed method can detect 0.5% v/v of Fried mustard oil in pure mustard oil.	Jamwal et al. (2021)

FTIR, Fourier-transform infrared spectroscopy; MIR, mid infrared spectroscopy; ATR, attenuated total reflectance; AnV, anisidine value; IV, iodine value; PV, peroxide value; FFAs, free fatty acids; VISC, viscosity; FAME, fatty acid methyl ester; TPC, total polar compound; PTG, polymer triacylglyceride; SFA, saturated fatty acids; PUFA, polyunsaturated fatty acids; MUFA, monounsaturated fatty acids; CV, carbonyl value; AV, acid value; MG, monoglycerides; DG, diglycerides; TG, triglycerides;Vit E, vitamin E; FA, fatty acid; PLS, partial least square regression; (UVE)-PLS, Uninformative variable elimination PLS; iPLS, interval PLS; HCA, Hierarchical cluster analysis; MLR, multiple linear regression analysis; LSD, least significant difference; PCA, principal component analysis; LDA, linear discriminant analysis; PLS-DA, partial least squares- discriminant analysis; PCR, principal component regression; SNV, standard normal variate; SG, Savitzkye-Golay smoothing; SPA, successive projections algorithm; UVE, uninformative variable elimination.

procedure was based on the absorbance of FTIR spectra at a particular wavenumber.

Furthermore, authors have explored the region of FTIR spectrum assigned to hydrogen's stretching (3050–2800 cm^{-1}) and ester carbonyl functional group of the triglycerides (1745 cm^{-1}) to predict the thermal degradation of various edible oils. Previously, researchers have heated the corn oil at numerous temperature ranges from 130 to 275 °C for 30 min. The changes emerged in FTIR spectra of oil samples in 3050–2800 cm^{-1} and 1745 cm^{-1} regions after thermal treatment were attributed to oxidation reactions. It was also reported that the addition of antioxidant compounds such as oregano decreased these spectral changes (Vlachos et al. 2006). Structural changes in the sunflower and olive oil were also monitored by FTIR after heating at frying temperature for 2 days. An increase in the heating time of oils resulted in a remarkable decrease in the degree of unsaturation (A3005 cm^{-1}/A2850 cm^{-1}). This degree of unsaturation was measured as the ratio of the absorbance at 3005 cm^{-1} (assigned to stretching vibration of the *cis* double bond) and 2850 cm^{-1} (allocated to the symmetric stretching vibration of aliphatic C-H bonds in methylene). Sunflower oil was observed to be more susceptible to the thermal stress compared to the olive oil (Valdés and Garcia 2006).

Attenuated Total Reflectance (ATR) is a widely employed sampling technique for IR spectroscopy. This technique hardly needs sample preparation. This sampling technique is compatible for quick and robust analysis of solid and liquid samples along with the samples that are otherwise difficult to handle such as paste. ATR elements are fabricated with relatively robust elements such as diamond, germanium, or zinc selenide. Thus, easy to clean and sample used for analysis can also be collected and reused for further characterization (Ramer and Lendl 2013).

ATR-FTIR was also efficiently employed to evaluate the thermal degradation of sunflower oil and mixed cooking oil based on the *cis/trans* isomerization, FFA contents, and *trans*-fatty acid contents. Partial least square regression 1 (PLS1) models based on the ATR-FTIR spectral data exhibit more accuracy for the prediction of oil heating conditions. The hierarchical cluster analysis (HCA) of ATR-FTIR spectra of thermally stressed oils separate both the oil samples into two different clusters along with the progression of these clusters based on increasing temperature and heating duration (Moros et al. 2009). The HCA of spectral data can be efficiently employed to determine the prediction capabilities of the model in case of new samples by comparing their cluster classification. ATR-FTIR spectroscopy was also employed for the spectral acquisition of virgin olive oil heated up to 94 h. The wavelength region from 978 to 960 cm^{-1} (represents the *trans*-fatty acids contents) was used to establish a model for the predicting TPC of virgin olive oil and excellent validation results (R^2 = 0.997) were reported by using an external set of samples (Tena, Aparicio-Ruiz, and García-González 2009).

In another study, the simultaneous thermal degradation and spectral data of sunflower, olive and canola oils were observed using mid-infrared (MIR) spectrometer equipped with a heated ATR apparatus. The major peaks at 3008, 985, 970 and 710 cm^{-1} indicated *cis-trans* isomerization of oil samples, the peak at 3539 cm^{-1} represent hydroperoxides formation, whereas, the peaks at 1732 and 1699 cm^{-1} correspond to the formation of secondary oxidation products comprising carbonyl groups such as aldehydes, ketones, and esters (Pinto et al. 2010). Researchers have also depicted the degradation of olive, cotton, corn, and sunflower oils followed by microwave heating (630 W) based on the reduction in FTIR absorbance ratios A3006/A2924 cm^{-1}, A3006/A2854 cm^{-1} and A3006/A1746 cm^{-1} of these samples. The decrease in these values was attributed to the reduction in 18:2 and 18:3 fatty acids content owing to the oxidation (Moharam and Abbas 2010). These studies will be useful in future for rapid and non-laborious detection of oil degradation based on the change in absorbance of peaks at particular wavenumber without employing wet analysis and chemometrics.

In addition, MIR spectra in conjunction with PLS identified two principal influential bands in MIR i.e. 1245-1180 cm^{-1} and 1150-1030 cm^{-1} that correspond to thermal oxidation degradation of virgin olive oil exposed to thermal treatment at 180 °C for 30, 60, 90, 120, 150 and 180 min (Maggio et al. 2011). C–O (1238, 1138, 1118, 1097 and 1033 cm^{-1}) was found to be the most affected band due to oxidation. In proceeding studies and real-world applications, these particular bands can be employed for the prediction of thermal degradation of cooked olive oils. In another study, the oxidative stability of different almond oils after thermal treatment (100 °C for 1, 3, 5, 7, 10, 15 and 20 days) was also assessed based on various volatile compounds using ATR-FTIR and head-space solid-phase microextraction/gas chromatography-mass spectrometry (HS-SPME/GC–MS). The oxidation of samples was reported to happen between 5 and 20 days of thermal treatment. The oxidation of linoleic acid resulted in the formation of (E, E)-2,4-decadienal. This volatile compound mentioned being responsible for the characteristic aroma of the oxidized almonds. A HS-SPME/GC–MS together with multivariate stepwise linear discriminant analysis (LDA) resulted in a successful categorization and distinction among Spanish and American almond cultivars (Beltrán et al. 2011).

Furthermore, the FTIR spectra of extra-virgin olive oil were also acquired for the variation in wavenumbers region 3100–3600 cm^{-1} in response to thermal treatment at 30, 60 and 90 °C for 35 days. The absorption profiles suggested the initial formation of hydroperoxides followed by an increase in the alcohols and secondary oxidation products (Navarra et al. 2011). In another study, the GC-FTIR and GC-MS were complementarily employed for the identification of oxidation compounds formed during thermal treatment (180 °C) of linoleate and methyl oleate. The study has primarily explored the compounds originated by hydroperoxide scission and still attached to the glyceridic backbone of the fats and oils that, in turn, form a part of nonvolatile molecules. The formation of various new compounds i.e., 20 non-esterified volatile compounds, 21 short-chain esterified
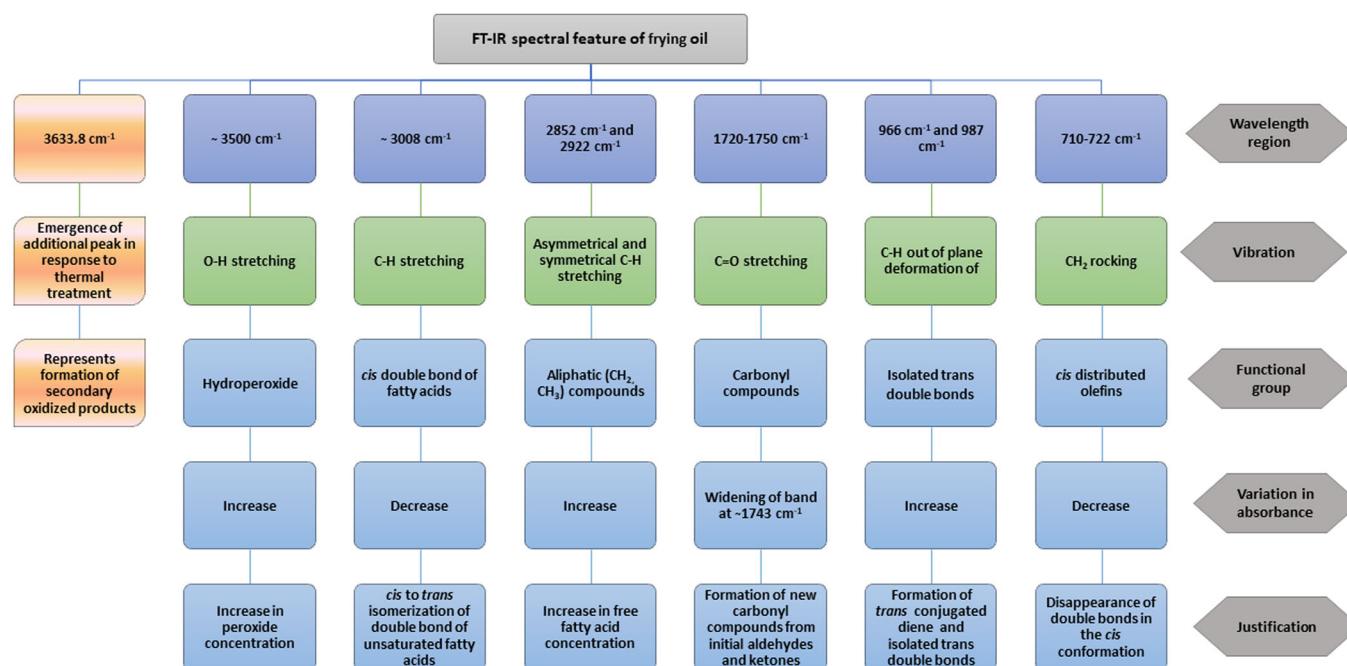
Figure 3. Typical FT-IR spectral bands associated with degradation of frying oil.

compounds and furanoid compounds were reported (Berdeaux et al. 2012). This model system revealed the complex evolution of small fractions of new compounds at frying temperature.

ATR-FTIR was also employed to monitor the oxidation process of virgin olive oils and different brands of the same cultivar at $100\,^{\circ}C$ until the initiation of sample polymerization. During this course, the band assigned to the stretching vibration of *cis* double bonds was reallocated to lower values (from $3006\,cm^{-1}$ to $970\,cm^{-1}$) related to the bending vibration of the *trans* double bond. The authors have also confirmed that *cis/trans* isomerization follows pseudo-first-order kinetics (Falcó et al. 2012). The kinetic parameters acquired from the data of FTIR absorbance bands around from $3006\,cm^{-1}$ to $970\,cm^{-1}$ can also be employed as an important tool for the cultivar classification of olive oil rather than using a fatty acid composition for cultivar classification. Furthermore, the FTIR spectra of sunflower oil, olive oil and their blend were collected for 8 and 16 h under simulated frying processes. It was observed that the changes in spectral region $3050\text{-}2800\,cm^{-1}$ and at $1745\,cm^{-1}$ in response to thermal treatment facilitate the monitoring of the oxidation process of oils. (Poiana et al. 2013).

