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A COMPARATIVE STUDY OF AUTOXIDATION OF VEGETABLE OIL DUE TO REPEATED DEEP FRYING

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ABSTRACT

The changes of chemical characterization such as formation of hydroperoxide (primary oxidative products) and aldehydes (secondary oxidative products) of the oils during four consecutive days of deep frying were studied. This is the comparative study of sunflower, soybean, groundnut and mustard oil focus on the oxidative degradation reactions on frying temperature. FT-IR spectra were recorded of all oil samples. The spectrum of all these oils shows band at 3473 cm^{-1} *assigned to O-H stretching vibration of hydroperoxide and also shows band at 1743 cm*$^{-1}$ *assigned to C=O stretching vibration of aldehydes with different intensity. Absorbance at 3473 cm*$^{-1}$ *and peroxide value and absorbances at 1743 cm*$^{-1}$ *and p-anisidine value are correlated to each other which indicate the decomposition of hydroperoxide and formation aldehydes are formed during the deep frying. The results illustrated, mustard oil is least degraded and produced less amount of hydroperoxide than other oils as it contained less concentration of polyunsaturated fatty acids and soybean oil is degraded maximum on four time of deep frying than other oils as it contained more concentration of polyunsaturated fatty acids.*

Keywords: Autoxidation, FT-IR Spectra, Hydroperoxide, Aldehydes,Chemical Changes

I. INTRODUCTION

Use of vegetable oil for deep frying has been one of the oldest and popular food preparations methods. Fried foods have the desirable flavor, golden brown color, and crispy texture, which make deep fried foods very popular trade. Frying is a process of immersing food in hot oil with a contact among oil, air, and food at a high temperature of 180^{0}C to 260^{0}C. Frying time, food surface area, moisture content of food, and type of frying oil influence the autoxidation of oil. During the deep frying process oxidation of fatty acids are commonly observed chemical reactions and these produce volatile or nonvolatile compounds. Most of volatile compounds evaporate during frying and the remaining volatile compounds in oil undergo further chemical oxidation reactions or are absorbed in fried foods. The nonvolatile compounds in the oil change the physical and chemical properties of oil as well as quality of fried foods. During the deep frying process at 180^{0}C triglyceride undergoes the oxidation reaction and hydroperoxide of fatty acids are formed. The formation of these hydroperoxide is termed as primary oxidative products. Peroxide value (PV) is used as a measure of the extent to which rancidity reactions have occurred during deep frying it could be used as an indication of the quality and stability of oils. This primary oxidative product such as hydroperoxide compounds of fatty acids are also analyzed by FT-IR spectroscopy method. The primary autoxidative product peroxides is highly unstable and instantaneously revolutionized into secondary products. Fatty acids such as linoleic acid and linolenic acid result from cleavage off the carbon bonds adjacent to the hydroperoxy group. The major chain-cleavage products formed from hydroperoxides are hydrocarbons and short chain aldehydes. This transformed lipids of sunflower, soybean, groundnut and mustard oils into simple hydrocarbon and aldehydes were comparatively studied by analyzing various parameters. Investigating and monitoring the degradation of oils during deep frying process is important to ensure the safety and quality of deep fried foods.

II MATERIAL AND METHOD

2.1Sampling

Deep frying experiments on the vegetable oil of sunflower, Groundnut, Soybean and Mustard oil were carried out simultaneously in electric stove. About 1 kg of each oil was introduced into fryer. Each day, the oil was heated at higher temperature (180^{0}C) and allows equilibrating at this temperature for 30 min then Poori (100 gm) was fired for period of 2 hr. per day for 4 days. The fryer was turned off at the end of the frying experiment and oil was allowed to cool to room temperature. The oil in the fryer was filtered to remove debris using separate filter. The oils were stored in the uncovered glass bottle for analysis.

2.2Determination of Peroxide value (PV)

The Peroxide values were determined according to ISO 3960-2007

2.3Determination of *p*-Anisidine value (p-AV)

p-Anisidine values were determined according to ISO 6885:2006

2.4Evaluation by FT-IR spectroscopy

The study was carried out on a Bruker-Tencer-37 FTIR-ATR spectrophotometer capable of covering 4000-400 cm^{-1}. For FT-IR spectra recording, small quantity of the oil samples in a thin film was used. All spectra, of fresh sunflower, soybean, groundnut and pure mustard oil and for four consecutive day of deep frying, were recorded from 4000 to 400 cm^{-1} and processed with computer OPUS software.

Chemically oils are molecules of glycerol esterifies with fatty acids. The importance if IR spectroscopy is to identify and obtained the information of molecular structure as different molecules is assigned to certain absorption band related to the specific functional group. Table number 1 exhibit the assignment of functional groups responsible for IR absorption at frequency region 4000 – 400 cm^{-1}

Table No. 1 Representing different frequency and related functional group

3633 cm^{-1}	secondary oxidized products
3473 cm^{-1}	O-H stretching vibration of hydro peroxide
3006-3009 cm^{-1}	C-H stretching vibration of the cis double bond
2854 cm^{-1}	C-H asymmetric stretching vibration aliphatic CH2
2825 cm^{-1}	C-H symmetric stretching vibration aliphatic CH2
1745. cm^{-1}	C=O ester carbonyl double bond stretching of triglycerides
1654- 1659 cm^{-1}	C=C stretching vibration of the cis olefins
1460–1462 cm^{-1}	deformations and bending of –C- H the CH2 and CH3 aliphatic groups
1373.2–1377 cm^{-1}	-C-H bending vibrations of CH2 group
1163.0–1236.3 cm^{-1}	Stretching vibration of C-O
908.2–970.2 cm^{-1}	CH=CH trans unsaturation
723.3 cm^{-1}	(-CH2),-CH=CH- overlapping of the CH2 rocking and the out of plane vibration of cis disubstituted olefins.

