

## Effect of temperature on frying oils: infrared spectroscopic studies

Muhammed Mizher Radhi ·  
Emad A. Jaffar Al-Mulla · Wisam H. Hoiwdy

Received: 23 August 2012 / Accepted: 20 September 2012  
© Springer Science+Business Media Dordrecht 2012

**Abstract** Frying oils were studied by Fourier-transform infrared (FT-IR) spectroscopy, in the range 4,000–200  $\text{cm}^{-1}$ , at different temperatures, in the liquid and solid states. The infrared spectrum at 15 °C was similar to that at 200 °C. The band at 730  $\text{cm}^{-1}$  which was assigned to the rocking mode of ( $-\text{CH}_2$ ) disappeared at higher temperature because of the rotational isomerism which occurred in the oil structure. The activation energy ( $E_a$ ) of the disappearing ( $-\text{CH}_2$ ) band, calculated by use of the chemical dynamic method using the Arrhenius equation, is 8.45  $\text{kJ mol}^{-1}$ . The enthalpy difference ( $\Delta H$ ) between the two rotational isomer bands of the conformational structures of the oil at 730 and 1,790  $\text{cm}^{-1}$ , at different high temperatures, was also calculated, by use of the Van't Hoff equation; the value obtained was  $-10.85 \text{ kJ mol}^{-1}$ .

**Keywords** Palm oil · Infrared spectroscopy · Isomerism · Different temperature

---

M. M. Radhi (✉)  
Department of Radiology, College of Health and Medical Technology, Baghdad, Iraq  
e-mail: mmradhi@yahoo.com

E. A. Jaffar Al-Mulla  
Department of Chemistry, College of Science, University of Kufa, P.O. Box 21,  
An-Najaf 54001, Iraq

E. A. Jaffar Al-Mulla  
Department of Chemistry, Faculty of Science, Universiti Putra Malaysia,  
43400 UPM Serdang, Selangor, Malaysia

W. H. Hoiwdy  
Department of Chemistry, College of Education, University of Al-Qadysia, Al Diwaniyah, Iraq

## Introduction

In previous studies, oils of many different compositions and origins have been investigated by use of a variety of methods, including spectral and analytical techniques, to determine the best ways of preventing damage to oils during their use in cooking or during storage. Physical properties and constants, particularly for isomerism of the oils, have been determined by use of infrared spectroscopy [1–3].

Soon et al. [4, 5] studied oil from sunflower seeds and from beans by use of NMR spectroscopy. Hard fat has also been studied by use of the same technique to determine its physical characteristics [6]; further studies have investigated the isomerization potential of the acids in fat, butter, and cream [7, 8]. It has been observed that trans isomers are more stable than cis isomers.

When sunflower oil was heated to 220 °C several times new chemical compounds were observed; these new species were blamed for changes in the composition of the oil as a result of oxidation of polyunsaturation [9, 10].

Analysis also revealed new structures of the metal compounds present in the oil; there is a low probability of the composition of monomers in the oil ring. The carboxylic acid content of fat or oil is also affected by raising the temperature [11, 12]. It has been shown that when sunflower oil is heated at high temperature the proportion of oleic acid is increased and that of linoleic acid is reduced.

On the basis of this background, it can be concluded that high temperatures during cooking will lead to changes in the composition of oil which will be reflected in alteration of their effects on the human body.

In this paper we discuss the infrared spectra of some vegetable oils heated at high and low temperatures. Changes in composition and changes in the physical characteristics of the oils, for example activation energy and enthalpy of isomerization, are also discussed.

## Experimental

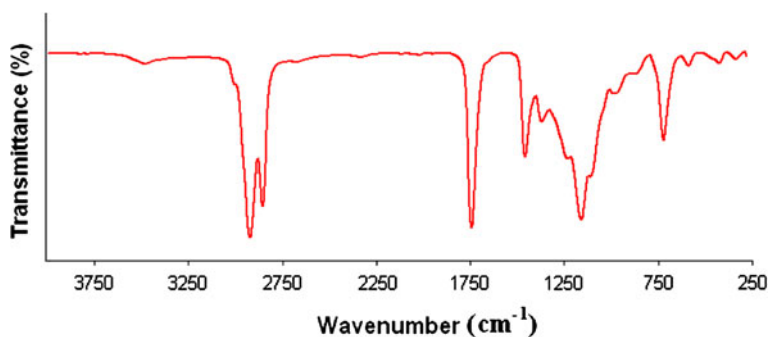
### Materials

Palm oil was a commercial product purchased by a local supplier from (Ngo Chew Hong Oils and Fats (M) Sdn. Bhd., Malaysia). Corn oil and sunflower oil were obtained from Mumbai, Maharashtra, India.