It was also reported that FTIR analyses of non-polar and polar fractions of thermoxidized virgin olive oil separately lead to an improved elucidation of neat oil spectra. The spectra of polar fraction found to be more informative as the absorption of bands assigned to epoxy, free fatty acids and peroxide compounds were more intense compared to the spectra of neat oil. The interpretation of the hydroxyl region was also simplified by segregating the alcohol and hydroperoxide bands in the polar fraction while retrieving ester linkage band through the non-polar fraction (Tena, Aparicio-Ruiz, and García-González 2013). ATR-FTIR spectroscopy was also employed to investigate the structural

variations stimulated in adulterated extra virgin olive oil due to thermal stress for 4 and 8 h at $185\,^{\circ}C$. The thermo-oxidative stress lowered the absorbance of the band at $3006\,cm^{-1}$ and $722\,cm^{-1}$, increase in the absorbance of the band at $987\,cm^{-1}$ and $967\,cm^{-1}$ (*cis-trans* isomerization) and widening of the band at $1743\,cm^{-1}$ (formation of secondary oxidation products) as shown in Figure 3. A weak vibration of the band at $885\,cm^{-1}$ representing the formation of epoxides was also observed in response to the thermal treatment (Poiana et al. 2015). In addition, ATR-MIR spectra of 24 different thermally treated (at $180\,^{\circ}C$ for 8 h) vegetable oils were also collected and it was reported that the intensity of the band at $3008\,cm^{-1}$ was directly proportional to the concentrations of the fatty acids as assessed by gas chromatography. The oils exhibited a higher degree of unsaturation demonstrated by the high intensity at $3008\,cm^{-1}$. After thermal treatment, a decrease in the intensity of this band and the slight increase in a band near $968\,cm^{-1}$ represented cis/trans isomerization (Rampazzo et al. 2018). Overall, the majority of researchers have explored the impact of thermal treatment on FTIR spectra of different oils. It was found to be a quite easy and rapid technique to access the chemical changes in the thermally treated oils samples depending on the increase or decrease in the absorption of particular bands of FTIR. However, only few studies have employed chemometrics for prediction of oil degradation products followed by thermal treatment and classified oil samples according to the level of thermal stress.

Application of FTIR spectroscopy for determination of thermal degradation of frying oils and fats with food material

As already discussed in the previous section that frying of food in oils or fats involves complex reactions compared to

heating oils and fats without food materials. It is also seems to be more practical to study the degradation of oils and fats with food materials as in real-life applications oils are repeatedly used by restaurants and street food vendors for frying of food. Several researchers have also explored the application of FTIR spectroscopy to determine the thermal degradation of frying media with food. Previously, ATR-FTIR technique was reported as a simple and accurate approach for the determination of FFA content in case of daily oil samples used to fry spring rolls at 180 to 190 °C for 90 s. For the prediction of FFA, multiple linear regression (MLR) model exhibiting root mean square error of cross-validation (RMSECV) of 0.10 and R^2 of 1.00 found to be more efficient compared to the univariate model (RMSECV = 0.12, R^2 = 0.996) (Engelsen 1997). In another study, the spectra of soybean oil employed for frying potato chips at 180 °C for 600 min was acquired using FTIR spectrometer. It was mentioned that with an increase in the frying time major alterations were observed at 3800-3200 cm^{-1} representing OH stretching region, 3050-2800 cm^{-1} corresponds to the CH stretching vibration, 1750-1650 cm^{-1} indicating carbonyl and olefin regions and 1000-900 cm^{-1} demonstrating trans double bond region. These alterations in FTIR spectra revealed an amplification in hydroperoxide and FFA contents, a decrease in triglyceride ester linkage, loss of *cis* double bonds, proliferation in *trans* saturation and formation of unsaturated aldehyde during the frying process (Goburdhun, Jhaumeer-Laulloo, and Musruck 2001).

Another study reported the implementation of ATR-FTIR and principal component analysis (PCA) to determine the chemical characteristics of frying oil samples fetched from fast-food restaurants. A significant correlation (0.84 to 0.94) was observed between the FFA content and FTIR absorbance at 3300 cm^{-1}. A good correlation (0.90 to 0.97) was also reported between the PV of different oils and FTIR absorbance at 3471 cm^{-1} (Innawong et al. 2004). Mid-FTIR along with the gel permeation chromatography (GPC) was employed as a detection technique to monitor the polymerized triacylglycerides (PTG) content in thermally stressed olive oil and throughout the deep-frying of French fries in olive oil. FTIR detection facilitated the confirmation of PTG content in olive oil along with its quantification. The developed method using GPC-FTIR (1900-1600 cm^{-1}) and extraction of a chromatogram using science-based calibration (a multivariate method) offered a detection limit of 0.19 mg mL^{-1} for PTG content in thermally stressed olive oil (Kuligowski et al. 2010a). The study involved the direct application of FTIR spectra for determination of thermal degradation of oils based on the absorption of particular bands assigned to the certain functional group seems to be an easy and less time-consuming method. However, some of the researchers have employed calibration models for the prediction of certain degradation products of oils followed by the thermal treatment. These methods also present high prediction efficiency and lower error values.

Furthermore, the thirty-nine samples of soybean and palm oil collected after frying Falafel for 48 h at 150-160 °C. The frying quality of these samples was predicted using PLS1 along with mid-FTIR data. The TPC, VISC, and FFA contents of the used oils were accurately predicted over the ranges of 5.09-33.42%, 20-144 pa s and 0.07-1.91 mg KOH/g, respectively (Al-Degs, Al-Ghouti, and Salem 2011). In another study, the FT-IR in combination with PLS regression was employed to determine chemical characteristics of frying oils collected from a college canteen and soybean oil (two different brands) used for frying various food products in terms of FFA and PV. For the prediction of FFA values, the developed model exhibited R^2 = 0.95, SEP = 0.14 and the ratio of standard deviation of reference values to SEP (residual predictive deviation: RPD) = 4.48. For PV, the developed model showed R^2 = 0.89, SEP = 6.17 and RPD = 2.93 (Du et al. 2012).

Hocevar et al. (2012) determine the composition of waste cooking oil (WCO) blends (palm oil, pure soybean oil or hydrogenated vegetable fat) collected from restaurants using MIR spectroscopy and chemometric techniques. PCA was executed using MIR spectra (3,000-600 cm^{-1}) to distinguish amongst pure cooking oils/fat and their blends. PLS models developed based on the MIR spectra observed to be suitable for prediction of oil contents in WCO blends with root mean square error of prediction (RMSEP) of 2.8% for palm oil, 4.7% for soybean oil and 5.5% for hydrogenated vegetable fat (Hocevar et al. 2012). In another study, the FTIR spectroscopy in conjunction with PLS regression was also employed for prediction of FFA, VISC and TPC of deep-frying oils samples obtained from various street vendors. It is interesting to note that this method resulted in poor prediction of FFA (for all oils including shortening predictability is R^2 =0.65-0.71, SEP = 0.15-0.14 and RPD = 1.66-1.83). However, exhibited an enormous potential for the prediction of VISC (for all oils including shortening predictability is R^2 = 0.92-0.95, SEP = 0.68-0.71 and RPD = 3.54-3.98) and TPC (for all oils including shortening predictability is R^2 = 0.79-0.93, SEP = 1.89-2.94 and RPD = 2.16-3.55) (Shen et al. 2014). The poor prediction ability of PLS models may be attributed to the involvement of complex reaction products in the oil samples that might have been interfered with the chemical analysis and spectral attributes of the oil samples.

In addition, researchers have also employed the transmission FTIR-PLS method for prediction of CV, CD, CT and TPC in canola oil during potato chips frying at 180 °C. An excellent R^2 and RMSEP were observed for TPC (0.999, 0.809), CV (0.992, 0.690), CD (0.998, 1.26) and CT (0.999, 0.735) (Talpur et al. 2015). Thus, this developed method can be efficiently employed for future prediction of CV, CD, CT and TPC in canola oil used for potato chips frying without using harmful chemicals within less than 2 min of analysis time. In another study, Chen et al. 2015a have also reported FTIR spectroscopy as a viable alternative to standard wet analysis methods for determination of thermal degradation of oils. They have predicted acid value (AV) and TPC, the most important parameter to determine thermal degradation of oils, in 156 samples of rapeseed oil used for frying French fries using ATR-FTIR in conjunction with PLS regression. The calibration model developed using second derivative of
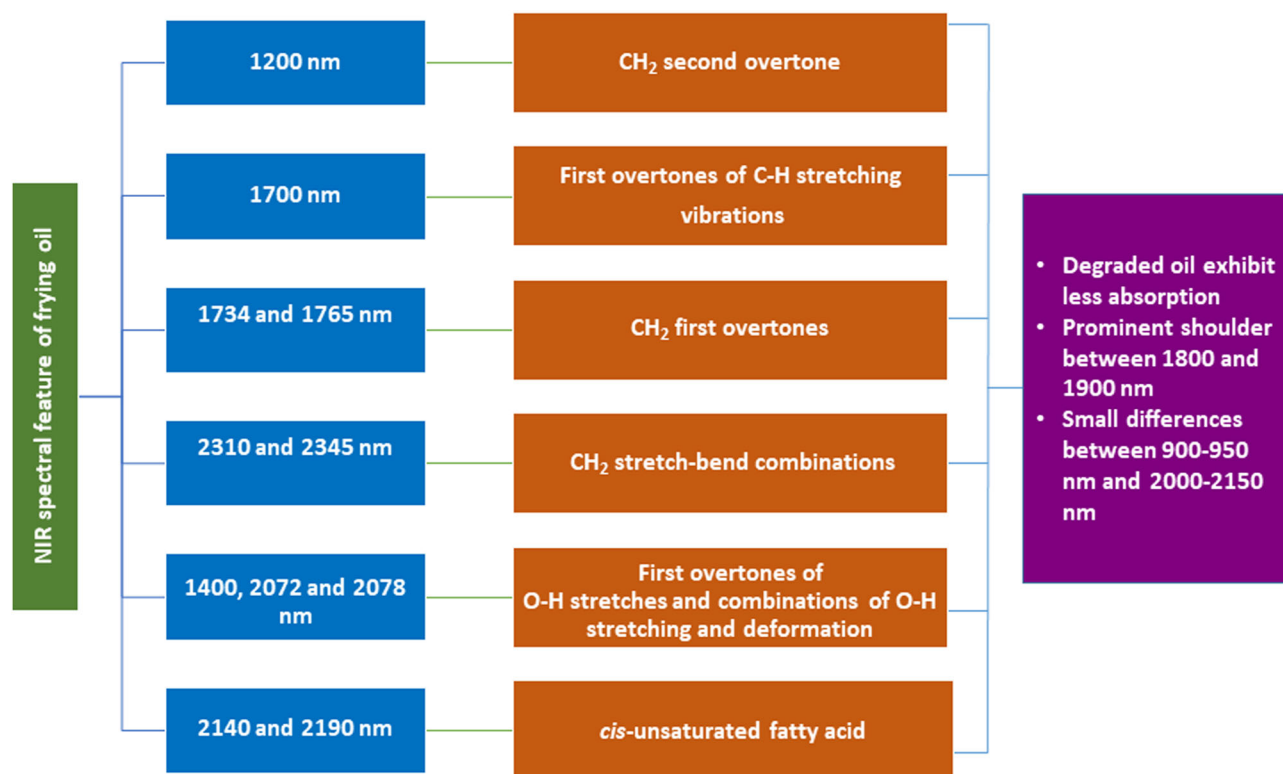
Figure 4. Typical NIR spectral bands associated with frying oil degradation study (Ng, Wehling, and Cuppett 2007, 2011).