III RESULT AND DISCUSSION

3.1Primary Oxidative Products formed on deep frying at 180^{0}C –

3.1.1Chemical Analysis - Peroxide Value

Peroxide value is useful as an indicator of oxidation at the initial stages of reaction between oxygen and unsaturated fatty acids, however, it not related to the frying duration, but to the formation hydroperoxide. The change in peroxide value (PV) of different oils during frying is shown in table No. 2 and Fig. No. 1

It is observed that after first deep frying peroxide value (PV) was increased in case of all oils as vegetable oils undergoes thermal oxidation and lipid peroxides has been identified as primary product. (1) After third day of deep frying of oils hydroperoxide are decomposed to secondary products as PV get decreased sharply. The PV increases during the first two days of frying and then decreases during the last few days of frying. The result showed that there was an initial sharp increase in PV from day 1 to 2 in all frying oils. While, the PV decrease after second day of frying in all frying oils. The results indicate that PV value of sunflower oil increased from first day to the second day of frying (1.82 to 5.83), while it decreased slightly from the second day to third day (5.83 to 5.52) and decreases sharply from third day to fourth day (5.52 to 1.98). Initially, a sharp increase in the PV of soybean was observed from first day to second day (1.6 to 6.2) and it sharply decreases from second day to fourth day (6.2 to 2.19) of the frying process. The result showed that a sharp increase in PV of groundnut oil during the first two days of frying (2.11 to 5.16), while it decrease slowly after second day of frying to fourth day of frying(5.16 to 3.96). The result also show that the PV of mustard oil increased sharply from first day to second day (2.66 to 5.35), while it decreased from second day to fourth day (5.35 to 2.38) of frying process. The result indicate that highest change in PV was observed in soybean and than in sunflower oil while, least change in PV was observed in groundnut (6) and than in mustard oil. After second day of frying PV of sunflower and soybean oil decreased sharply as it contain more (60% to 70%) polyunsaturated fatty acids. Peroxide value of groundnut and mustard oil decreased less as it contain more (50% to 60%) monounsaturated fatty acids. This may be due to presence of natural antioxidant such as tocopherols in oil and fatty acid composition.

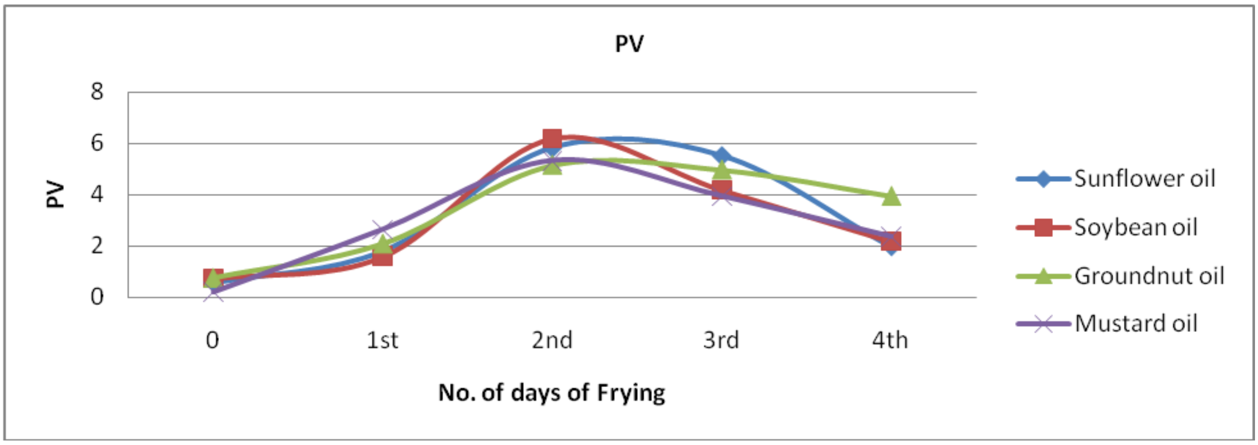

Fig.No. 1 Evaluation of the Peroxide Value depending on the numbers of frying at 180^{0}C

3.1.2Instrumental analysis – FT-IR spectra

FT-IR spectroscopy is an excellent tool for analysis as the intensities of the bands in the spectrum are proportional to concentration. Triglycerides are the main components of edible fats and oils; as a consequence, FT-IR spectra of triglycerides dominate in FTIR spectra of fats and oils (I. N. Hayati et al 2009).

