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Thermal degradation of fatty acids during repeatedly frying of vegetable oil: A survey review

KEY WORDS: degradation, fatty acids, vegetable oil, oxidation

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ABSTRACT

Fried food has been very popular around the world. Deep frying of foods enhanced the crispy texture, flavor, golden brown colour of the food. Different vegetable oils are used for deep frying depending on availability in that area. During deep frying process chemical reaction like oxidation, hydrolysis, isomerization, polymerization etc. take place, which cause the phisico-chemical changes in fatty acids of oil. Frying at high temperature also affect the quality of fried food. Repeatedly used frying oil is harmful to human health. Repeatedly used frying oil produced primary oxidative product i.e. hydroperoxide and secondary oxidative products like aldehydes, ketones etc. which cause the degradation of oil. Therefore, it is necessary to study the chemical changes of oil occurred during deep frying process of commonly used vegetable oils. In this review, we constituted the previous study on physic-chemical changes in oil during deep frying and methods used for evaluation the degradation of fried oil in order to explore the area which requires further research.

I. Introduction

Vegetable oils

Vegetable oils consists primary a large molecules are called triglyceride of fatty acids. Triglycerides are insoluble in water and greasy to touch [16].They are extracted from seeds of plants such as sunflower, soybean, groundnut and mustard oil. Vegetable oils are used for various purposes like for cooking, for industrial use, for pet food additive etc. In India vegetable oil are widely used in frying, backing and other types of cooking. It is also used in food preparation and flavoring such as salad dressing etc. So it is also term as edible oil.

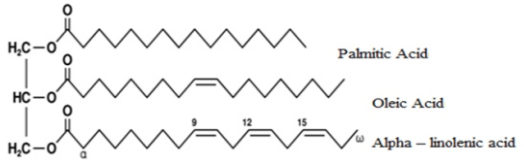

Fig. no. 1 Triglyceride

Cooking oil like sunflower, soybean oil, groundnut oil, mustard oil containing polyunsaturated and monounsaturated fatty acids like linoleic acid, linolenic acid and oleic acid, although some oils that contains saturated fat, such as coconut oil, palm oil are solid. Lipid comprise a group of naturally occurring molecules that includes fats, waxes, sterols, fat soluble vitamins such as vitamin A,D,E and K, monoglycerides, diglycerides, triglycerides, phospholipids and others. Lipid may define as hydrophobic small molecules. Lipids also encompass molecules such as fatty acids and their derivatives including mono-, di- and triglycerides.

Vegetable oil Types

Sunflower oil

Sunflower oil is extensively used for frying in India. The refined sunflower oil is clear and slight amber coloured with slight fatty odor. It is the mixture of monounsaturated and polyunsaturated fatty acids with low saturated fatty level. However, the high level of unsaturated fatty acids enhances its susceptibility to oxidation. On frying sunflower oil significantly losses the essential fatty acid (linoleic acid) [17]. Sunflower oil also contains nutrients: Vitamin B, Lecithin, Tocopherols, Carotenoids, Selenium, Proteins, Copper, Iron, Zinc, and Calcium.

Groundnut oil

Groundnut oil is also known as peanut oil. The oil is available in refined, unrefined, cold pressed and roasted varieties. It is an olive coloured with mild flavor. It contained high level of monounsaturated fatty acid. Refined groundnut oil also contained externally added ingredient such as vitamin A, vitamin D, vitamin E.

Soybean oil

It is the most wildly consumed cooking oil. Soybean oil has a high smoke value, so it is used extensively as oil for frying. Soybean oil contained high level of polyunsaturated fatty acids. Refined soybean oil also contains externally added ingredients such as vitamin A, D, E and dimethyl polysiloxane.

Mustard oil

Pure mustard oil is mostly used for cooking but also used for body massage to improve blood circulation, muscular development and skin texture. It contains high level of monounsaturated fatty acids. Mustard oil contains the pungent Allyl isothiocyanate.

Table no.1 Composition of Fatty Acids in sunflower, groundnut, soybean and mustard oil.

