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RESEARCH ARTICLE

Fourier transform-infrared spectroscopy techniques used to study sunflower oil after thermally exposure

Allaa Hussein Mhdi[1], Ghalib A. Atiya[2]

1. Dept. of Chemistry, College of Science , Diyala university
2. Dept. of Chemistry, College of Education of Pure Sciences, Diyala university

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Corresponding Author

Allaa Hussein Mhdi

Abstract

In this study we demonstrated that the IR spectroscopy can be used to follow the variations can be occurred during the exposure of the oil to a high heat. Also we figured out the specific frequencies that should be looked at during the analyses of tested samples. We conformed that major changes will happened when the temperature elevated to up to 270 °C. As the peroxide derivative of fatty acids, formed during the storage, through the reaction of air oxygen, with the oil, had disappeared during the heating at up to 150 °C. The shift of the combinations bands ranged from 4000 cm^{-1} to 3000 cm^{-1} formed from the fundamental and overtone of C-C and O-H bands can be considered to make quantifications for the chemical changes that expected during working temperatures, through the industrial processes or consumptions. Such region can be used instead of using the fundamental fingerprint regions of the cocking oils and their mixtures.

INTRODUCTION

E presented in this paper the use of Fourier Transform-Infrared (FTIR) spectroscopy technique as a powerful method to inspect the major changes when the cocking oil exposed to extreme temperature. Sunflower oil forms one of the main editable oils available for consumptions[1,2]. It is also fined many industrial applications like pharmaceutical, cosmetic and adhesives and other modified chemicals. Such techniques mainly applied for the identifications of edible oils[3]. Also used to detect the industrial adulteration[4] that can be made through the industrial process.

Many researchers found that many changes can occurs during the storage or in unconditioned stores[5].

Adding antioxidants[6] found that to have a great impact on heat resistibility properties.

Liu, et. al.[7] stated sunflower oil, form genetic point view, and found such technique can be used to identify the origin of the variety extracted from. Many other techniques like thermogravimatric (TG), derivative thermogravimetry (DTG) and NMR, were involved to study the stability of sunflower oil under range of temperatures[8] which proved that the oil suffering several changes and decompositions to its fatty acids, polyunsaturated, monounsaturated and saturated compounds as well as the presence of dimmers, trimmers' and polymer forms of such decomposed products. A study of oxidation process for the sunflower oil, using GC-mass, under extreme storage conditions at 70°C. Maria D. Guillen, et. al, they detect more than 82 compounds during 11 days of the air oxidation process[9]. Also many studies were done to determine the purity of oil, in which they observed band shifts in the range from 3050 cm^{-1} to 1745 cm^{-1}ecpecially for the C-H stretching vibration of the cis-double bond. They also notice that the antioxidants may have some involvements in such process. Adding such compounds it is essential now a days that they have grate impact to protect the products in both storage or from the exposure to high heat during the cooking

or industrially through the food processing. Such compounds like primary antioxidants, oxygen scavengers, secondary antioxidants, enzymatic antioxidants and chelating agents or sequestrantes.
Such compounds includes ascorbic acid, glucose oxidase, glutathione peroxideas, vitamins: A, C, E; fruits phenolics and amino acids these are oftenlly added to play as antioxidant[10, 11]
Sunflower oil was studded elevated temperature for about 350°C with presence of water mist, they found it hydrolyzed and some of Hydroperoxides related products had appeared with a strong broad band started from 3700 cm^{-1} to 3100 cm^{-1} with an approximate peak originated at 3430 cm^{-1}. This oil degradation products accumulates quickly such as high molecular weight alcohols and shorter acids and starts to evaporate and auto ignited at 365°C.[10,11]
The physical properties noticed by some researchers had changed, when the oil exposed to temperatures more than 120°C, like density, refractive index, viscosity, specific heat and composition heat, smoke and flash points and milting characteristics. Such changes can be attributed to the change of the structure of the triglycerides fatty acids orientations to be for example twisted or uncoiled changed from *cis*- linkage bent from the unsaturated bands of either conjugated or olefinic chain of the fatty acid[2,6].