FTIR spectra of sunflower, soybean, groundnut and mustard oil samples for four consecutive days of frying at 180^{0}C showed that there exists a notable difference in band between the same oil used for frying four times with Poories. The oil composition affects the exact position of the band and yield of a shift when the proportion of the fatty acids changes. The spectrum of all oils shows band at 3473 cm^{-1} assigned to O-H stretching vibration of hydroperoxide. The change in absorbance at 3473 cm^{-1} with four consecutive days of deep frying is show in table No.2.Figure no. 2,3,4,and 5 illustrate the spectrum of sunflower, soybean, groundnut and mustard oil samples before (fresh) and after four consecutive days of deep frying of Poories. FT-IR spectra of sunflower, soybean, groundnut and mustard oil samples shows that their exits a remarkable with difference in the band at before deep frying and between the same oil used for deep frying for four times with Poories. During deep frying for two times with Poories of all the four oils under this study, shows at 3473 cm^{-1} absorbance band increased indicating an increase in absorbance which may be due to formation of hydroperoxides: primary oxidative products. On third and fourth time of deep frying it is observed that absorbance band at 3473 cm^{-1} is decreased gradually which may be due to decomposition of hydroperoxides and formation of secondary oxidative products. A large change in absorbance is seen in soybean oil which shows maximum increase of absorbance at 3473 cm^{-1} band than other oils and mustard oil shows minimum increase of absorbance at 3473 cm^{-1} band which may be due to fatty acid composition ratio. Soybean oil consist about 54% linoleic acid, sunflower oil consist about 48%, groundnut oil consist about 33 % and mustard oil consist about 15 % linoleic acids. It is indicated that the concentration of polyunsaturated fatty acid may affect the degradation of oil at frying temperature. Increased in rate of absorbance at 3473 cm^{-1} is as follows which indicates the stability of oils at frying temperature. Mustard oil < Groundnut oil < Sunflower oil < Soybean oil

Table no. 2 Change in PV, *p*-AV, absorbance at 3473 cm^{-1} and 1743 cm^{-1} during four consecutive days of frying oil samples.

Types of oil	No. of days of frying	PV	*p*-AV	Absorbance at	
				3473 cm^{-1}	1743 cm^{-1}
Sunflower oil	Fresh	0.59	8.3	0.00201109	0.19316907
	1	1.82	19.26	0.00216819	0.25596532
	2	5.83	19.80	0.00285509	0.25834425
	3	5.52	20.30	0.00268848	0.26216534
	4	1.98	21.85	0.00222057	0.26549135
Soybean oil	Fresh	0.74	6.12	0.00188894	0.194030438
	1	1.6	15.06	0.002255492	0.255910518
	2	6.2	18.61	0.002786135	0.25735341
	3	4.19	20.42	0.002551279	0.264522878
	4	2.19	22.72	0.002255492	0.267789451
Groundnut oil	Fresh	0.78	5.2	0.00156192	0.189149244
	1	2.11	9.61	0.00212455	0.239022465
	2	5.16	15.81	0.00228622	0.247060817
	3	4.98	17.98	0.00217265	0.248155687
	4	3.96	18.19	0.00200673	0.248851623
Mustard oil	Fresh	0.21	7.5	0.00171886	0.1910467
	1	2.66	8.85	0.00175343	0.218718702
	2	5.35	10.83	0.0020562	0.219884397
	3	3.96	12.65	0.00210056	0.239750127
	4	2.38	17.11	0.00191075	0.242643157

3.1.3Regression coefficient of oils

Changes in the RT-IR spectrum at 3473 cm^{-1} have been used as a relative measure of primary oxidation. The absorbance increase due to the formation of hydroperoxide is proportional to the uptake of oxygen and formation of peroxides during the early stages of oxidation. Peroxide value is the determination of hydroperoxide produced on deep frying by chemical method and the spectrum at 3473 cm^{-1} is also determined the presence of hydroperoxide (5). Therefore peroxide value and spectrum at 3473 cm^{-1} is correlated to each

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other and is expressed in correlation coefficient. Correlation coefficients (R2) between absorbance at 3473 cm^{-1} with peroxide value for four consecutive days of deep frying for all oil samples is shown in table no. 3 and Fig.no. 6 for sunflower, soybean, groundnut and mustard oil it was found to be positive and strong; 0.985, 0.889, 0.688 and 0.708 respectively.

Table No. 3 Correlation coefficients (R2) between absorbance at 3473 cm^{-1} with PV

Type of Oil	Correlation coefficient (R^2)
Sunflower oil	$R^2 = 0.985$
Soybean oil	$R^2= 0.889$
Groundnut oil	$R^2 = 0.688$
Mustard oil	$R^2 = 0.708$