FTIR spectra exhibited $R^2 = 0.98$ and standard errors of cross-validation (SECV) = 1.17% for TPC and $R^2 = 0.99$ and SECV = 0.16 mg KOH/g for the AV of the samples under investigation. For validation procedure, SEP for TPC and AV was reported to be 1.10% and 0.16 mg KOH/g, respectively (Chen et al. 2015a). Furthermore, the ATR-FTIR in conjunction with PLS was employed for an efficient prediction of carbonyl value, an indicator of the quantity of carbonyl compounds, of 156 samples of rapeseed oil used for frying frozen par-fried French fries. A good calibration model ($R^2 = 0.98$, standard error of calibration (SEC) = 1.68, SEP = 1.93 μmol g^{-1}, RPD = 5.8) was developed based on the second derivation spectra (Zhang et al. 2015). Thus, the calibration model reported in this study can be successfully employed for the prediction of carbonyl value of rapeseed oil. However, if this particular calibration model has been used for the prediction of carbonyl value of some other type of oils, further experimentation is required to confirm the adaptability of the present calibration.

FTIR spectroscopy was also used to assess the oxidation of mustard and corn oil after frying pieces of potato for multiple times and after heating the mustard oil and corn oil at boiling point i.e. 170 and 140 °C, respectively. Authors have mentioned a significant change in a band at 2852.7-2926.0 cm^{-1} after heating the oils at boiling point and using the same frying oil for multiple times. Whereas, at boiling point, mustard oil exhibited a supplementary peak at 3633.8 cm^{-1} represented the formation of secondary oxidized product (Zahir et al. 2017). These observations will be useful in future to detect the repeatedly used corn and mustard oil by simply observing the change in particular bands

and peaks of FTIR spectra of these oil samples. A recent review has also discussed the successful application of FTIR spectroscopy along with the chemometrics to determine thermal degradation of various edible fats and oils such as corn, mustard, canola, and virgin coconut oil (Rohman 2017). Recently, ATR-FTIR along with LDA were reported to classify pure mustard oil and adulterated with mustard oil used to fry potato pieces with 100% accuracy. PLS regression of FTIR spectral region 1260–1080 cm^{-1} presented best prediction with high R2 (0.999) and residual RPD of 31.91 with low RMSE and relative prediction error (RE %) of 0.53% v/v and 3.37%, respectively. This method reported to detect 0.5% v/v of fried mustard oil in pure mustard oil (Jamwal et al. 2021).

Researchers have extensively explored the application of FTIR spectroscopy for determination of thermal degradation of oils used for frying various food items. FTIR spectral data in conduction with standard wet analysis has been employed to develop calibration models for several properties representing thermal degradation oils such as FFA, PV, PTG, TPC, VISC, CV, CD, CT, and AV with high efficiency. These models can be used in future for prediction of a particular property of specific thermally degraded oil. Whereas, only a few studies have reported the thermal degradation of oils with food presented by the change in particular FTIR absorption band. However, in case of thermal degradation of oils without food, comparatively less number of studies have been reported and most of the studies have reported the change in absorption of a specific peak or FTIR band assigned to particular functional group. The calibration models were only developed for AnV, FFA and TPC by

employing PLS and FTIR data. The calibration and prediction efficiency of developed models were found to be high. It is important to note that individually the prediction efficiency of developed models for various properties of thermally stressed oils with and without food is quite high, but we were not able to compare the results as different authors have studied different properties, by employing different methods, using different oil sample thermally treated at different temperature for different time durations.

Application of near-infrared spectroscopy for determination of thermal degradation of frying oils and fats without food material

NIR spectroscopy along with chemometrics has also been employed to determine the thermal degradation of frying oils and fats with and without food. The detailed description of thermal treatment, oil samples, parameters studied, mathematical treatment and instrumentation used by various researchers in this field are summarized in Table 2.

NIR spectra of oil samples are complex due to the overtone vibrations and combinational bands of N-H, C-H and O-H bonds present in the samples. Therefore, the multivariate statistical analysis must be carried out using data generated by chemical analysis as primary data and spectral data as secondary data for better understanding of spectra, extraction of useful information and quantitative analysis of various degradation products in thermally stressed oil samples. Previously, the polar, polymeric, and linoleic acid contents of thermally treated sunflower oil were predicted by using NIRS and MLR. It was found that at a thermal load of 170-180 °C and 200-210 °C, the SEC in case of polar content was reported to be 0.991% and 0.915%, in case of polymer content observed to be 1.21% and 1.65%, for linoleic acid content found to be as 0.436% and 0.446%, respectively. The multiple correlation coefficients were ranged from 0.994 to 0.999 (El-Rafey et al. 1988).

Later, NIRS along with modified PLS was also employed for the quality prediction of commercial frying vegetable oils and animal fats (Szabó et al. 2010). Szabó et al. reported an improved estimation accuracy of sampling event and heat-sum ($R^2 = 0.94$ and cross-validation values more than 0.9) was reported compared to the previous study carried out by Engelsen (1997). The study conducted by Szabó et al. (2010) had also mentioned that the calibrations for AV (SEC: 0.174, SECV: 0.196), PV (SEC: 3.08, SECV: 3.43), pAnV (SEC: 20.9, SECV: 21.9), DPTG (SEC: 2.62, SECV: 2.35) and TPM (SEC: 3.97, SECV: 4.15) reach to the practical application levels (Szabó et al. 2010). An innovative method based on near-infrared emission spectroscopy was also reported for monitoring the oxidative stability of edible oils exposed to frying temperatures (160°C). The oxidative stability of samples under investigation was explained by an increase in the intensity and broadening of the band at 2900 nm. The area under this band dictates the degree of oxidation of cooking oil under thermal stress (Gonzaga and Pasquini 2006). It was the only study with home-made spectrometer equipped with an acousto-optical tunable filter as a monochromator. This study has also used the concept of induction time, the time in which an oil sample resists to oxidation, to study the impact of nitrogen insertion and antioxidant addition on thermal degradation of oils. It was indicated that the involvement of nitrogen gas reduces the oxidation rate, but the degradation of oil was unavoidable. Whereas the addition of antioxidant can enhance the induction time and reduced the oxidation rate of oil samples.

NIRS along with chemometrics was reported to predict TPM and FFAs in the soy-based oil thermally treated at 190°C for 8 h per day. In the wavelength region of 700-1100 nm, PLS models exhibited a notable correlation (r) between NIR and reference method for TPM (r = 0.983) and for FFA (r = 0.943). Whereas, in 1100-2500 nm, forward stepwise multiple linear regression models found to be better compared to PLS for predicting TPM (r = 0.999) and FFA (r = 0.983) (Ng, Wehling, and Cuppett 2007). For future applications, NIR region ranging from 1100 to 2500 nm can be employed for the satisfactory prediction of TPM and FFA. Furthermore, specific NIR bands by employing interval PLS regression models need to be explored for prediction of a particular oil degradation products that, in turn, can be employed to develop cost-effective handheld devices for on-site applications. Another study in this field has employed a polar qualification system based NIR spectra analysis for identifying the category of frying oils or fats along with the magnitude of heating. It was mentioned that an increase in the difference of heating extent leads to accurate discrimination of oil/fat samples in different groups or categories. The water peak at 1440 nm was used for the identification of heat-sum classes. With the increase in heating extent, water content present in oil/fat sample was evaporated that, in turn, reveal the characteristic NIR bands for C–H bonds for the precise identification of heat-sum classes. For animal fats, polar sensitivity values were observed to be lowered compared to vegetable oils. (Bázár, Szabó, and Romvári 2010). Thus, based on polar sensitivity values, it can be concluded that vegetable oils are sensitive to thermal degradation compared to animal fats. In addition, method used to identify the extent of oil/fat heating based on water peak at 1440 nm can also be successfully employed for the rapid identification of thermal degradation of other types of edible oils. In addition, researchers have also collected visible-Near infrared (VIS-NIR) spectra of virgin olive oil samples subjected to thermal treatment at 180 °C for different time intervals. This spectral data was explained with PLS modeling to identify the principal influential regions. The critical variations in response to thermal treatment were reported to be in a band ranges from 2200 to 1325 cm^{-1} (Maggio et al. 2011). Furthermore, VIS/NIRS in conjunction with PLS was also employed for the prediction of olive oil stability. The performance of olive oil stability index model was found to be satisfactory with RPD values of 3.30 and 3.02, SEP being 6.68 and 7.38. Satisfactory predictive models were also reported for the prediction of FFAs (RPD = 3.14), PV (RPD = 2.84), and CD (RPD = 2.56) content of olive oil under thermal stress (Sánchez, Moreda, and García 2013). Recently, rice bran oil was heated from 25 °C to 120 °C and

Table 2. Summary of application of NIR spectroscopy for determination of thermal degradation of oils and fats.

Sample (n)	Treatment	Spectrometer, Spectral range, resolution	Attributes	Preprocessing	Multivariate analysis	Remarks	Reference
Refined sunflower oil (42)	170-180 °C and 200-210 °C for 60 h	NEOTEC 6450 Research Composition Analyze, 1100-2500 nm, 2 nm	TPC, Polymer contents and FA composition	Second derivative	Multiple regression analysis (computer program)	Efficient models were developed based on the NIRS and MLR (R = 0.994-0.999)	El-Rafey et al. (1988)
Soya bean, peanut, and palm oil (50 in calibration set)	190 °C for 60h (21 h with foodstuffs)	FT-NIR universal spectrometer from Buhler, 4000-10000 cm⁻¹	Total polar parts	Normalization and first derivative	PLS (bcap 6.0-software)	NIR reported to efficiently substitute column chromatography to determine total polar parts	Hein, Henning, and Isengard (1998)
Deep frying fats (50)	Samples used for deep frying were collected from canteens, snack bars and restaurants	Buhler/BUECHI FT-NIR spectrometer, 10000-4000 cm⁻¹	AV, TPM, DPTG and FOS values	First and second derivative	MPLS (NIRVIS/NIRCAL software ver. 2.0)	Addition of sample in calibration set recommended to improve model performance	Büning-Pfaue and Kehraus (2001)
Soybean oils with three levels of linolenic acid (141)	Initial frying temperature:190 °C for 165 s for 6 h per day for 23 days.	LabSpec reflectance spectrometer, 350-2500 nm	FFA, TPC and CDA	–	PLS (Unscrambler 9.6)	Efficient method to determine the FFA (R^2 = 0.973) TPM (R^2 = 0.984) and CDA (R^2 = 0.902)	Gerde et al. (2007)
Partially hydrogenated soy-based frying oil(103)	190°C for 8 h	Foss NIRSystems model 6500 scanning spectrometer, 400-2500 nm	TPM and FFAs	First and second derivative	FSMLR and PLS (Spectral analysis software NSAS, ver. 3.53)	Performance of FSMLR models were better than PLS models in1100-2500 nm.	Ng, Wehling, and Cuppett (2007)
Soy-based frying oil (186)	Various foods fried at 190°C for 8 h	Foss NIRSystems model 6500 scanning spectrometer, 400-2500 nm	TPM and FFAs	First and second derivative	FSMLR and PLS (NSAS software)	Frying different foods in oil had no impact on the reliability of TPM and FFA determination	Ng, Wehling, and Cuppett (2011)
Rapeseed, sunflower seed oil, pig and goose fat (256)	140, 150, 160, 165, 170, 175 and 180°C for 36h	FOSS NIRSystem 6500 spectrometer, 800-2400 nm, 2 nm	AV, PV, Carbonyl number, pAnV, TPM, DPTG	Second derivative	MPLS (WinISI II ver. 1.5 spectral analytical program)	Estimation of AV, PV, pAnV and TPM meet practical requirements while prediction of polymer content and CV was less satisfactory	Szabó et al. (2010)
Sunflower seed oil, rapeseed oil, lard and goose fat (252)	140, 150, 160, 165, 170, 175 and 180 °C for 36 h	FOSS NIRSystems 6500 spectrometer, 1100-2500 nm, 2 nm	Classification of samples on the basis of heat treatment	Second derivative	Polar Qualification System (QS32 Evaluation Software)	Vegetable oils experienced more prominent deterioration during heating compared to animal fats	Bázár, Szabó, and Romvári (2010)
Refined hazelnut and peanut oils (156)	Dough frying for 5 and 35 h	Bruker multi-purpose analyzer FT-NIR spectrometer, 780-2500 nm, 8 cm⁻¹	FFAs, TPM, VISC and smoke points	Straight line subtraction	PLS (OPUS 5.5 software)	NIRS-PLS reported to be effective in predicting FFA (r = 92.58), TPM (r = 94.61), VISC (r = 81.95) and smoke point (r = 84.07)	Öğütcü et al. (2012)