### Techniques

#### *Fourier-transform infrared (FT-IR) spectroscopy*

The infrared spectra of the oils were recorded on a Perkin-Elmer FT-IR 1650 spectrophotometer, in the region 4,000–200  $\text{cm}^{-1}$ , using CsI windows for both liquid and solid phases. Temperature treatment of the solid and liquid phases was performed by use of a VLT-2 variable temperature cell type fitted with a chromel–alumel thermocouple wire with a constantan wire lead.



**Fig. 1** FT-IR spectrum of frying oil (palm oil)

## Results and discussion

### Assignment of fundamental vibration frequencies of bands

Figure 1 shows the FT-IR spectrum of frying oil (palm oil) in the liquid phase at room temperature. In general, characteristic bands in the FT-IR spectra of oils were observed at 2912, 2853, and 1744  $\text{cm}^{-1}$ , resulting from C–H asymmetric stretching of  $\text{CH}_2$ , C–H symmetric stretching of  $\text{CH}_2$ , and C=O stretching of ester (glyceride), respectively.

The intensities of some of the vibrational frequency bands of the oil samples increased with increasing temperature whereas the intensities of others decreased or disappeared, for example that at 720  $\text{cm}^{-1}$ , assigned to the frequency of vibration of the rocking mode, as shown in Table 1.

**Table 1** Assignment of fundamental vibration frequencies of frying oil (palm oil) in the liquid phase

Vibration assignment	
Increasing bands	
3,020 (m.b.sh)	$\nu_a$ ( $\text{CH}_3$ )
2,919 (v.s.)	$\nu_a$ ( $\text{CH}_3$ )
1,790 (v.w.sh)	$\nu_s$ C=C
1,470	$b_a$ ( $\text{CH}_3$ )
1,370 (w.b.sh.)	$b_a$ ( $\text{CH}_3$ )
Decreasing bands	
2,980 (v.s.sh.)	$\nu_a$ (CH)
2,860 (v.s.)	$\nu_s$ (CH)
1,760 (v.w.sh.)	$\nu_s$ C–C
1,745 (m.sh)	$\nu_s$ C=C
1,200 (s.b.)	$\nu_s$ C=C–C=C
1,120 (m.b.sh.)	$b_a$ C=C
770 (v.w.sh.)	$b_a$ C=C
720 (m)	$r$ ( $-\text{CH}_2$ )

*s* strong, *v* very, *m* medium,  
*w* weak, *sh* shoulder, *b* broad

## Effect of different temperatures on the structure of oil samples

FT-IR spectra of different oils were investigated in the liquid and solid states at different temperatures; samples of the oils were heated to temperatures between 15 and 250 °C or cooled to temperatures between 0 and −196 °C (by use of liquid nitrogen). The peak at 730  $\text{cm}^{-1}$  corresponding to the rocking vibration mode  $r(-\text{CH}_2)$  was clearly observed at high temperatures, confirming the sample was in the liquid state. This peak was split into two peaks (720 and 730  $\text{cm}^{-1}$ ) in the solid state at low temperature. The disappearance of the peak at 730  $\text{cm}^{-1}$  at high temperature and its re-appearance at low temperature is apparent from Fig. 2.

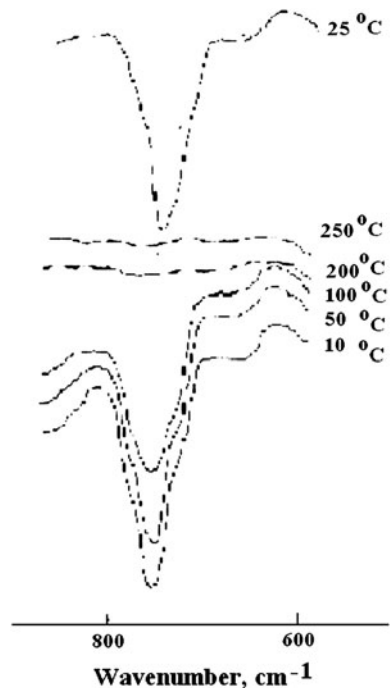
Thermal study ( $\Delta H$ )

The enthalpy differences ( $\Delta H$ ) between the conformers in the liquid and solid phases were determined by use of the modified Van't Hoff equation, Eq. (1):

$$\text{Log} \frac{D(t)}{D(c)} = Z e^{-\frac{\Delta H}{2.3RT}} \quad (1)$$

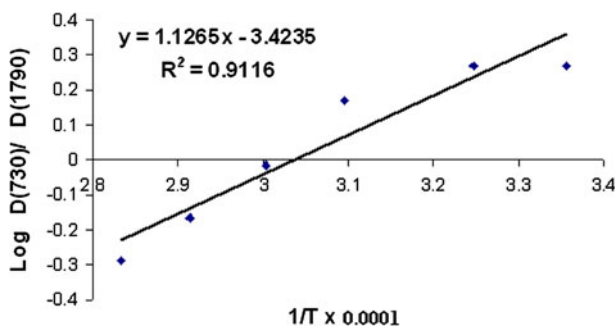
where  $D(t)$  and  $D(c)$  are the absorptivities of trans and cis conformers in the oil.  $Z$  and the molar extinction coefficient  $e^{-\Delta H/RT}$  are both assumed to be constant for small temperature intervals [13, 14].