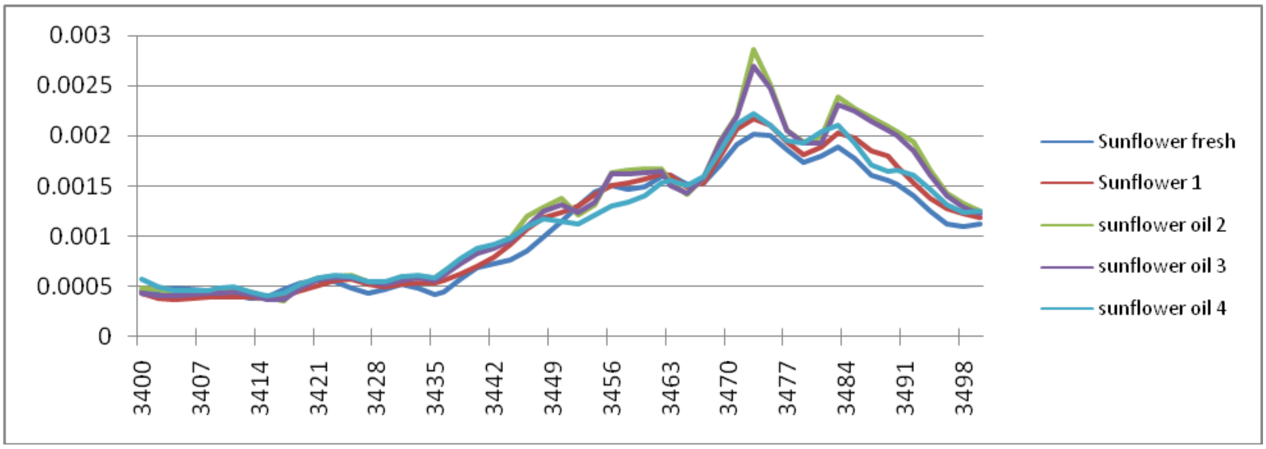

Fig. No. 2 FT-IR Spectrum from 3400 cm^{-1} to 3500 cm $^{-1}$ of Fresh , after 1st ,2nd 3rd and 4th frying of Sunflower oil

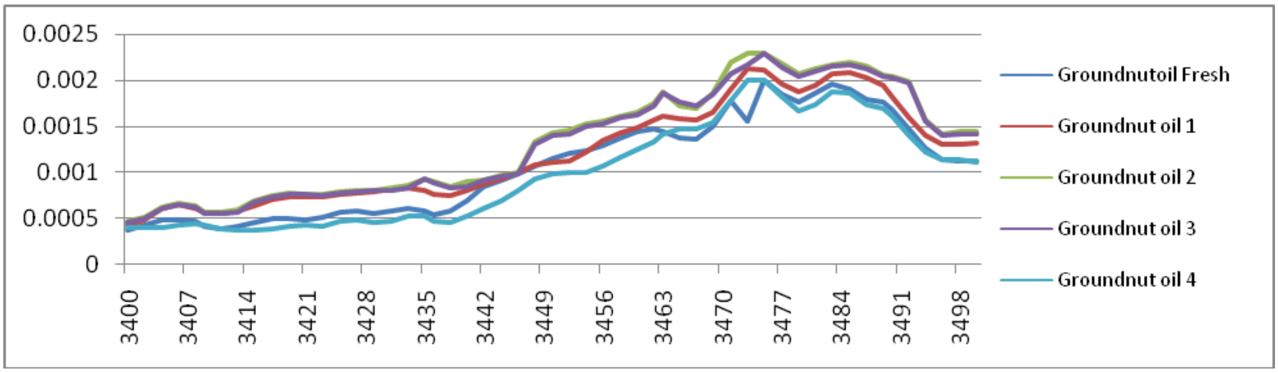

Fig. No.3 FT-IR Spectrum from 3400 cm^{-1} to 3500 cm $^{-1}$ of Fresh , after 1st ,2nd 3rd and 4th frying of Groundnut oil

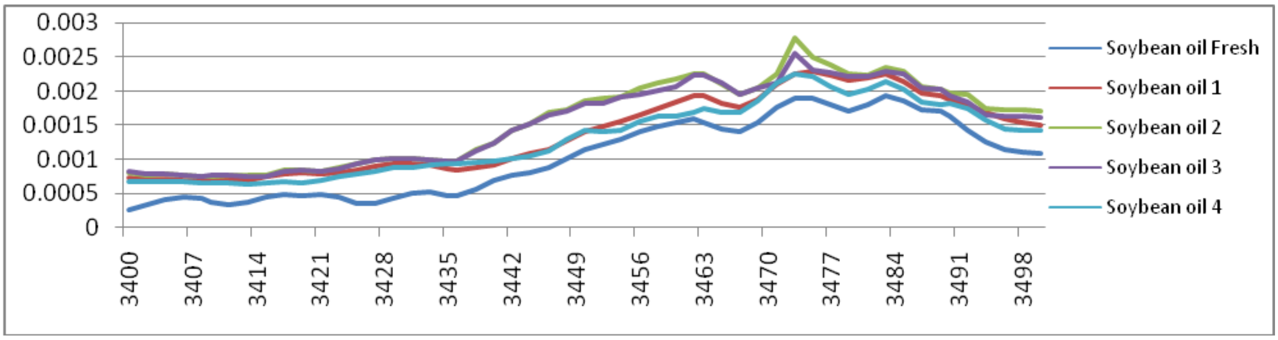

Fig. No.4 FT-IR Spectrum from 3400 cm^{-1} to 3500 cm $^{-1}$ of Fresh , after 1st ,2nd 3rd and 4th frying of Soybean oil