Table 2. Continued.

Sample (n)	Treatment	Spectrometer, Spectral range, resolution	Attributes	Preprocessing	Multivariate analysis	Remarks	Reference
Olive, sunflower seed, corn, and Seeds oil (369)	At 190°C with/without foodstuff for several hours,	Bruker Multipurpose Analyzer (MPA) FT-NIR spectrometer, 15,000–3800 cm⁻¹, 8 cm⁻¹	PTG	First derivative	PLS (iPLS and UVE-PLS) (Matlab7.7.0)	Global PLS model was recommended for the determination of PTG	Kuligowski et al. (2012)
Fresh, used and abused fried fats and oils (400)	Collected from several fast food cafeterias, caterers and bakeries	Bruker MPA FT-NIR spectrometer, 12 4000–500 cm⁻¹, 8 cm⁻¹	TPC, DPTG, AnV, AV, FA, IV, monomeric oxidized tri-acylglycerols	First derivative and Vectornormalization	PLS (OPUS software ver. 7.2.)	Efficient models were developed for the prediction of all parameters	Gertz and Behmer (2014)
Two types of rapeseed oil (156)	Frozen French fries fried for 3 min at 80, 200 and 220 °C at an interval of 22 min for 7 h per day for 4 successive days	Foss NIRSystems model 6500 scanning spectrometer, 700–2500 nm, 2 nm	AV and TPC	First derivative and second derivative	PLS (Spectral analysis software NSAS, ver. 3.53)	Calibration models with very high accuracy were reported for prediction of various parameters	Ma et al. (2014)
Mixture of several vegetable oils (144)	Potato frying at 105 °C-180 °C for 6 h a day for 3 successive days	A MPA-TM FTNIR system, 12000–4000 cm⁻¹, 4 cm⁻¹	CV	Second derivative, SNV and MSC	PLS (OMNIC 7.3 and TQ Analyst 7.2)	PLS model developed using pretreated spectra (9702 cm⁻¹ to 4531 cm⁻¹) performed best for the prediction of CV	Wang et al. (2014)
Mixture of various oils (126)	105 °C–190 °C for 8 h a day for 3 consecutive days	Bruker FTNIR spectrometer, 12000–4000 cm⁻¹, 4 cm⁻¹	PC	Savitzky-Golay smoothing, Norris derivative smoothing, first and second derivative	PLS (TQ Analyst 7.2)	The optimal PLS calibration was obtained for the prediction of PC	Chen et al. (2015b)
Rice bran oils from Brazil, Uruguay, and Thailand	25 °C to 120 °C with increment of 20 °C	microNIR JDSU spectrometer, 900 – 1680 nm Ocean Optics UV-Vis spectrometer, 200–800 nm, 1 nm	γ- oryzanol, tocopherol, and oxidation products	Baseline correction, Savitzky-Golay smoothing,	Parallel Factor Analysis (Matlab version 3.1)	Reduction in antioxidants start at 70 °C and pronounced increase in oxidation products start after 90 °C.	Rosa et al. (2019)
Soybean oils mixed with antioxidants	French fries cooked at 180 °C, same oil used for five days with same cooking procedure	XDS Rapid Content, Foss NIR spectrometer, 400–2500 nm	AV, PV, pAnV, TPC, VISC, Conjugated diene and triene, oxidative stability, FA composition, color, sensory analysis	–	PCA (Python 3.6)	NIRS proved to be an efficient technique to monitor quality change of oils that also present a good consistency with physicochemical indices of oil samples	Li et al. (2021)

NIR, near infrared; FT-NIR, Fourier transform-near infrared; SNV, standard normal variate; MSC, multiplicative scatter correction; AnV, anisidine value; IV, iodine value; PV, peroxide value; FFAs, free fatty acids; VISC, viscosity; TPC, total polar compound; PTG, polymer triacylglyceride; CV, carbonyl value; AV, acid value; DPTG, dimeric and polymeric triglycerides; TPM, total polar material; PLS, partial least square regression; FOS, food oil sensor; pAnV, para-anisidine value; FA, fatty acid; PC, polar compound; MPLS, modified partial least squares; FSMLR, forward stepwise multiple linear regression; CDA, conjugated dienoic acids.

NIR and UV-Vis spectrum was collected after an increment of 20 °C. Parallel Factor Analysis was employed to process the data. The reduction in antioxidants was reported to start at 70 °C and pronounced increase in oxidation products start after heating at 90 °C (Rosa et al. 2019). ATR-FTIR along with Raman spectroscopy was also employed to predict PV and AV content of soybean, rapeseed, sunflower and peanut oil heated twice for 30-35 min at 50 °C to 260 °C using data fusion technique. It was reported that successive projections algorithm along with data fusion results in best prediction of PV (R_c^2 =0.964, R_p^2 = 0.939 and RMSEC =0.060, RMSEP = 0.080) and AV (R_c^2 =0.955, R_p^2 = 0.919 and RMSEC =0.025, RMSEP = 0.027) (Liu et al. 2020).

Only a few studies have explored the application of NIR spectroscopy to identify thermal degradation of oils without food. The development and validation of high-performance calibration models for various parameters such as FFAs, PV, CD, TPM, AV, pAnV and DPTG by various researchers illustrate the interest of employing NIRS as a multiparametric technique. However, as mentioned previously, in real-world applications edible oils are exposed to a higher temperature while frying the food products that involve significantly complex reactions and resultant products compared to the thermally stressed oils without food. In the following section, application of NIRS has been discussed for the prediction of thermal degradation of frying media with food.

Application of near-infrared spectroscopy for determination of thermal degradation of frying oils and fats with food material

Several types of food products are developed by employing deep-frying in different types of oils and fats by small-scale food canteens and food industries. Application of rapid and nondestructive such as NIRS is desirable at industrial level as well as in small-scale food processing units to monitor and maintain the quality of frying media. Table 2 and Supplemental Table 1 summarizes thermal treatment employed by various researchers, oil samples and food material used for frying, oil degradation parameters studied in different studies, mathematical treatment and NIR instrumentation used by various researchers.

Previously, VIS-NIR spectroscopy altogether employed to develop efficient models for determination of VISC and monoglycerides (MG) content of frying oils obtained from commercial spring roll plant. Accurate NIR/VIS correlations were also observed for the DPTG (dimeric and polymeric triglycerides), MG (monoglycerides), DG (diglycerides), TG (triglycerides) and FFA measurements for these frying oils. However, a poor correlation was observed for the PV of frying oil (Engelsen 1997). Overall, VIS-NIR spectroscopy in conjunction with chemometrics can replace traditional method based on titration and chromatographic techniques for analyzing and optimizing thermal degradation of frying media used in commercial spring roll plant. In addition, NIR in conjunction with PLS was also used to predict the amount of polar components present in the palm, peanut and soya bean oil heated with various foodstuffs for different times at 190 °C. The correlation amongst the amount of polar parts determined by NIR and column chromatography was reported to be 0.996 (Hein, Henning, and Isengard 1998).

Previously, fiber optic probe connected to NIRS was also applied to predict the quality of deep-frying fats collected from various snack bars, canteens, and restaurants. An efficient determination of AV (SEC = 0.15, SEP (standard error of prediction) = 0.21, SECV (standard error of cross-validation) = 0.19, R^2 = 0.98) and food oil sensor values (SEC = 0.30, SEP = 0.30, SECV = 0.31, R^2 = 0.98) were reported. However for total polar material (SEC = 2.37, SEP = 1.60, SECV = 2.30, R^2 = 0.99) and DPTG (SEC = 0.91, SEP = 1.30, SECV = 1.05, R^2 = 0.98) poorer statistical terms of calibration were observed (Büning-Pfaue and Kehraus 2001). The application of a fiber optic probe seems to be more practical to collect the NIR spectra data of the actual site where the deep-frying of foods take place. This technique may result in the precise prediction of real-time degradation of frying oil. By using NIR data, PLS and one-out cross-validation, calibration models were established to predict TPM, FFA and conjugated dienoic acids (CDA) of soybean oils used to make French fries. The R^2 values between lab values and predicted values were reported to be 0.984 for TPM, 0.973 for FFA and 0.902 for CDA (Gerde et al. 2007). Thus, the capability of predicting different oil degradation parameters simultaneously with high accuracy proves NIRS a potentially valuable technique for quality assurance of frying media used in food preparation.

In another study, the NIR spectrum of fresh and highly degraded oil used for frying three different foodstuffs was collected. The absorption of degraded frying oil was less compared to the spectrum of fresh oil. The observed bands in the spectrum of oil and corresponding vibrations and functional groups are described in Figure 4. The best correlations 0.999 and 0.983 for TPM and FFA were observed in wavelength region 1100-2500 nm by applying forward stepwise multiple linear regression, respectively (Ng, Wehling, and Cuppett 2007; 2011). In an extension of this study by Ng, Wehling, and Cuppett (2007), it was reported that frying the several varieties of foods in soy-based oil does not affect the credibility of TPM and FFA prediction carried out by using NIR spectroscopy (Ng, Wehling, and Cuppett 2011). Thus, this finding indicates that a calibration model developed to predict the degradation of specific edible oil, used to fry particular food, can be successfully employed to predict the degradation of that specific oil irrespective of the food item being fried in it. However, still, a detailed study is required to prove if this finding is applicable to predict another degradation parameter of other types of oils used to fry different types of food material.