Type of oil	Saturated	Monounsaturated	Polyunsaturated	Oleic acid C18:1 (%)	Linoleic acid C18:2 (%)ω 6	Linolenic acid C18:3 (%)
Sunflower oil	12 %	25.6 %	62.3 %	14-40	48-74	0-0.3
Groundnut oil	20.9 %	51.2 %	27.6 %	35-69	12-43	0-0.28
Soybean oil	17.1 %	26.6 %	55.9 %	17-30	48-59	4.5-11
Mustard oil	5.5 %	69.5 %	24.6 %	8-23	10-24	6-18

Fatty acids

Fatty acids are a hydrocarbon chain that terminates with carboxylic acid group; this arrangement confers the molecules with a polar, hydrophilic end and a nonpolar hydrophobic end that is insoluble in water. The fatty acid carbon chain typically between 4 to 28 carbon long may be saturated or unsaturated . If fatty acid contained double bond; there is a possibility of either a cis or trans geometric isomerism. Cis-double bonds cause the fatty acid chain to bend. Most naturally occurring fatty acids are of the cis configuration although the trans form does exist in some natural and partially hydrogenated fats and oils.

Saturated and unsaturated both types of fatty acids are occurring in vegetable oil. Myristic acid, palmitic acid, stearic and arachidic acid are most observed saturated fatty acids in vegetable oil. Monounsaturated fatty acids such as oleic acid (cis 9- octadecenoic acid) are occurs most frequently in nature. It is so known as Omega -9. It is not essential fatty acid. It can be created by the human body from unsaturated fatty acids and are therefore not essential for the diet. There are two main PUFA such as linoleic (Omega 6) fatty acids and linolenic (Omega – 3) fatty acid. Polyunsaturated fatty acids such as linoleic acid and linolenic acid especially in the edible vegetable oils are necessary for normal development and functioning of human tissue and are called as essential fatty acids. These are essential fatty acids because these cannot not be synthesize by body and need to be supplied through diet. Vegetable oils are essential in the diet for the absorption and mobilization of fat soluble vitamins such as vitamin A, vitamin E

and fat soluble antioxidants in the body.

Autoxidation of vegetable oil on frying

Lipid oxidation is a major cause of food quality deterioration as during deep frying of food products, vegetable oil undergoes thermal oxidation. Thermal oxidation is also called as autooxidation. Autooxidation of unsaturated fatty acids occurs via free radical chain reaction. Lipid hydroperoxides have been identified as primary oxidative product (ROOH). The hydroperoxide are very unstable and quickly decompose to secondary oxidation product, such as aldehydes, alcohols, ketones and epoxy compound. During deep frying process of food, primary and secondary oxidative products can be absorbed by fried food [18]. Lipid oxidation not only changes the colour, texture and essential nutrients and micronutrients of food but also generate a lot of harmful biological effects to human health [19].

I. Literature Review

Abdul Rohman et al [1].This paper monitored the oxidative stability of corn oil, rice bran oil, soybean oil and sunflower oil by FT-IR. He was observed the absorbance intensity at 3470 cm^{-1}, 1655 cm^{-1} and 967 cm^{-1} were increased and at 3008 cm^{-1} and 722 cm^{-1} were decreased. There was a strong positive (R2) correlation between absorbance at 3008 cm^{-1} and conjugated dienes and with specific absorptivities of conjugated trience and p-Anisidine value.

Amit K Das [2]. This paper compared intensity of deterioration of refined groundnut oil occurred during the continuous frying and intermittent frying. It was predicted that peroxide value, anisidine value, diene value, oxidized fatty acids and viscosity were higher due to intermittent frying. Also, as compared to continuous frying, there were significant decreased in iodine value, unsaturated fatty acids, saponification value and smoke value in intermittent frying.Result shows that quality degradation of refined groundnut oil on intermittent frying process is caused more degradation than continuous frying process.

Anwar Ahmed et al [3] This paper study the physiochemical changes of the excessively used vegetable oils for frying process. Acid value, saponification value, peroxide value, free fatty acids and total polar compounds were increased after frying operation. Stearic acid, palmitic acid and oleic acid content were increased after frying. However, linoleic acid and linolenic acid content were decreased after frying. The highest values of total polar compounds were due to excessive number of frying and low quality oil. This study concluded that the changes in the chemical profile of excessively used oil were cause several health hazard and rendered oils unfit for human consumption.