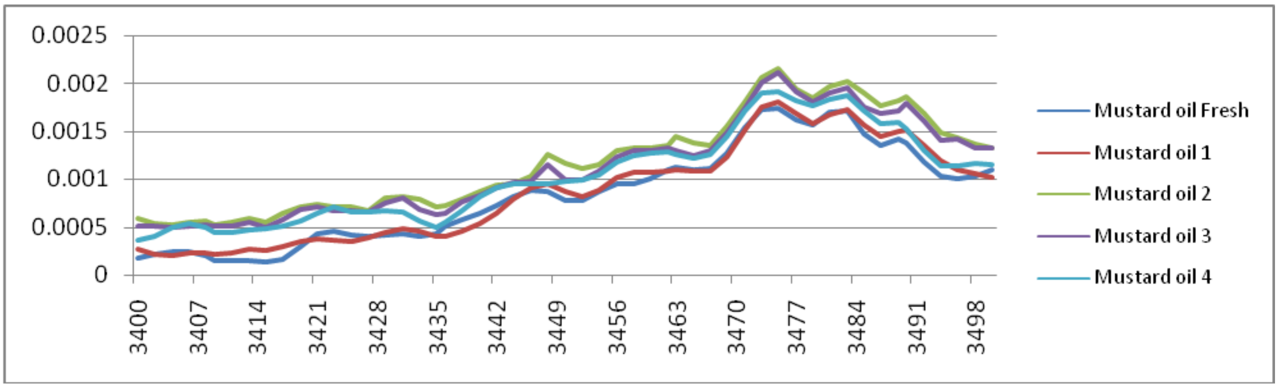

Fig. No.5 FT-IR Spectrum from 3400 cm^{-1} to 3500 cm $^{-1}$ of Fresh , after 1st ,2nd 3rd and 4th frying of Mustard oil

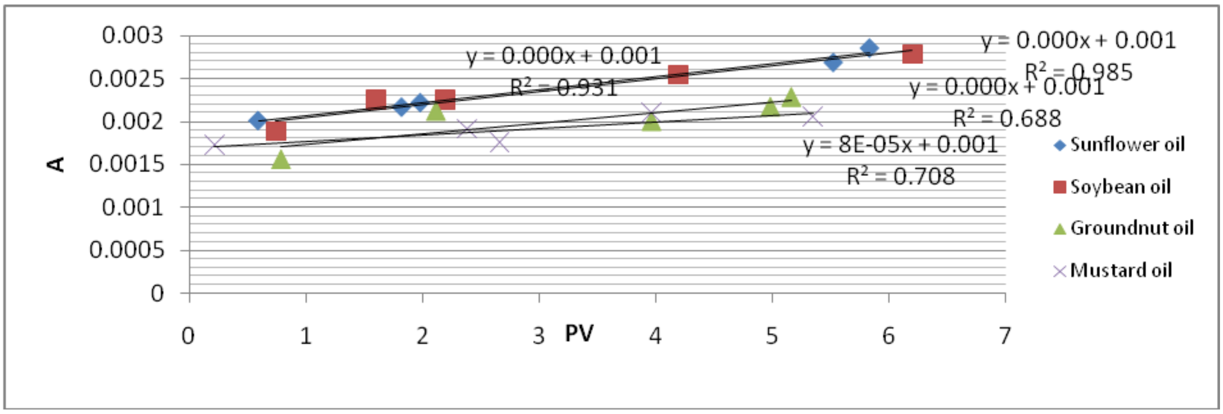

Fig. No. 6 Change in PV and Absorbance at 3473 cm-1 during four consecutive days of frying of oils at 180^{0}C

3.2Secondary Oxidative Products formed on deep frying at 180^{0}C

3.2.1Chemical Analysis – *p*-Anisidine Value (*p*-AV)

The changes in the *p*-Anisidine value of all the oils during the four consecutive days of deep frying process are shown in Fig.7 and table no.2. An increase in the *p*-AV of all frying oils was observed with prolonging deep frying time (5). This finding could be explained by the fact that less stable primary oxidized compound (hydroperoxide) decomposed further to form aldehydes and ketones compounds. Aldehydes and ketones compounds are secondary oxidized compounds which formed at frying temperature. *P*-anisidine value, indicate the level of secondary oxidative compounds, produced during deep frying of oils. The results illustrate that *p*-anisidine value was increased as the level of aldehydes and ketones increased with increasing number of deep frying for all four oils (7). The highest significant change in *p*-AV was observed in the soybean oil (6.12 to 22.72) followed by sunflower oil (8.3 to 21.85), while least significant change observed in the mustard oil (7.5 to 17.11) followed by groundnut oil (5.2 to 18.19). This observation could be due to presence of high concentration of polyunsaturated fatty acids (linoleic acid) that were oxidized, in soybean (54.2%) and sunflower (39.4) oils. The minimum degradation of fatty acids are observed in mustard oil it is may be due to presence of natural antioxidants and pure form.