Furthermore, NIRS along with PLS was also employed to predict the quality of hazelnut and peanut oil used for frying dough. Best correlations were reported between reference data and NIR predicted data for frying oil properties such as FFA (r = 92.58, RMSEP = 0.121), TPM (r = 94.61, RMSEP = 3.96) along with the physical properties namely, VISC (r = 81.95, RMSEP = 22.30) and smoke point (r = 84.07,

RMSEP = 8.74) (Öğütcü et al. 2012). In addition, FT-NIR in conjunction with PLS was also employed for the estimation of FFA values and PV of deep-frying oil samples collected from college canteen and soybean oil used for frying different kind of foodstuffs. An efficient prediction results were reported for FFA content (R^2 = 0.948, SEP = 0.14 and RPD = 4.38) and PV (R^2 = 0.953, SEP = 4.15 and RPD = 4.36) of these deep-frying oil samples (Du et al. 2012). However, previously Engelsen (1997) has reported poor prediction of PV of frying oils obtained from commercial spring roll plant. This poor prediction may be attributed to the complexity of oil sample, frying procedure, oil sample replenishment and sample collection.

Previously, the "Joint Committee for the Analysis of Fats, Oils, Fatty products, Related Products and Raw Materials (GA FETT)" had also established FT-NIR based method for the prediction of polar compounds, PTG, AnV, and AV of fats and oils employed for frying of different kinds of foods. The R^2 for calibration model was reported to be 0.956-0.966 and root mean square error of estimation (RMSEE) ranges from 0.27 to 6.84 and RMSEP were in the range of 1.38 to 6.23. This method had also been verified with 11 laboratories (Gertz, Fiebig, and Hancock 2013). This is an appreciable effort made by the researchers to generate a standard FT-NIR based method for simultaneous determination of various oil degradation parameters. However, to implement this particular method with the same statistical performance, researchers need to install spectrometer with similar specification along with using the same operating parameters as mentioned in this study. Moreover, FT-NIR along with PLS was also employed to estimate degradation of 400 frying fats and oils samples fetched from various canteens, bakeries, and caterers. This method predicted various properties of deep-frying oils and fats such as TPC (R^2 = 97.6, RMSEP = 1.56%), DPTG (R^2 = 99.4, RMSEP = 0.47%), AnV (R^2 = 95.7, RMSEP = 6.8) and AV (R^2 = 97.4%, RMSEP = 0.17%) with high accuracy. This method was also successfully employed for monitoring total oxidized products of deep-frying oil and fat samples with R^2 = 96.8 and RMSEP = 0.57% (Gertz and Behmer 2014). This study was carried out to develop a universally applicable FT-NIR based method to detect the quality of all kinds of used frying oils at all stages of degradation. Therefore, about 400 samples of fresh, used as well as abused fried fats and oils from several fast-food restaurants, bakeries, caterers, or industrial producers were included in this study. However, successful transfer with efficient performance of this method from one laboratory to another laboratory is still a major challenge that need to be considered.

In another study, NIR along with PLS was also employed to predict the degradation of rapeseed oil samples obtained after deep frying frozen French fries using disposable glass test tube of 13 mm diameter. Calibration models were established using PLS regression with full cross-validation for the prediction of AV (R^2 = 0.99, SECV = 0.17 mg KOH/g and SEP = 0.17 mg KOH/g) and TPC (R^2 = 0.98, SECV = 1.25% and SEP = 1.04%) with reasonable accuracy (Ma et al. 2014). This study was again carried out to develop a practical NIR model for prediction of AV and TPC. Thus, two different types of rapeseed oils namely, refine and unrefined heated at different temperature were considered in this study. In addition, the use of disposable glass test tube of 13 mm diameter as a sample holder makes this technique more convenient as the washing of sample holder after every use is quite impractical and the infusion of repeated heated oil with high viscosity is easy in these tubes compared to quartz tube with a smaller diameter. FT-NIR spectroscopy combined with PLS was reported to predict carbonyl value for the mixture of various oils used for frying potato pieces. The performance of PLS model was observed to be best (RMSEC = 1.47 mmol kg^{-1} and RMSEP = 1.73 mmol kg^{-1}) with pretreated spectra from 9702 cm^{-1} to 4531 cm^{-1}. This method also reported to be an efficient method for the online prediction of the CV of frying oils (Wang et al. 2014). This spectral range covers the absorption bands ranging from 4513–5369 cm-1 assigned to the second overtone of the C=O stretching vibration related to carbonyl compounds. Thus, it is advisable to further narrow down spectral range close to the band responsible to carbonyl compounds to develop a statistical model with reasonable efficiency. That, in turn, will reduce the analysis time and cost of an instrument for this particular application.

In addition, FT-NIRS has also been employed to determine TPC, DPTG, and AnV of vegetable oils used for frying potato slices. NIRS data in conjunction with multivariate analysis demonstrated lowest thermal degradation in refined olive oil at 160°C during deep-frying and highest degradation in case of refined sunflower oil at 180°C during pan-frying. The blend of refined olive oil and refined palm oil has also shown high stability as compared to the blend of refined soybean oil and refined palm oil during 50 consecutive deep-frying sessions of potato fries at 180 °C (Zribi et al. 2014; 2016). The high stability of olive oil is attributed to its high level of monounsaturated fatty acids, especially oleic acid. In another study, FT-NIR spectroscopy combined with PLS was successfully employed for the prediction of polar components in a mixture of various oils used for frying potato chips. The optimal PLS calibration was obtained for estimation of polar components with r = 0.998 and RMSE = 1.0% in wavelength range 4963-4616, 5222-5037 and 5688-5499 cm^{-1}. The PLS calibration of these deep-fried oil samples was also validated with high efficiency (r = 0.997, RMSEP = 1.3%) (Chen et al. 2015b). Application of NIR spectroscopy for quality analysis of various frying oils has also been discussed in previously published reviews papers (Weisshear 2014; Wang et al. 2016; Juan and Shu-Yu 2016; Wang et al. 2017). Recently, soybean oils mixed with antioxidants were used for cooking French fries at 180 °C, same oil used for five days with same cooking procedure followed by observation of NIR spectrum of samples. PCA of oil spectrum ranging from 1100 to 2200 nm revealed NIRS as an efficient technique to monitor quality change of oils that also present a good consistency with physicochemical indices of oil samples (Li et al. 2021).

Some researchers have also considered frying oil with and without foodstuffs while developing NIR and FTIR

based models for the quality prediction of frying oils (Kuligowski et al. 2010b; Kuligowski et al. 2011; Kuligowski et al. 2012; Cascant, Garrigues, and de la Guardia 2017). For the calibration purpose, they have considered the samples of oils used for frying various food items and sample of thermally stressed oils without food material. In this way, the developed model can be employed to predict the different level of degradation of a wide range of oil samples including oils samples heated without food and oil samples employed for frying various food products. As mentioned previously, NIRS combined with PLS was employed to predict PTG content of four different types of vegetable oils heated with or without foodstuff. Variables used for establishing PLS models were selected by using interval PLS (iPLS) and uninformative variable elimination PLS (UVE-PLS). However, a PLS model established by using spectra of altogether four types of oils was recommended for the determination of PTG over the specific PLS models developed for individual oil. The global PLS model displayed an excellent performance in terms of high R^2 calibration $= 0.985$, R^2 cross-validation $= 0.984$, R^2 prediction $= 0.983$ and low root mean square error of calibration (RMSEC) $= 1.79\%$ (w/w), RMSEP $= 2.28\%$ (w/w) (Kuligowski et al. 2012). In another study, the total polar materials (TPM) content of heated olive oil and sunflower oil with and without foodstuff was predicted using ATR-MIR spectroscopy along with the PLS regression. This method provides satisfactory prediction results with relative root mean square error of prediction (RRMSEP) $= 11.8\%$ and RPD $= 5.8$ (Cascant, Garrigues, and de la Guardia 2017).

A PLS regression model was developed using ATR-FTIR spectra of thermally treated olive oil samples with and without various foodstuffs for the prediction of polymeric triacylglyceride (PTG). The PLS model based on expert knowledge variable selection approach exhibited high R^2 (0.991); low calibration error (1.14%), validation error (1.21%), and prediction error (1.40%) along with the low prediction bias (-0.0023% w/w) and calibration bias (-0.0017% w/w). The prediction capability of the developed model was reported to be independent of the kind of foodstuff used for frying (Kuligowski et al. 2010b).

ATR-MIR spectra of corn, olive and sunflower oil heated with and without various foodstuffs were employed for estimation of PTG content in these samples. An improved RMSEP was observed with PLS models based on the selected calibration sets (based on the type of oil) compare to the pooled calibration set that includes samples from all classes. PLS-DA also provided a correct classification of oil samples fried without food independent of their PTG content. However, this classification of oil samples fried with food was less evident (Kuligowski et al. 2011).

Determination of thermal degradation of frying oils and fats using Raman spectroscopy

Raman spectroscopy is based on the Raman scattering effects and molecular vibrations. It is an important analytical tool employed to fetch information regarding molecular fingerprinting as well as monitoring changes in the molecular bond structure. As a nondestructive method, it requires small sample size and minimum sample preparation. Raman spectroscopy along with chemometrics has also been used to detect the thermal degradation of edible oils and fats. Details regarding the sample, sample size, thermal treatment, instrument used, parameter analyzed, and multivariate analysis are mentioned in Supplemental Table 2.

Previously, the Raman spectra of 20 oil samples obtained from a Chinese spring roll plant was collected. The peaks observed at 1440 and 1302 cm^{-1} assigned to polymethylene scissoring and twisting, respectively. A sharp peak at 1656 cm^{-1} represented $C=C$ stretching of cis olefins. In carbonyl region, a weak peak at around 1748 cm^{-1} assigned to ester $C=O$ stretch. The peaks at 2925 and 2852 cm^{-1} assigned to polymethylene asymmetric and symmetric C-H stretching, respectively and a peak at 3009 cm^{-1} correspond to olefinic $=C–H$ stretching in the cis conformations. The full Raman spectra (300 to 3300 cm^{-1}) of these oil samples along with the PLS were used for the prediction of different quality parameters of oils with R^2 ranging 0.74 to 0.96 and RMSECV of 0.15 to 45.41. (Engelsen 1997). Further, individual peaks responsible for particular degradation product need to be identified followed by the development of PLS models using these regions. Another study investigated the time-dependent thermal degradation of edible oils at 160 °C using FT-Raman spectroscopy. The formation of conjugated double bonds and cis/trans isomerization was reported at 1655 cm^{-1} corresponding to the $C=C$ stretching region. This study has considered the model development using a particular Raman peak and a specific oil degradation product related to this peak. A high correlation ($R^2 = 0.96$) was observed between AnV and the time-dependent intensity changes in Raman bands at 1693 cm^{-1}. A good correlation ($R^2 = 0.92$) was also reported between K_{270} (spectrophotometric absorption at 270 nm represents the formation of conjugated trienes) and intensity of the band at 1635 cm^{-1} (Muik et al. 2005).