Experimental:
Instruments
Perken Elmer FTIR spectrometer Model spectrum 65.
Heating mantel.
IR Liquid cell was used KBr windows, drilled for injecting samples.

Materials:

We obtained sunflower oil from the market (Turkish origin).

Procedure and sampling:
A quantity of 25 ml of sunflower oil was heated in aluminum vessel, the temperature elevated to 190°C and pointed at different grade as the following 240, 260, 280, and 300°C.

Results and Discussion:

Figure 1 revels the major noticeable changes in the range from 4000 cm^{-1} to 3000cm^{-1}, particularly for the peak 3648 cm^{-1} which assigned for the hydroperoxide that degraded rapidly and disappeared completely after one hour of heating at temperature 280°C especially for the sample's spectra 4 and 5. A spectrum ranged from 4000cm-1 down to 450 cm-1 was taken before heating as in Fig. 1
We noticed also a regular degradation in the intensity of the peak centered 3546 cm^{-1}, Figure 2, which assigned for as discussed in the introduction a combination band as a result of red shift under the oxidation conditions from 1746 cm^{-1} to 1744 cm^{-1} for the aster carbonyl group[8,9], which have an overtone lays approximately at 3488 cm^{-1} which can combined with the O-H bond, strong vibrational frequency, υ , at 3629 cm^{-1} which easily collapsed associatively with the overtone to get the band 3546 cm^{-1} that is why most of the researchers avoided to study it. The regular degradation of it can be used to follow kinetically the pyrolysis of sunflower oil or its mixtures with additives.
As shown in table 1 , different compositions appear due to sunflower oil analysis [9] .

Table **1: Main compositions of the sunflower oils of fatty acids.**

Composition	*Sunflower oil*
Monounsaturated %	22.8
Polyunsaturated %	65.2
Saturated %	12.0

Source: ref. 9

Such variation of the location of the combination bands can be expected to be approximately around 15 wavenumbers especially for the liquid samples as in ours mainly red shift compared with gas phase spectra.

This band shows regular intensity changes had happened under the heat conditions, that reflects the decomposition of the hydroperoxides which expected to form during the storage or during the heating under the presence of air[9, 11]. Also can be used to follow the sunflower degradation under heat conditions or can be used to study the sunflower oil kinetically.

Unfortunately, we noticed, that most of the researchers not give it more emphasis, probably it is combination band.

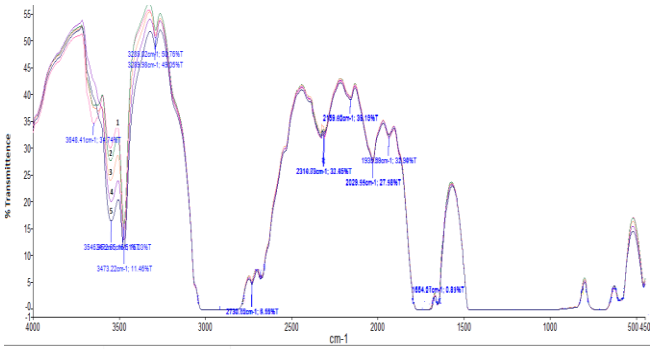

Figure 1: Transmittance spectra for sunflower oil starting one not heated marked with 1 and the other overlay spectra, for samples exposed to high temperatures started from 240C, 260C, 280C and 300C where marked with 2, 3, 4,and 5. Heating period was one hour.

Next band centered at 3473 cm^{-1} which not showed big changes compared with last two bands. Figure 3, which covers the finger print of the oil, revels variations for the fundamental bands that belongs to the groups forming the backbone of the triglycerides oils, as in the sunflower oil Table 2.

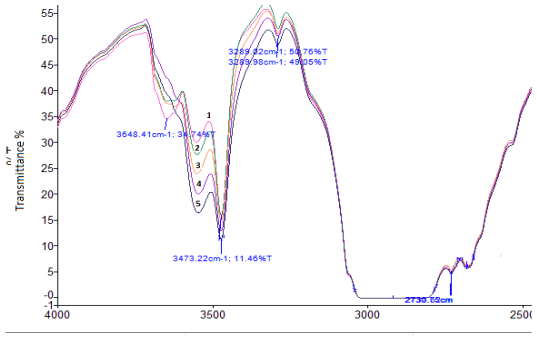

Figure 2: Expanded section for the region A from the frequency 4000 cm^{-1} to 3000 cm^{-1}, in which the frequency 3648.41cm^{-1} had disappeared after exposure for 260^0 C and one hour heating.