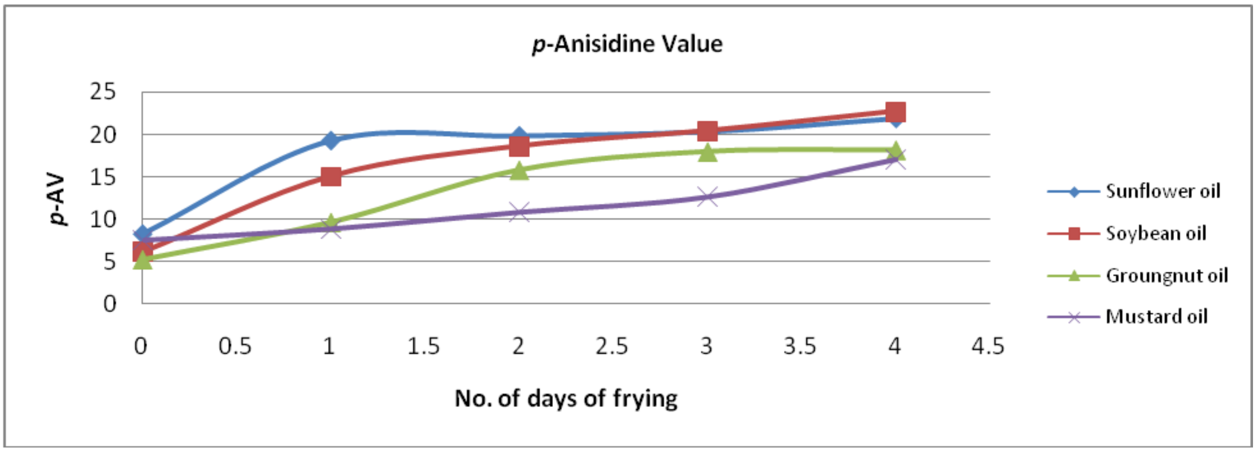

Fig.No. 7 Evaluation of the *p*-Anisidine Value depending on the numbers of frying at 180^{0}C

3.2.2Instrumental analysis – FT-IR spectra

The carbonyl functional group of the oil in the FTIR spectra appeared in the frequency region 1700–1600 cm^{-1}. The aldehydic C=O exhibited a stretched band in 1730– 1680 cm^{-1} (2), which is close to and may overlap with the absorption band of the ester carbonyl functional group of palm oil in 1748–1746 cm^{-1}, especially because under oxidative conditions, the frequency of this band can decrease to 1743 cm^{-1} depending on the carbonyl absorbencies of the saturated aldehydes (3). Hamilton (4) also reported the generation of aldehydes during the auto-oxidation of oils, which reduces the band frequency from 1746 cm^{-1} to below 1744 cm^{-1}. The band at 1730–1728 cm^{-1} could only be detected as the difference spectrum between the oxidized and unoxidized oils (2). Aldehydes also showed weak absorption bands in the frequency region 2700–2800 cm^{-1} which indicate the presence of C-H stretching in aldehydes.

FTIR spectra of sunflower, soybean, groundnut and mustard oil samples for four consecutive days of frying at 180^{0}C showed that there exists a notable difference in 1743 cm^{-1} band between the same oil used for frying four times with Poories. The oil composition affects the exact position of the band and yield of a shift when the proportion of the formation aldehydes changes. The change in absorbance at 1743 cm^{-1} with four consecutive days of deep frying is show in table No2.Figure no. 8,9,10 and 11 illustrate the spectrum of sunflower, soybean, groundnut and mustard oil samples before (fresh) and after four consecutive days of deep frying of Poories. On frying temperature (180^{0}C) and during deep frying for four times with Poories of all the four oils under this study at 1743 cm^{-1} band indicating an increase in absorbance which may be due to formation of aldehydes:

secondary oxidative products. On deep frying it is observed that absorbance band at 1743 cm^{-1} is increased gradually which may be due to decomposition of hydroperoxides and formation of secondary oxidative products. From the result obtained it is indicated that from first day of deep frying to fourth day absorbance is increased gradually as the formation of aldehydes during oxidation of fatty acids carried out at high temperature for all four oils. A large change in absorbance is seen in soybean oil which shows maximum increase of absorbance at 1743 cm^{-1} band than other oils and mustard oil shows minimum increase of absorbance at 1743 cm^{-1} band which may be due to fatty acid composition ratio. This results may be due to soybean oil consist higher amount of polyunsaturated than other oils and mustard oil consists higher amount of monounsaturated oil and presence of natural antioxidants. Polyunsaturated fatty acid may affect the degradation of oil at frying temperature. Increased in rate of absorbance at 1743 cm^{-1} is as follows which indicates the stability of oils at frying temperature. Mustard oil < Groundnut oil < Sunflower oil < Soybean oil

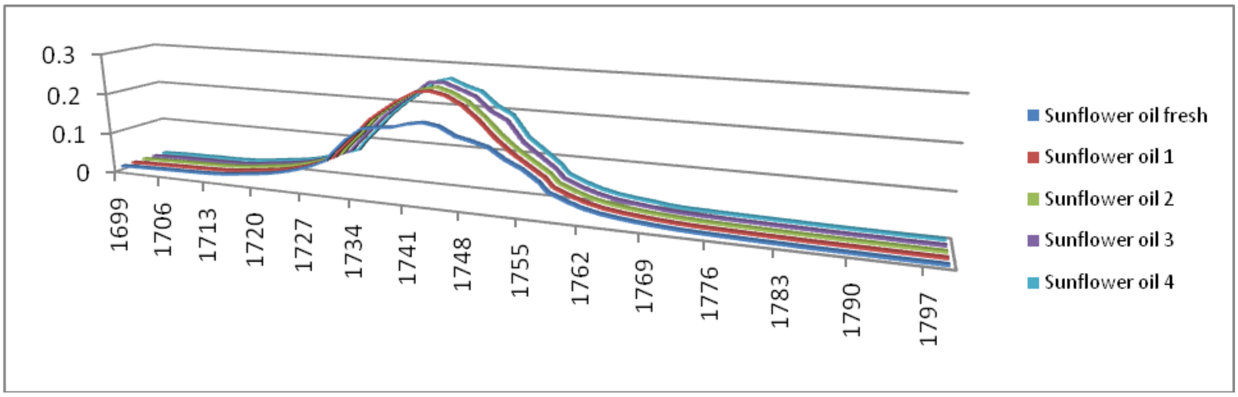

Fig. No. 8 FT-IR Spectrum from 1700 cm^{-1} to 1800 cm^{-1} of Fresh , after 1st ,2nd 3rd and 4th frying of Sunflower oil