Furthermore, Raman spectroscopy was also employed to determine deterioration of carotenoids contents present in extra virgin olive oil while a microwave and conventional heating. Raman bands ranging from 900 to 1570 cm^{-1}, assigned to carotenoids, were entirely vanished at 203 °C with conventional heating, although these bands were spotted up to 225 °C during microwave heating. A precise calibration model ($R^2 = 0.99$, RMSEC $= 0.027$ and RMSEP $= 0.079$) was also established using PLS and Raman spectra (900-1570 cm^{-1}) for the prediction of carotenoid content of oil samples (El-Abassy, Donfack, and Materny 2010). The spectral collection time in this study was just 15 s and Raman spectroscope set up enable in-situ determination of oil quality while heating. Raman spectra of edible oils under thermal stress (sunflower, canola and olive oils) used to determine oxidative degradation of oils via the amount of increasing degradation products represented by particular band mainly at 1640 cm^{-1}. Application of PCA on spectral data revealed a significant difference in thermally degraded sunflower, canola, and olive oils. The least effect of thermal

treatment was observed in case of olive oil followed by canola oil attributed to a high level of oleic acid and antioxidants, respectively (Vaskova and Buckova 2015).

Raman spectroscopy was also employed to acquire the spectra of oil used for frying French fries at $185 \pm 5\,°C$ for 40 h. An increase in the Raman intensity of the oil samples was observed in spectral region 945 to $1600\,cm^{-1}$ that were mentioned to be associated with the formation of FFA (Ibrahim, Aziz, and Hashim 2017). A review published previously has also concluded that Raman spectroscopy can be successfully employed for assessing the oxidative degradation of vegetable oils under thermal stress (Jiménez-Sanchidrián and Ruiz 2016).

Previous studies have explored the short range of temperature and large temperature increments due to which it was difficult to analyze the degradation process as a function of temperature in detail. To overcome this shortcoming, in another study, Raman spectra of 8 different thermally stressed vegetable oils were collected. The oil samples were heated at $25\,°C$ to $205\,°C$ and samples were collected after every $10\,°C$ increments in temperature. The intense bands at $1301\,cm^{-1}$, $1439\,cm^{-1}$ (corresponding to C-H bending) and $1655\,cm^{-1}$ (representing $=$C-H bending) were employed to analyze the degradation of oil samples. The thermal treatment above $165\,°C$ leads to prominent changes in above-mentioned bands in case of olive, extra virgin olive and coconut oils. PCA was reported to be a robust and reliable method for monitoring oil stability compared to univariate analysis (Alvarenga et al. 2018). In another study, Raman spectra of various grades of olive oil heated at $190\,°C$ for 2 h was collected and the extra virgin olive oil was reported as stable oil as compared to the pomace and refined oil as it has shown least decrease in the intensity at $3008\,cm^{-1}$. The stability of the thermally stressed oil has been attributed to the presence of tocopherols (Carmona et al. 2014). Furthermore, the variations in the ratio of vibrational signals of unsaturated ($1265\,cm^{-1}$) to saturated fat ($1440\,cm^{-1}$) of thermally stressed edible oils were studied using surface enhanced Raman spectroscopy (SERS). It was observed that olive and coconut oil, contain less C$=$C double bonds, presented high Ea, are more stable against thermal degradation (Lam, Roy, and Chattopadhyay 2020).

Unlike infrared spectroscopy, Raman spectroscopy is least explored to study thermal degradation of edible oils. Only a few studies have explored the impact of thermal treatment and frying of food material on oil quality using Raman spectroscopy. Only a few researchers have explored degradation parameters of oil after thermal treatment and limited reports are available for the development of calibration model for prediction of degradation products by using chemometrics and specific peak assignments to the degradation products. Moreover, the availability of portable Raman devices can further enhance the in-situ analysis of thermal degradation of oil samples.

Conclusions and future perspective

Due to the enhanced consumer's awareness, the demand for quality control of deep-frying fats and oils has been increased from the last few decades. This led to an increase in the number of studies related to the application of vibrational spectroscopy in this field. These spectroscopic techniques have gained the attention of researchers due to their advantages such as fast measurement, no or minimum sample preparation, being reagent-free and cost-effective. All the studies reviewed in this paper reported that vibrational spectroscopic techniques (FTIR, NIR and Raman spectroscopy) in conjunction with chemometrics can successfully be used to detect, identify, and quantify the intensity of degradation of oils and fats used for repeated frying of various food products. NIR spectroscopy in conjunction with various statistical tools is reported as a fast and accurate method to determine various physiochemical parameters as an indicator of frying oil degradation. FTIR spectroscopy combined with chemometrics is also successfully employed to predict various physiochemical parameters of frying oil. The change in a particular FTIR band of oil samples under thermal stress exemplifies thermal degradation. An increase in the intensity of bands at $2852\,cm^{-1}$ and $2922\,cm^{-1}$ represents an increase in the FFA concentration and an intensification of the band at $966\,cm^{-1}$ and $987\,cm^{-1}$ corresponds to the formation of *trans* conjugated diene and isolated trans double bonds. However, Raman spectroscopy is still a least explored technique in this field. The comparison between the performances of these three techniques is observed to be unfeasible as the design of the experiment for all the studies was not similar. Different studies have considered different oil samples thermally stressed at different temperature and time, different types of oil samples were used for frying different food materials. In addition, the spectral data were processed with different mathematical treatments and different mathematical models were developed for qualitative and quantitative analysis of oil degradation. Moreover, IR and Raman spectroscopy possess their own advantages and disadvantages. In the case of IR spectroscopy, water exhibit strong interference that is absent in Raman spectroscopy. Whereas fluorescence interference is a major problem in Raman spectroscopy that is minor in IR spectroscopy. Few researchers have compared the performance of NIR and FTIR spectroscopy for quality prediction of deep-frying oils under the same conditions. Thermal stress of leads to major alterations in two band of MIR spectra ($1245–1180\,cm^{-1}$ and $1150–1030\,cm^{-1}$) and $2200–1325\,cm^{-1}$ in case of Vis-NIR spectra. Certain studies have also mentioned that among NIR/VIS spectroscopy as a good general-purpose technique for determining frying oil deterioration while comparing it with FTIR and FT-Raman spectroscopic techniques. NIR spectroscopy was also reported as a better technique because of its less cost compared to MIR instruments. The availability of portable NIR and Raman spectrometer allow its application for on-site monitoring of frying oil quality in restaurants and food industries. However, the efficient applicability of both FTIR and FT-NIR for determination frying oil quality has also been observed in the literature.

Despite these extensive studies, there are still a few gaps in this field that have to be satisfied. In literature, only a single study is reported on the simultaneous degradation

and measurement of frying oil quality by employing ATR-FTIR spectroscopy. Thus, considerable efforts have to be done to explore the feasibility of IR and Raman spectroscopy for real-time monitoring of frying oil quality. Only a few studies have reported the impact of deep-frying food on the predictive ability models of developed based on IR techniques. Thus, more studies need to be carried out to ascertain the effect of type of foods being fried on the predictive ability of mathematical model developed based on the IR and Raman spectral data. In addition, more experiments need to be performed based on large data set including different type of oils, different frying treatments and food materials to ensure the reliability and robustness of the models. Another important issue that needs to be addressed is poor device-to-device reproducibility while transferring spectral databases and chemometric models between devices of the same brand. The lack of validated spectral databases and inter-laboratory studies are other issues that need to be addressed. However, some degree of standardization is expected in near future due to the introduction of new hardware, development of sensitive probes, efficient optical systems, processing software and sophisticated processing algorithms to benefit inter-laboratory comparisons.

Funding

ORCID

Baojun Xu ⬤ http://orcid.org/0000-0003-0739-3735

References

Al-Degs, Y. S., M. Al-Ghouti, and N. Salem. 2011. Determination of frying quality of vegetable oils used for preparing falafel using infra-red spectroscopy and multivariate calibration. *Food Analytical Methods* 4 (4):540–9. doi: 10.1007/s12161-011-9201-9.

Alvarenga, B. R., F. A. N. Xavier, F. L. F. Soares, and R. L. Carneiro. 2018. Thermal stability assessment of vegetable oils by Raman spectroscopy and chemometrics. *Food Analytical Methods* 11 (7):1969–76. doi: 10.1007/s12161-018-1160-y.

Bázár, G., A. Szabó, and R. Romvári. 2010. NIR based quality control of frying fat samples by means of polar qualification system. *Food Control.* 21 (7):992–7. doi: 10.1016/j.foodcont.2009.12.017.

Beltrán, A., M. Ramos, N. Grané, M. L. Martín, and M. C. Garrigós. 2011. Monitoring the oxidation of almond oils by HS-SPME–GC–MS and ATR-FTIR: Application of volatile compounds determination to cultivar authenticity. *Food Chemistry* 126 (2):603–9. doi: 10.1016/j.foodchem.2010.11.058.

Berdeaux, O., S. Fontagné, E. Sémon, J. Velasco, J. L. Sébédio, and C. Dobarganes. 2012. A detailed identification study on high-temperature degradation products of oleic and linoleic acid methyl esters by GC-MS and GC-FTIR. *Chemistry and Physics of Lipids* 165 (3):338–47. doi: 10.1016/j.chemphyslip.2012.02.004.

Büning-Pfaue, H., and S. Kehraus. 2001. Application of near infrared spectroscopy (NIRS) in the analysis of frying fats. *European Journal of Lipid Science and Technology* 103 (12):793–7. doi: 10.1002/1438-9312(200112)103:12<793::AID-EJLT793>3.0.CO;2-D.

Carmona, M. Á., F. Lafont, C. Jiménez-Sanchidrián, and J. R. Ruiz. 2014. Raman spectroscopy study of edible oils and determination of the oxidative stability at frying temperatures. *European Journal of Lipid Science and Technology* 116 (11):1451–6. doi: 10.1002/ejlt.201400127.

Cascant, M. M., S. Garrigues, and M. de la Guardia. 2017. Comparison of near and mid infrared spectroscopy as green analytical tools for the determination of total polar materials in fried oils. *Microchemical Journal* 135:55–9. doi: 10.1016/j.microc.2017.07.012.

Chen, J. Y., H. Zhang, J. Ma, T. Tuchiya, and Y. Miao. 2015a. Determination of the degree of degradation of frying rapeseed oil using Fourier-transform infrared spectroscopy combined with partial least-squares regression. *International Journal of Analytical Chemistry* 2015:185367. doi: 10.1155/2015/185367.

Chen, X., X. Yu, Y. Wang, Y. Yang, and J. Zhang. 2015b. Determination of polar components in frying oils by Fourier-transform near-infrared spectroscopy. *Journal of Oleo Science* 64 (3):255–61. doi: 10.5650/jos.ess14227.

Choe, E., and D. B. Min. 2007. Chemistry of deep-fat frying oils . *Journal of Food Science* 72 (5):R77–R86. doi: 10.1111/j.1750-3841.2007.00352.x.

Craig, A. P., A. S. Franca, and J. Irudayaraj. 2015.Chapter 7: Vibrational spectroscopy for food quality and safety screening. In *High throughput screening for food safety assessment*, 165–94. Oxford,UK: Woodhead Publishing.

deMan, J. M. 1999. Chapter 2: Lipids. In *Principles of food chemistry*, eds A. K. Bhunia, M. S. Kim, and C. R. Taitt, 66–70. New York: Springer.

Du, R., K. Lai, Z. Xiao, Y. Shen, X. Wang, and Y. Huang. 2012. Evaluation of the quality of deep frying oils with Fourier transform near-infrared and mid-infrared spectroscopy. *Journal of Food Science* 77 (2):C261–266. doi: 10.1111/j.1750-3841.2011.02551.x.