**Fig. 2** FT-IR showing the ( $-\text{CH}_2$ ) rocking band at a vibration frequency of 730  $\text{cm}^{-1}$  at different temperatures



**Table 2** Optical densities,  $D$ , of the bands at 730 and 1,790  $\text{cm}^{-1}$  at different temperatures

$T$ ( $\text{K}^\circ$ )	$1/T \times 10^{-3}$	$D$ 730 ( $\text{cm}^{-1}$ )	$D$ 1,790 ( $\text{cm}^{-1}$ )	$\log D$ 730/ $D$ 1,790
298	3.356	0.239	0.128	0.271
308	3.247	0.233	0.125	0.270
323	3.096	0.185	0.125	0.170
333	3.003	0.094	0.097	-0.014
343	2.915	0.058	0.085	-0.166
353	2.833	0.034	0.066	-0.288

**Fig. 3** Plot of  $\log D(t)/D(c)$  against  $1/T$  for palm oil at different high temperatures

A plot of  $\log D(t)/D(c)$  against  $1/T$  for an oil in the liquid phase should give a straight line (Table 2 and Fig. 3). The value of  $\Delta H$  was calculated from the slopes obtained for the bands at 730 and 1,790  $\text{cm}^{-1}$ . The value of  $\Delta H$  for conversion of cis isomers to trans isomers is  $-10.85 \text{ kJ mol}^{-1}$ .

### Activation energy study

The activation energy ( $E_a$ ) for conversion of structure I (trans isomer) into structure II (cis isomer) was estimated by plotting time against temperature and use of the Arrhenius equation (Eqs. 2 and 3) [15–17].

$$K = Z \exp(-E_a/RT) \quad (2)$$

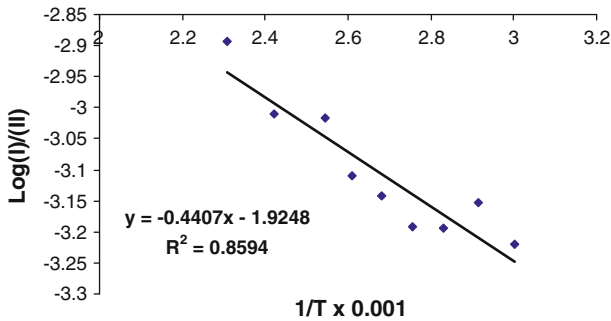
$$K = (1/t) \ln \{D(\infty) - D(0)\} / \{D(\infty) - D(t)\}, \quad (3)$$

where the pre-exponential factor  $Z$  is constant. The average rate constant  $k$  ( $\text{s}^{-1}$ ) is obtained for each temperature. The same band of structure I used for the  $\Delta H$  value was used in Eq. (3). The symbols  $D(0)$ ,  $D(t)$ , and  $D(\infty)$  denote absorbances measured at times  $t = 0$ ,  $t = t$ , and  $t = \infty$ , respectively. The value of  $E_a$  is obtained from the slope of a plot of  $\log k$  against  $1/T$  (Table 3 and Fig. 4). The value of  $E_a$  is  $8.45 \text{ kJ mol}^{-1}$  which has a support by summing up  $E_a$  of the less stable trans isomer with the corresponding  $\Delta H$  value.

It was noted that the physical characteristics (color and viscosity) of the oil changed when heated several times to high temperatures. The effect of temperature

**Table 3** Optical density of the rocking vibration mode band at  $730\text{ cm}^{-1}$  with time and increasing temperature

$T$ (K)	$1/T \times 10^{-3}$	$t$ (s)	$D$	$\log 1/t \log\{D(\infty) - D(0)/D(\infty) - D(t)\}$
323	3.096	0	0.580	0
333	3.003	90	0.515	-3.221
343	2.915	210	0.420	-3.153
353	2.830	285	0.390	-3.195
363	2.755	330	0.365	-3.191
373	2.681	390	0.315	-3.141
383	2.611	435	0.280	-3.110
393	2.545	495	0.210	-3.016
413	2.421	540	0.190	-3.011
433	2.309	600	0.120	-2.894
473	2.114	$\infty$	0.025	-

**Fig. 4** Plot of  $\log D(\infty) - D(0)/(D(\infty) - D(t))$  versus  $1/T$  for disappearance of the band  $730\text{ cm}^{-1}$ . (I) =  $D(\infty) - D(0)$  and (II) =  $D(\infty) - D(t)$ 

on the oils can also be studied by infrared spectroscopy, by monitoring the disappearance of peaks of the unstable isomers at high temperature. Use of oil several times for cooking will affect the composition of the boiled oil. Without any doubt, oil isomers are converted by oxidation to isomers harmful to human health.