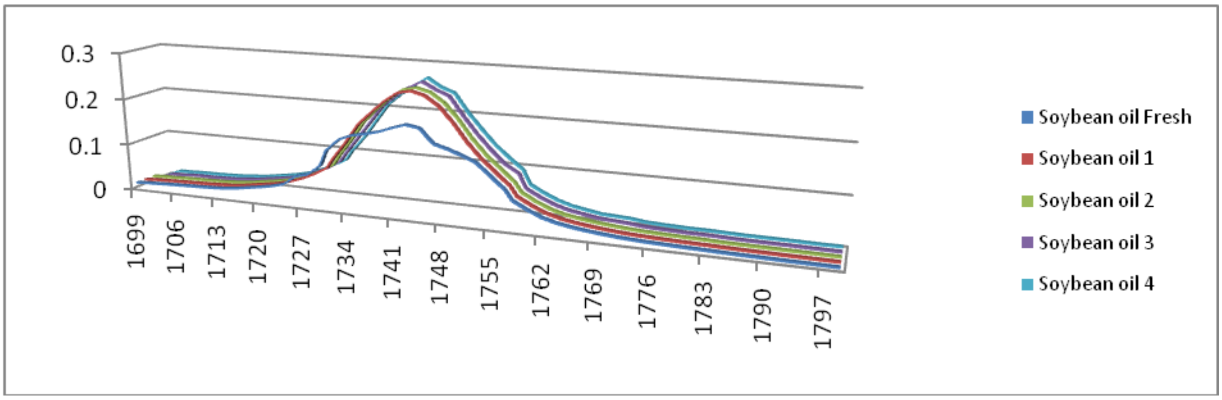

Fig. No.9 FT-IR Spectrum from 1700 cm^{-1} to 1800 cm^{-1} of Fresh , after 1st ,2nd 3rd and 4th frying of soybean oil

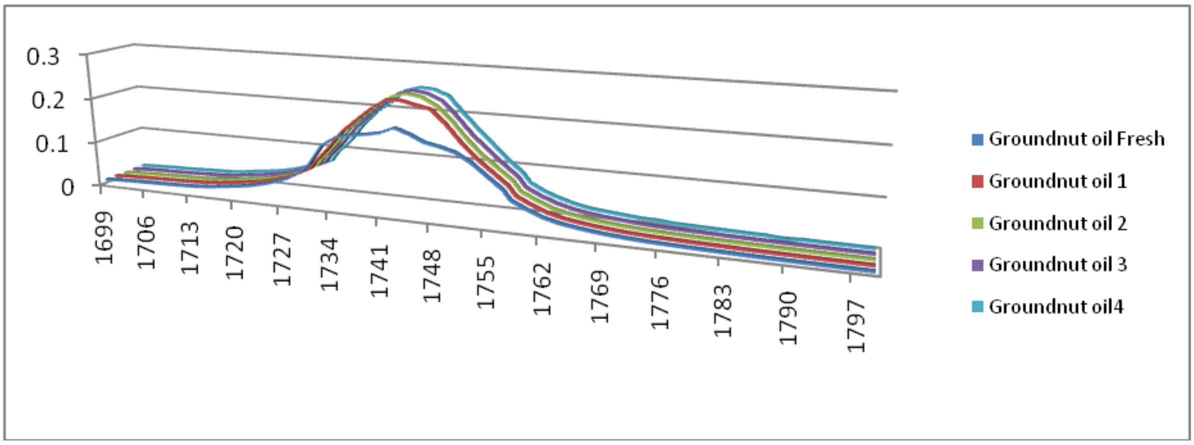

Fig. No. 10 FT-IR Spectrum from 1700 cm^{-1} to 1800 cm $^{-1}$ of Fresh , after 1st ,2nd 3rd and 4th frying of groundnut oil

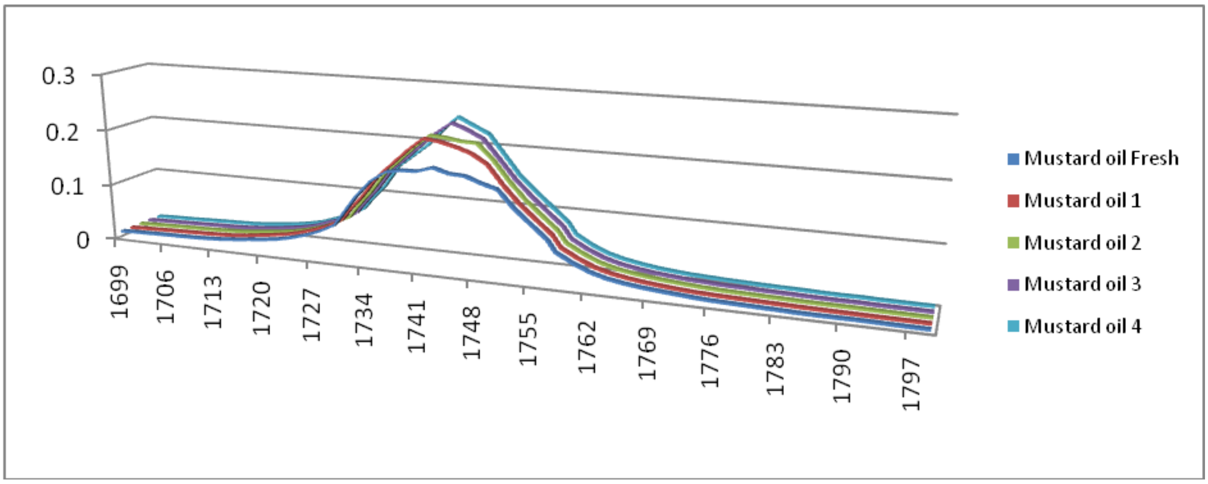

Fig. No. 11 FT-IR Spectrum from 1700 cm^{-1} to 1800 cm $^{-1}$ of Fresh , after 1st ,2nd 3rd and 4th frying of mustard oil