Dubois, J., F. R. van de Voort, J. Sedman, A. A. Ismail, and H. R. Ramaswamy. 1996. Quantitative Fourier transform infrared analysis for anisidine value and aldehydes in thermally stressed oils. *Journal of the American Oil Chemists' Society* 73 (6):787–94. doi: 10.1007/BF02517956.

El-Abassy, R. M., P. Donfack, and A. Materny. 2010. Assessment of conventional and microwave heating induced degradation of carotenoids in olive oil by VIS Raman spectroscopy and classical methods. *Food Research International* 43 (3):694–700. doi: 10.1016/j.foodres.2009.10.021.

El-Rafey, H. H. A., J. Perédi, K. Kaffka, B. Náday, and A. Balogh. 1988. Possibilities of application of NIR technique in the analysis of oil-seeds and their derivatives - examination of used frying oil. *Fett Wissenschaft Technologie/Fat Science Technology* 90 (5):175–9. doi: 10.1002/lipi.19880900504.

Engelsen, S. B. 1997. Explorative spectrometric evaluations of frying oil deterioration. *Journal of the American Oil Chemists' Society* 74 (12):1495–508. doi: 10.1007/s11746-997-0068-2.

Falcó, I. P. R., N. G. Teruel, S. P. Moya, and M. L. M. Carratalá. 2012. Kinetic study of olive oil degradation monitored by Fourier transform infrared spectrometry. Application to oil characterization. *Journal of Agricultural and Food Chemistry* 60:11800–10.

Farhoosh, R., and S. M. R. Moosavi. 2008. Carbonyl value in monitoring of the quality of used frying oils. *Analytica Chimica Acta* 617 (1-2):18–21. doi: 10.1016/j.aca.2007.11.049.

Ganesan, K., K. Sukalingam, and B. Xu. 2019. Impact of consumption of repeatedly heated cooking oils on the incidence of various cancers- A critical review. *Critical Reviews in Food Science and Nutrition* 59 (3):488–505. doi:10.1080/10408398.2017.1379470. PMC: 28925728

Gerde, J. A., C. L. Hardy, C. R. Hurburgh, and P. J. White. 2007. Rapid determination of degradation in frying oils with near-infrared spectroscopy. *Journal of the American Oil Chemists' Society* 84 (6):519–22. doi: 10.1007/s11746-007-1068-y.

Gertz, C., and D. Behmer. 2014. Application of FT-NIR spectroscopy in assessment of used frying fats and oils. *European Journal of Lipid Science and Technology* 116 (6):756–62. doi: 10.1002/ejlt.201300270.

Gertz, C., H. Fiebig, and J. N. S. Hancock. 2013. FT-near infrared (NIR) spectroscopy – screening analysis of used frying fats and oils for rapid determination of polar compounds, polymerized triacylglycerols, acid value and anisidine value [DGF C-VI 21a (13)]. *European Journal of Lipid Science and Technology* 115:1197. doi: 10.1002/ejlt.201300221.

Goburdhun, D., S. B. Jhaumeer-Laulloo, and R. Musruck. 2001. Evaluation of soybean oil quality during conventional frying by FTIR and some chemical indexes. *International Journal of Food Sciences and Nutrition* 52:31–42.

Gonzaga, F. B., and C. Pasquini. 2006. A new method for determination of the oxidative stability of edible oils at frying temperatures using near infrared emission spectroscopy. *Analytica Chimica Acta* 570 (1):129–35. doi: 10.1016/j.aca.2006.03.109.

Hein, M., H. Henning, and H. Isengard. 1998. Determination of total polar parts with new methods for the quality survey of frying fats and oils. *Talanta* 47 (2):447–54. doi: 10.1016/S0039-9140(98)00148-9.

Hocevar, L., V. R. B. Soares, F. S. Oliveira, M. G. A. Korn, and L. S. G. Teixeira. 2012. Application of multivariate analysis in mid-infrared spectroscopy as a tool for the evaluation of waste frying oil blends. *Journal of the American Oil Chemists' Society* 89 (5):781–6. doi: 10.1007/s11746-011-1968-8.

Ibrahim, N., S. Abd Aziz, and N. Hashim. 2017. Oil quality monitoring during deep fat frying using Raman spectroscopy. *Acta Horticulturae* (1152):307–12. doi:10.17660/ActaHortic.2017.1152.41.

Innawong, B., P. Mallikarjunan, J. Irudayaraj, and J. E. Marcy. 2004. The determination of frying oil quality using Fourier transform infrared attenuated total reflectance. *LWT – Food Science and Technology* 37 (1):23–8. doi: 10.1016/S0023-6438(03)00120-8.

Jamwal, R., Amit, S. Kumari, B. Balan, S. Kelly, A. Cannavan, and D. K. Singh. 2021. Rapid and non-destructive approach for the detection of fried mustard oil adulteration in pure mustard oil via ATR-FTIR spectroscopy-chemometrics. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 244:118822. doi: 10.1016/j.saa.2020.118822.

Jiménez-Sanchidrián, C., and J. R. Ruiz. 2016. Use of Raman spectroscopy for analyzing edible vegetable oils. *Applied Spectroscopy Reviews* 51 (5):417–30. doi: 10.1080/05704928.2016.1141292.

Juan, L., and L. Shu-Yu. 2016. The research progress on near Infrared spectroscopy in the non-destructive detection of the quality of edible oil. *Food & Machinery* 11:225–8.

Ku, S. K., M. S. M. Ruhaifi, S. S. Fatin, M. Saffana, K. T. Anna, S. Das, and J. Kamsiah. 2014. The harmful effects of consumption of repeatedly heated edible oils: A short review. *La Clinica Terapeutica* 165:217–21.

Kuligowski, J., D. Carrion, G. Quintas, S. Garrigues, and M. de la Guardia. 2011. Sample classification for improved performance of PLS models applied to the quality control of deep-frying oils of different botanic origins analyzed using ATR-FTIR spectroscopy. *Analytical and Bioanalytical Chemistry* 399 (3):1305–14. doi: 10.1007/s00216-010-4457-2.

Kuligowski, J., D. Carrión, G. Quintás, S. Garrigues, and M. de la Guardia. 2012. Direct determination of polymerised triacylglycerides in deep-frying vegetable oil by near infrared spectroscopy using partial least squares regression. *Food Chemistry* 131 (1):353–9. doi: 10.1016/j.foodchem.2011.07.139.

Kuligowski, J., G. Quintás, S. Garrigues, and M. Guardia. 2010a. Monitoring of polymerized triglycerides in deep-frying oil by on-line GPC-FTIR spectrometry using the science based calibration multivariate approach. *Chromatographia* 71 (3-4):201–9. doi: 10.1365/s10337-009-1426-z.

Kuligowski, J., G. Quintás, S. Garrigues, and M. de la Guardia. 2010b. Direct determination of polymerized triglycerides in deep-frying olive oil by attenuated total reflectance-Fourier transform infrared spectroscopy using partial least squares regression. *Analytical and Bioanalytical Chemistry* 397 (2):861–9. doi: 10.1007/s00216-010-3546-6.

Lalas, S. 2009. Chapter 4: Quality of frying oil. In Sahin, S., Sumnu, S. G.(Eds.), *Advances in deep-fat frying of foods*, 58–63. Boca Raton, FL: CRC Press.

Lam, H.-Y., P. K. Roy, and S. Chattopadhyay. 2020. Thermal degradation in edible oils by surface enhanced Raman spectroscopy calibrated with iodine values. *Vibrational Spectroscopy* 106:103018. doi: 10.1016/j.vibspec.2019.103018.

Li, P., X. Yang, W. J. Lee, F. Huang, Y. Wang, and Y. Li. 2021. Comparison between synthetic and rosemary-based antioxidants for the deep frying of French fries in refined soybean oils evaluated by chemical and non-destructive rapid methods. *Food Chemistry* 335: 127638 doi: 10.1016/j.foodchem.2020.127638.

Liu, H., Y. Chen, C. Shi, X. Yang, and D. Han. 2020. FT-IR and Raman spectroscopy data fusion with chemometrics for simultaneous determination of chemical quality indices of edible oils during thermal oxidation. *Lwt* 119:108906. doi: 10.1016/j.lwt.2019.108906.

Ma, J., H. Zhang, T. Tuchiya, Y. Miao, and J. Y. Chen. 2014. Rapid determination of degradation of frying oil using near-infrared spectroscopy. *Food Science and Technology Research* 20 (2):217–23. doi: 10.3136/fstr.20.217.

Maggio, R. M., E. Valli, A. Bendini, A. M. Gómez-Caravaca, T. G. Toschi, and L. Cerretani. 2011. A spectroscopic and chemometric study of virgin olive oils subjected to thermal stress. *Food Chemistry* 127 (1):216–21. doi: 10.1016/j.foodchem.2010.12.018.

Man, Y. B. C., and I. Jaswir. 2000. Effect of rosemary and sage extracts on frying performance of refined, bleached and deodorized (RBD) palm olein during deep-fat frying. *Food Chemistry* 69:301–7.

Man, Y. B. C., and G. Setiowaty. 1999. Determination of anisidine value in thermally oxidized palm olein by Fourier transform infrared spectroscopy. *Journal of the American Oil Chemists' Society* 76 (2): 243–7. doi: 10.1007/s11746-999-0225-x.

Meenu, M., Q. Cai, and B. Xu. 2019. A critical review on analytical techniques to detect adulteration of extra virgin olive oil. *Trends in Food Science & Technology* 91:391–408. doi: 10.1016/j.tifs.2019.07.045.

Meenu, M., U. Kamboj, A. Sharma, P. Guha, and S. Mishra. 2016. Green method for determination of phenolic compounds in mung bean (*Vigna radiata* L.) based on near-infrared spectroscopy and chemometrics. *International Journal of Food Science & Technology* 51 (12):2520–7. doi: 10.1111/ijfs.13232.

Meenu, M., and B. Xu. 2019. Application of vibrational spectroscopy for classification, authentication and quality analysis of mushroom: A concise review. *Food Chem* 289:545–57. doi: 10.1016/j.foodchem.2019.03.091.

Meulenaer, B. D., R. Medeiros, 2016. and, and F. Mestdagh. Chapter 18: Acrylamide in Potato Products. In J. Singh, L. Kaur (Eds.), *Advances in Potato Chemistry and Technology*, 527–62. Academic Press, USA.

Moharam, M. A., and L. M. Abbas. 2010. A study on the effect of microwave heating on the properties of edible oils using FTIR spectroscopy. *African Journal of Microbiology Research* 4:1921–7.

Moreno, M. C. M. M., D. M. Olivares, F. J. A. López, J. V. G. Adelantado, and F. B. Reig. 1999a. Determination of unsaturation grade and trans isomers generated during thermal oxidation of edible oils and fats by FTIR. *Journal of Molecular Structure* 482-483: 551–6.

Moreno, M. C. M. M., D. M. Olivares, F. J. A. Lopez, J. V. G. Adelantado, and F. B. Reig. 1999b. Analytical evaluation of polyunsaturated fatty acids degradation during thermal oxidation of edible oils by Fourier transform infrared spectroscopy. *Talanta* 50:269–75.

Moros, J., M. Roth, S. Garrigues, and M. de la Guardia. 2009. Preliminary studies about thermal degradation of edible oils through attenuated total reflectance mid-infrared spectrometry. *Food Chemistry* 114 (4):1529–36. doi: 10.1016/j.foodchem.2008.11.040.