Barbara Maik et al [4] In this paper oxidative degradation of six vegetable oil at 160^{0}C were investigated by Fourier transform Raman spectroscopy. Formation of saturated and unsaturated aldehydes, conjugated double bond system and isomerization of cis and trans bands was observed in the C-C stretching region and found to be follow different pattern for each oils.

C.A. Andrew et al [5] This paper is an comparative study of deterioration of cottonseed oil and groundnut oil, heating at high temperature (1800C) used for frying. The result shows that cottonseed oil possesses higher changes in free fatty acids than in groundnut oil. The change in refractive index and peroxide value were increased with heating time. This paper predicted that cottonseed oil is more susceptible to deterioration than groundnut oil at heating temperature.

Eran Zahir et al [6] In this paper physiochemical properties of corn and mustard oil were studied used for repeated frying. Result revealed that due to temperature change in the oil there is a notable difference in the spectral band which showed that the proportions of the fatty acids were changed. The spectra of corn oil at frying temperature showed frequencies in range of 2853.7 – 2926.0 cm^{-1} while in mustard oil an additional peak was observed at 3633.8 cm^{-1} which exhibits the secondary oxidized products formed.

Felix A Aladedunge [7] This paper reports the changes in regular canola oil as affected by frying temperature. The results shows that total polar compounds, p-anisidine value, colour and trans fatty acids content increased significantly during the frying process for seven consecutive days of frying. The amount of polyunsaturated fatty acids reduced by half and the trans isomer contribution increased 2.5 times during frying. Total polar components formation correlated inversely with the reduction of tocopherols.

Garima Goswami [8] In this paper attempt is being made to trans the harmful effect of repeated used oil for frying on human health. Increased viscosity and darkening in colour can alter the fatty acid composition of the cooking oil. Oxidation, hydrolysis and thermal polymerization are the chemical reaction occurring as a repeated heating of oil. This paper suggested that oil should not be heated again and again as formation of harmful products can be minimized by discarding it for making soap or using it with certain antioxidant.

Goburdhun D [9] This paper evaluated the quality of soybean oil during continuous frying by FT-IR and chemical analysis method. The results illustrated that hydroperoxide and free fatty acids concentration has been increased during frying process. Triglycerides ester linkage, iodine number increased a general loss of cis double bond and increased in trans double bond of unsaturated fatty acids and also the formation of unsaturated aldehydes during frying process.

Rashmi Sharma et al [10] This paper compared the vegetable oil namely mustard, groundnut, soybean and safflower treating with deep frying. The analysis suggest that the soybean and safflower oil possessing high polyunsaturated fatty acids should not be used for deep frying and longer storage. Also, natural oil rich in natural antioxidants should be a best choice for both chemical and nutritional point of view.

R.P. Yadav et al [11] This paper reported that mustard oil is heart friendly oil. Mustard oil is cholesterol and trans fat free, low in saturated fat and high in monounsaturated fat and polyunsaturated fat, a high smoke point and with ideal N6 to N3 acid ratio, which is very essential for healthy heart. Mustard oil meet all these criteria, therefore it is a best cooking oil.

Priyanka Rastogi [12] This paper investigated the changes in chemical properties occur due to cooking in Indian ghee, hydrogenated oil, coconut oil, mustard oil, groundnut oil, soybean oil, multiple deep frying cooking method. Peroxide value, formation of free fatty acids and trans fatty acids increased significantly during cooking process in all edible oil and fat. Auther investigated that single deep frying appears to be the least harmful method and soybean oil is the least susceptible to degradation.

Pravin S More et al [13] This paper studied the rapid characterization of oxidative deterioration in edible oil by optical photospectrometry. Investigation shows that the kinetic reaction of reused sunflower oil which is undergoes the autoxidation reaction has variation of absorption coefficient. Result shows that free fatty acids, acid and saponification value get reduce in exposed oil.

Nasivullah et al [14] This paper studied the oxidative stability of sunflower oil, groundnut oil, mustard oil and palm oil blended with rice brane and sesame oils during deep frying process. Sunflower oil shows maximum p-Anisidine value, which indicates the deterioration products. But, deterioration product were absent in the mustard oil and palm oil. The result shows that sunflower oil preparation product had the lowest oxidation stability and the palm oil preparation had the highest stability.