3.2.3 Correlation coefficients (R2)

Changes in the RT-IR spectrum at 1743 cm^{-1} have been used as a relative measure of secondary oxidation of fatty acid cause during deep frying. The absorbance increase due to the formation of aldehydes is proportional to the decomposition of hydroperoxides during the termination stages of autoxidation. *p*-anisidine value is the determination of aldehydes produced on deep frying by chemical method and the spectrum at 1743cm^{-1} is also determined the presence of aldehydes. Therefore *p*-anisidine value and spectrum at 1743 cm^{-1} is correlated to each other and is expressed in correlation coefficient. Correlation coefficients (R2) between absorbance at 1743 cm^{-1} with *p*-anisidine value for four consecutive days of deep frying for sunflower, soybean, groundnut and mustard oil it was found to be positive and strong; 0.995, 0.912, 0.772 and 0.729 respectively (table.no. 4 and fig. no. 12).

Table No. 4 Correlation coefficients (R2) between absorbance at 1743 cm^{-1} with *p*-Anisidine value for four consecutive days of deep frying

heType of Oil	**Correlation coefficient (R^2)**
Sunflower oil	$R^2 = 0.995$
Soybean oil	$R^2= 0.912$
Groundnut oil	$R^2 = 0.772$
Mustard oil	$R^2 = 0.729$

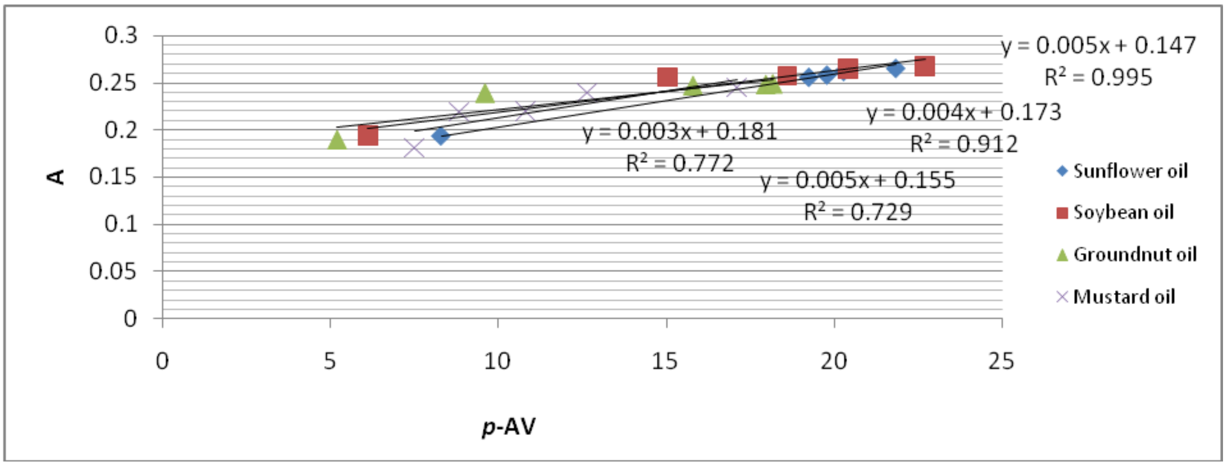

Fig. No.12 Change in p-AV and absorbance at 1743 cn-1 of oils during four consecutive days opf frying at 180^{0}C

IV. CONCLUSION

FT-IR spectroscopy was used to evaluate the degree of oxidation after heating and frying processes. The spectra of sunflower, soybean, groundnut and mustard oil at the frying temperature and at multiple frying times with a poories showed frequencies in range of 3400 cm^{-1} to 3500 cm $^{-1}$ and 1700 cm^{-1} to 1800 cm $^{-1}$ of fresh , after 1st ,2nd 3rd and 4th days frying. The spectrum of all these oils shows band at 3473 cm^{-1} assigned to O-H stretching vibration of hydroperoxide and also shows band at 1743 cm^{-1} assigned to C=O stretching vibration of aldehydes with different intensity. Absorbance at 3473 cm^{-1} and peroxide value are correlated to each other which indicate the formation of hydroperoxides. Absorbances at 1743 cm^{-1} and *p*-anisidine value are correlated to each other which indicate the decomposition of hydroperoxide and formation of the secondary oxidative product: aldehydes are formed during the deep frying. The results illustrated, mustard oil is least degraded and produced less amount of hydroperoxide on four time of deep frying than other oils as it contained less concentration of polyunsaturated fatty acids. Soybean oil is degraded maximum on four time of deep frying than other oils as it contained more concentrated polyunsaturated fatty acids.

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