Mossoba, M. M., R. E. McDonald, D. J. Armstrong, and S. W. Page. 1991. Hydrogenation of soybean oil: A thin-layer chromatography and gas chromatography/matrix isolation/Fourier transform infrared

study. *Journal of Agricultural and Food Chemistry* 39 (4):695–9. doi: 10.1021/jf00004a014.

Muik, B., B. Lendl, A. Molina-Díaz, and M. J. Ayora-Cañada. 2005. Direct monitoring of lipid oxidation in edible oils by Fourier transform Raman spectroscopy. *Chemistry and Physics of Lipids* 134 (2): 173–82. doi: 10.1016/j.chemphyslip.2005.01.003.

Navarra, G., M. Cannas, M. D'Amico, D. Giacomazza, V. Militello, L. Vaccaro, and M. Leone. 2011. Thermal oxidative process in extravirgin olive oils studied by FTIR, rheology and time-resolved luminescence. *Food Chemistry* 126 (3):1226–31. doi: 10.1016/j.foodchem.2010.12.010.

Ng, C. L., R. L. Wehling, and S. L. Cuppett. 2007. Method for determining frying oil degradation by near-infrared spectroscopy. *Journal of Agricultural and Food Chemistry* 55 (3):593–7. doi: 10.1021/jf061841d.

Ng, C. L., R. L. Wehling, and S. L. Cuppett. 2011. Near-infrared spectroscopic determination of degradation in vegetable oils used to fry various foods. *Journal of Agricultural and Food Chemistry* 59 (23): 12286–90. doi: 10.1021/jf202740e.

Öğütcü, M., B. Aydeniz, M. B. Büyükcan, and E. Yılmaz. 2012. Determining frying oil degradation by near infrared spectroscopy using chemometric techniques. *Journal of the American Oil Chemists' Society* 89 (10):1823–30. doi: 10.1007/s11746-012-2087-x.

Pedreschi, F., P. Moyano, K. Kaack, and K. Granby. 2005. Color changes and acrylamide formation in fried potato slices. *Food Research International* 38 (1):1–9. doi: 10.1016/j.foodres.2004.07.002.

Pinto, R. C., N. Locquet, L. Eveleigh, and D. N. Rutledge. 2010. Preliminary studies on the mid-infrared analysis of edible oils by direct heating on an ATR diamond crystal. *Food Chemistry* 120 (4): 1170–7. doi: 10.1016/j.foodchem.2009.11.053.

Poiana, M., E. Alexa, M. Munteanu, R. Gligor, D. Moigradean, and C. Mateescu. 2015. Use of ATR-FTIR spectroscopy to detect the changes in extra virgin olive oil by adulteration with soybean oil and high temperature heat treatment. *Open Chemistry* 13 (1): 689–98. doi: 10.1515/chem-2015-0110.

Poiana, M., G. A. Mousdis, C. A. Georgiou, E. Alexa, D. Moigradean, and I. Cocan. 2013. Detection of thermal processing impact on olive and sunflower oil quality by FTIR spectroscopy. *Journal of Agroalimentary Processes and Technologies* 19:48–56.

Ramer, G., and B. Lendl. 2013. Attenuated Total Reflection Fourier Transform Infrared Spectroscopy. In *Encyclopedia of analytical chemistry*, edited by R. A. Meyers and R. A. Meyers. Chichester, UK: John Wiley and Sons, Ltd. doi: 10.1002/9780470027318.a9287.

Rampazzo, V., L. F. Ribeiro, P. M. Santos, M. C. M. Ferreira, E. Bona, G. M. Maciel, and C. W. I. Haminiuk. 2018. Multi-block analysis coupled with GC-FID and ATR-MIR for the evaluation of thermal degradation in vegetable oils. *Journal of Chromatography. B, Analytical Technologies in the Biomedical and Life Sciences* 1081-1082:118–25. doi: 10.1016/j.jchromb.2018.02.031.

Rodriguez-Saona, L. E., and M. E. Allendorf. 2011. Use of FTIR for rapid authentication and detection of adulteration of food. *Annual Review of Food Science and Technology* 2:467–83. doi: 10.1146/annurev-food-022510-133750.

Rohman, A. 2017. The use of infrared spectroscopy in combination with chemometrics for quality control and authentication of edible fats and oils: A review. *Applied Spectroscopy Reviews* 52 (7):589–604. doi: 10.1080/05704928.2016.1266493.

Rosa, L. N., A. Coqueiro, P. H. Março, and P. Valderrama. 2019. Thermal rice oil degradation evaluated by UV-Vis-NIR and PARAFAC . *Food Chemistry* 273:52–6. doi: 10.1016/j.foodchem.2018.03.065.

Saguy, I. S., and D. Dana. 2003. Integrated approach to deep fat frying: Engineering, nutrition, health and consumer aspects. *Journal of FoodEngineering* 56 (2-3):143–52. doi: 10.1016/S0260-8774(02)00243-1.

Sanahuja, A. B., M. S. P. Moya, S. E. M. Pérez, N. G. Teruel, and M. L. M. Carratalá. 2009. Classification of four almond cultivars using oil degradation parameters based on FTIR and GC data. *Journal of the American Oil Chemists' Society* 86:51–8.

Sánchez, J. A. C., W. Moreda, and J. M. García. 2013. Rapid determination of olive oil oxidative stability and its major quality parameters using Vis/NIR transmittance spectroscopy. *Journal of Agricultural and Food Chemistry* 61 (34):8056–62. doi: 10.1021/jf4021575.

Shen, Y., S. Chen, R. Du, Z. Xiao, Y. Huang, B. A. Rasco, and K. Lai. 2014. Rapid assessment of the quality of deep frying oils used by street vendors with Fourier transform infrared spectroscopy. *Journal of Food Measurement and Characterization* 8 (4):336–42. doi: 10.1007/s11694-014-9194-3.

Stevens, J. F., and C. S. Maier. 2008. Acrolein: Sources, metabolism, and biomolecular interactions relevant to human health and disease. *Molecular Nutrition & Food Research* 52 (1):7–25. doi: 10.1002/mnfr.200700412.

Szabó, A., G. Bázár, L. Locsmándi, and R. Romvári. 2010. Quality alterations of four frying fats during long-term heating (conventional analysis and NIRS calibration). *Journal of Food Quality* 33 (1): 42–58. doi: 10.1111/j.1745-4557.2009.00285.x.

Talpur, M. Y., Hassan, S. S. S. T. H. Sherazi, S. A. Mahesar, H. Kara, and A. A. Kandhro, Sirajuddin. 2015. A simplified FTIR chemometric method for simultaneous determination of four oxidation parameters of frying canola oil. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* 149:656–61. doi: 10.1016/j.saa.2015.04.098.

Tena, N., R. Aparicio-Ruiz, and D. L. García-González. 2013. Time course analysis of fractionated thermoxidized virgin olive oil by FTIR spectroscopy. *Journal of Agricultural and Food Chemistry* 61 (13):3212–8. doi: 10.1021/jf305422d.

Tena, N., R. Aparicio, and D. L. García-González. 2009. Thermal deterioration of virgin olive oil monitored by ATR-FTIR analysis of trans content. *Journal of Agricultural and Food Chemistry* 57 (21): 9997–10003. doi: 10.1021/jf9012828.

Valdés, A. F., and A. B. Garcia. 2006. A study of the evolution of the physicochemical and structural characteristics of olive and sunflower oils after heating at frying temperatures. *Food Chemistry* 98 (2): 214–9. doi: 10.1016/j.foodchem.2005.05.061.

Vaskova, H., and M. Buckova. 2015. Thermal degradation of vegetable oils: Spectroscopic measurement and analysis. *Procedia Engineering* 100:630–5. doi: 10.1016/j.proeng.2015.01.414.

Velasco, J., S. Marmesat, 2009. and, and M. C. Dobarganes. Chapter 3-Chemistry of Frying. In Sahin, S., Sumnu, S. G.(Eds.), *Advances in Deep-Fat Frying of Foods*, 34–41. CRC Press.

Vlachos, N., Y. Skopelitis, M. Psaroudaki, V. Konstantinidou, A. Chatzilazarou, and E. Tegou. 2006. Applications of Fourier transform-infrared spectroscopy to edible oils. *Analytica Chimica Acta* 573-574:459–65. doi: 10.1016/j.aca.2006.05.034.

Wang, L., D. Sun, H. Pu, and J. Cheng. 2017. Quality analysis, classification, and authentication of liquid foods by near-infrared spectroscopy: A review of recent research developments. *Critical Reviews in Food Science and Nutrition* 57 (7):1524–38. doi: 10.1080/10408398.2015.1115954.

Wang, P., J. Sun, T. Zhang, and W. Liu. 2016. Vibrational spectroscopic approaches for the quality evaluation and authentication of virgin olive oil. *Applied Spectroscopy Reviews* 51 (10):763–90. doi: 10.1080/05704928.2016.1176034.

Wang, Y., X. Yu, X. Chen, Y. Yang, and J. Zhang. 2014. Application of Fourier transform near-infrared spectroscopy to the quantification and monitoring of carbonyl value in frying oils. *Analytical Methods* 6 (19):7628–33. doi: 10.1039/C4AY00703D.

Weisshear, R. 2014. Quality control of used deep-frying oils. *European Journal of Lipid Science and Technology* 116:716–22.

Zahir, E., R. Saeed, M. A. Hameed, and A. Yousuf. 2017. Study of physicochemical properties of edible oil and evaluation of frying oil quality by Fourier transform-infrared (FT-IR) spectroscopy. *Arabian Journal of Chemistry* 10:S3870–S3876. doi: 10.1016/j.arabjc.2014.05.025.

Zeb, A. 2019. Chapter 5: Chemistry of fried foods. In *Food frying: Chemistry, biochemistry and safety*, 124–5. John Wiley & Sons.doi: 10.1002/9781119468417.ch5.

Zhang, H., J. Ma, Y. Miao, T. Tuchiya, and J. Y. Chen. 2015. Analysis of carbonyl value of frying oil by Fourier transform infrared spectroscopy. *Journal of Oleo Science* 64 (4):375–80. doi: 10.5650/jos.ess14201.

Zhang, Q., A. S. M. Saleh, J. Chen, and Q. Shen. 2012. Chemical alterations taken place during deep-fat frying based on certain reaction products: A review. *Chemistry and Physics of Lipids* 165 (6): 662–81. doi: 10.1016/j.chemphyslip.2012.07.002.

Zribi, A., H. Jabeur, F. Aladedunye, A. Rebai, B. Matthäus, and M. Bouaziz. 2014. Monitoring of quality and stability characteristics and fatty acid compositions of refined olive and seed oils during repeated pan- and deep-frying using GC, FT-NIRS, and chemometrics. *Journal of Agricultural and Food Chemistry* 62 (42):10357–67. doi: 10.1021/jf503146f.

Zribi, A., H. Jabeur, B. Matthäus, and M. Bouaziz. 2016. Quality control of refined oils mixed with palm oil during repeated deep-frying using FT-NIRS, GC, HPLC, and multivariate analysis. *European Journal of Lipid Science and Technology* 118 (4):512–23. doi: 10. 1002/ejlt.201500149.solve find the solution to (a problem or question) or understand the meaning of More (Definitions, Synonyms, Translation)