## Conclusions

Frying oils were studied by infrared spectroscopy at different high and low temperatures. FT-IR spectra of palm oil, corn oil, and sunflower oil were investigated in the liquid and solid states at different temperatures; samples of the oils were heated to temperatures between 15 and  $250\text{ }^{\circ}\text{C}$  or cooled to temperatures between 0 and  $-196\text{ }^{\circ}\text{C}$  (by use of liquid nitrogen). It was clearly observed that the peak at  $730\text{ cm}^{-1}$ , corresponding to rocking vibration mode  $r(-\text{CH}_2)$ , confirmed the oil was in the liquid state at high temperature. This peak was split into two peaks

(720 and 730  $\text{cm}^{-1}$ ) in the solid state at low temperature, i.e. the peak at 730  $\text{cm}^{-1}$  disappears at high temperatures but re-appears at low temperatures. It was noted that the physical characteristics (color and viscosity) of the oil changed when the oil was heated several times to high temperatures. The effect on the oil can also be observed by infrared spectroscopy, by studying and the disappearance of some peaks from the unstable isomers at high temperature. Use of oil several times for cooking will affect its composition. Without any doubt, oil isomers are converted by oxidation to isomers harmful to human health.

**Acknowledgments** The authors wish to express their thanks to Professor Dr Abdul Kareem Hamed Maroof, Dean of Al Mansour University College-Baghdad.

## References

1. B. Maurizio, Q.L. Jose, R.H. Jesus, M.R.T. Carmen, C. Modesta, M. Mariano, L. Magdalena, M. Jose Mataix, J. Bioenerg. Biomemb. **34**, 127 (2002)
2. Y.B. Che Man, G. Setiowaty, F. R. J. Am. Oil Chem. Soc. **76**, 693–699 (1999)
3. H.W. Hoidy, M.B. Ahmad, E.A.J. Al-Mulla, W.M.Z. Yonus, N.A. Ibrahim, J. Oleo Sci. **59**, 229 (2010)
4. E.A.J. Al-Mulla, N.A.B. Ibrahim, K. Shameli, M.B. Ahmad, W.M.W. Yunus, Res. Chem. Intermed. (2012). doi:[10.1007/s11164-012-0687-6](https://doi.org/10.1007/s11164-012-0687-6)
5. S.N. Soon, J. Am. Oil Chem. Soc. **77**, 749 (2000)
6. G. Vlahov, J. AOAC Int. **89**, 1071 (2006)
7. E.A.J. Al-Mulla, N.A.B. Ibrahim, I.H.T. AlKarkhi, K. Shameli, M. Zidan, M.B. Ahmad, W.M.W. Yunus, Res. Chem. Intermed. (2012). doi:[10.1007/s11164-012-0745-0](https://doi.org/10.1007/s11164-012-0745-0)
8. L.N. Choo, L.W. Randy, L.C. Susan, J. Agric. Food Chem. **55**, 593 (2007)
9. S. Kazemi, N. Wang, M. Ngadi, S.O. Prasher, Agric. Eng. Int. **7**, 581 (2005)
10. E.A.J. Al-Mulla, J. Oleo Sci. **60**, 41 (2011)
11. T. Ahmad, S. Atta, A. Ahmad, S.A. Nagra, Sains Malaysiana **32**, 171 (2003)
12. Y.B. Che Man, M.H. Moh, J. Am. Oil Chem. Soc. **75**, 557 (1998)
13. E.A.J. Al-Mulla, A.H. Suhail, S.A. Aowda, Ind. Crop. Prod. **33**, 23 (2011)
14. M.M. Radhi, M.F. El-Bermani, Spectrochim. Acta **46A**, 33 (1990)
15. N.A. Jassem, M.F. El-Bermani, Spectrochim. Acta Part A **76**, 213 (2010)
16. W.H. Hoidy, E.A.J. Al-Mulla, K.W. Al-Janabi, J. Polym. Environ. **18**, 608 (2010)
17. I.A. Hussain, M.F. El-Bermani, Spectrochim. Acta Part A **57**, 2659 (2001)