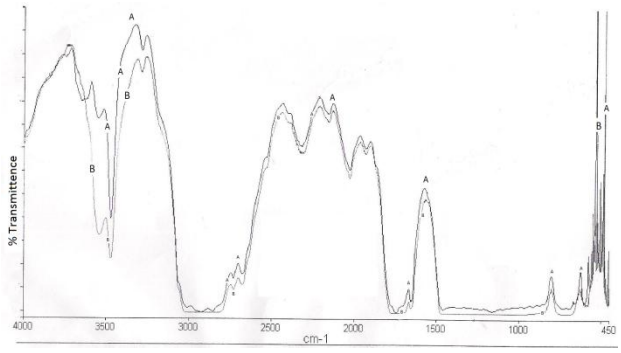

Figure 3: Transmittance spectra, of unheated sunflower oil marked with A and a spectrum of the same sample after exposure for 300^0 C for 1 hour contanuace heat marked with B. Note the majure change were observed at the combenation region bands from 4000 Cm^{-1} to 3000 Cm^{-1} wheather the other foundemantal regions no signifecent oservable changes.

Figure 4, which is an expanded part of Figure 1, reveling intensity changes, were also occurred to the fundamental bands, but relatively very small compared to the first two bands A and B, here forms less than 90% of the intensity of the peak of the band C, whether the first band, range of the band A was disappeared and the combination band, band B, shows 50% variations in either the peak intensity and the peak area as well.

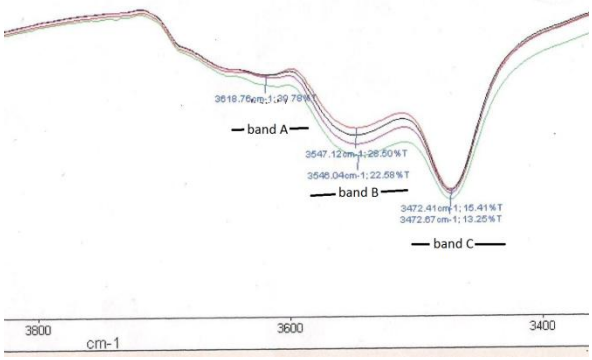

Figure 4: Expanded range of Figure 1, major change of the band range A, band B reveled regular changes in either the peak intensity and peak area. Band C, indicate no significant changes compared with band A and B.

Table 2: lists main observed bands the shows noticeable intensity changes.

Band center Frequency/ cm^{-1}	Band Assignments	Description of Band change	Ref. No.
3648	For O-H of Hydroperoxides, Shoulder of Characteristic band of mono oxidized oil consist of several bands next to the band centered at 3546 cm^{-1}.	Strong and Broad, Shoulder, with noticeable changes, Disappeared in gradual manner, after exposed to heat above 240^0 C,	7, 9

3546	**A combination band, of an overtone of the carbonyl group of ester associated with**	**Broad band, with regular and measurable intensity change with heat exposure.**	**7,13**
3473	**Overtone of -C=O of ester**	**Sharp and strong, with minor intensity changes.**	**12, 13**
3289	**For symmetrical and asymmetrical vibrations C-H, CH2 and CH3 for aliphatic groups.**		**5**
2730	**C-H of alkynes groups**		**14, 15**
1935			
1554	**Center of a range of strong Spectral band for the vibration of the deformation bending of C-H attached to unsaturated and *ces*-unconjugated carbon groups.**	**Very strong, Not noticeable change.**	**5**
Region from 1550 to 450 cm^{-1}	**This contains several strong bands belongs to the C-C links, C=O carbohydrate vibration.**	**Very strong, Not noticeable change.**	**5**

Conclusion

We demonstrated in this publication that the combination band can be followed to study the degradation of sunflower oil under heat environments. Also we confirmed that intensity change play an important role in the identification of oil resultant from heat exposure especially in the band of an overtone of the carbonyl group of ester .

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