Narasimhamurthy et al [15] This paper studied the changes in physiochemical characteristic of groundnut, sesame and coconut oil during heating and frying. The results indicates relatively greater alteration in heated oils compared to fried oils. the fatty acids analysis showed significantly increased in the level of saturated fatty acid and decrease in the level of unsaturated fatty

acids in both heated and fried oil.

II. Chemical evaluation methods

A. Peroxide value

The peroxide value gives the information about the number of peroxide compound in the oil and hence of the age and quality of the edible oil. 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 and breakdown of oxidation products. Peroxides are unstable and decomposed at frying temperature. The oil with peroxide value between 1 and 5 mEq/Kg are at low oxidation state and between 5 and 10 mEq/Kg are at average oxidation stage. Lower the peroxide value, better the quality of oil.

B. p-Anisidine value

The p-anisidine value (p-AV) method measures the content of aldehydes (principally 2-alkenals and 2,4-alkadienals) present in oil samples at acidic conditions generated during the decomposition of hydroperoxides [20] and can be used as markers to determine degradation of peroxidised materials produced by the heating process .

C. Totoxo value

The Totoxo value is a measure of the total oxidation, including primary and secondary oxidation products. It is a combination of PV and p-AV. Totoxo value measures both hydroperoxides and their breakdown products, and provides a better estimation of the progressive oxidative deterioration of fats and oils. The lower the Totoxo value, the better the quality of oil.

D. Iodine number

The iodine number (IN) of oil is a direct representation of the degree of unsaturation present in the oil. Iodine is used to halogenate the double bonds present in unsaturated fatty acids of oil. The vegetable oil sample reacts with an excess of iodine monochloride solution (Wijs reagent) under controlled conditions. Halogens add quantitatively to the double bonds in the unsaturated fatty acids, principally oleic and linoleic acids. Unreacted halogens are determined by titrating with thiosulfate. The iodine number is defined as the grams of halogen, expressed as iodine, reacting with 100 g of oil.

E. Estimation of conjugated dienes and trienes by UV spectroscopy

The UV spectrum involves the electronic absorption of fatty acids; in particular, the 230-270 nm band shows high absorption when conjugated dienes and trienes of unsaturated fatty acids are present. For this reason, the absorbance measured at 232 nm and 270 nm, namely K232 and K270, which is capable of detecting product oxidation and rectified oils. The analysis of primary oxidation compounds is always carried out either by the peroxide value or alternatively, by the determination of specific extinction at 232 nm, since the hydroperoxides of polyunsaturated fatty acids, the most susceptible fatty acids to undergo oxidation have a strong absorbance at 232 nm. The latter is especially useful for small samples and has the advantage of being nondestructive [21]. UV absorption at K268 is one of the markers used to follow secondary oxidation formation [22].The increment of absorptivity at 268 nm, which is an indicator for the formation of conjugated trienes.

F. FTIR spectroscopy

FT-IR spectra shows notable difference in the band near 3009cm^{-1}assigned C-H stretching vibration of the cis-double bond (=CH), near 966 cm^{-1} assigned trans –CH=CH– bending out of plane and 722 cm ^{1} assigned cis –CH=CH– bending out of plane. primary and secondary oxidative products by FTIR spectroscopy.

Spectra shows notable difference in the band near 3800-3200 cm^{-1}, -OH stretching [23], 1746 cm^{-1} assigned ester carbonyl functional group of the triglycerides, near 3470cm^{-1} assigned –OH stretching frequency of hydro peroxide [24], The aldehydes C=O exhibited stretched band in 1730-1680 cm^{-1}. Aldehydes also showed weak absorption band in the frequency region 2700-2800 cm^{-1} which indicate the presence of C-H stretching in aldehydes.

III. Conclusion

Vegetables oils used for deep frying process is degraded at high temperature. The change in physiochemical properties of oils is various with types of vegetable oils. Intensity of deterioration of vegetable oil at high temperature it depend on quantity of polyunsaturated fatty acids, monounsaturated fatty acids, presence of antioxidants in oil. From review it is observed that oil containing high amount of polyunsaturated fatty acids were degraded greatly than the types of oil containing monounsaturated fatty acids and saturated fatty acids. Quantity of Linoleic acid and linolenic acid in oil were decreased significantly during frying at high temperature and stearic acid, palmitic acid, oleic acid were increased. Change in peroxide value, p-anisidine value, viscosity, free fatty acids, refractive index, total pour compounds, colour, trans fatty acids content, conjugated diene and triene were increased during frying process. Saponification values, iodine number, cis fatty acid content were decreased during frying. Formation of saturated and unsaturated aldehydes, conjugated double bond, isomerization of cis and trans, these changes in the chemical profile of excessively used oil were cause several health hazards and rendered oils unfit for human consumption. Further comparative study is required to investigate the deterioration of commonly used vegetable oil for repeated frying process.

Reference

[1]. Abdul Rohman Y.B. Che Man.(2013). Application of FTIR spectroscopy for monitoring the stabilities of selected vegetable oils during thermal oxidation. Article in International Journal of Food Properties,16(7)

[2]. Amit, K. Das and Babylatha , R. and Pavithra , A. S. and Sakina, Khatoon (2013) Thermal degradation of groundnut oil during continuous and intermittent frying. Journal of Food Science and Technology, 50(6): 1186-1192

[3]. Anwaar Ahmed, Nisar Ahmed Malik, Muhammad Atif Randhawa, Saeed Akhtar, Asif Ahmad, Hajra Ahmed And Syed Shahzad Shah (2012).Changes in vegetable oil used for commercial frying:a case study from rawalpindi , Pakistan J.Chem.Soc.Pak., 34(5)

[4]. Barbara Muik, Bernhard Lend, Antonio Molina-Diaz, Maria Jose Ayora-Canada,(2005). Direct monitoring of lipid oxidation in edible oils by Fourier transform Raman spectroscopy. Journal of Chemistry and Physics of Lipid, 134: pp 173-182

[5]. C.Andrew; Buba A. A.; A.U. Itodo; E.E.Etim (2012). Thermoxidative Degradation of Commonly Used Vegetable Oils: A Comparative Study. Journal of Emerging Trends in Engineering and Applied Sciences (JETEAS), 3 (6) :924-928

[6]. Erum Zahir, Rehana Saeed, Mehwish Abdul Hameed, Anjum Yousuf. (2014) Study of hysicochemical properties of edible oil and evaluation of frying oil quality by Fourier Transform-Infrared (FT-IR) Spectroscopy. Arabian Journal of Chemistry, Article.

[7]. Felix A. Aladedunye, Roman Przybylski. (2009). Degradation and Nutritional Quality Changes of Oil During Frying. Journal of the American Oil Chemists Society, 86(2):149-156

[8]. Garima Goswami, Rajni Bora, Mahipat Singh Rathore. (2015). Oxidation of cooking oils due to repeated frying and human health. International Journal of Science Technology and management, 04(01).

[9]. Goburdhun D, Jhaumeer-Laulloo SB Musruck. (2001). Evaluation of soybean oil quality during conventional frying by FTIR and some chemical indexes. International Journal of Food Science Nutrition, 52(1):31-42

[10]. Rashmi Sharma, Renu Bhutra, Shveta Acharya and M R K Sherwani. (2007) Comparative analysis of four edible oils for stability against longer storage and heat deterioration during frying. Journal of lipid science technology 39:111-113

[11]. R. P. Yadav, Bibha Kumari. (2013). Ultrasonic Studies on Mustard Oil: A Critical Review. International Journal of Science and Research (IJSR) 6(14).

[12]. Priyanka Rastogi, Beena Mathur, Shweta Rastogi, V.P. Gupta, Rajeev Gupta. (2006). Fatty acid oxidation and other biochemical changes induced by cooking in commonly used Indian fats and oils. Nutrition & Food Science, 36(6):407 – 413

[13]. Pravin S More , Anil V Shelke,and Dattatray J Late. (2015). Rapid characterization of oxidative deterioration in edible oil by optical photospectrometry research & reviews. Journal of Food and Dairy Technology RRJFPDT , 3(2)

[14]. Nasirullah, Baby Latha Rangaswamy. (2005). Oxidative stability of healthful frying oil medium and uptake of inherent nutraceuticals during deep frying. Journal of American oil Chemists' Society October, 82(10): 753-757

[15]. Narasimhamurthy, K. and Raina, P. L. (1998). Studies on the physico-chemical characteristics of some vegetable oils during heating and frying. Journal of Food Science and Technology, 35 (5): 432-434.

[16]. M.C. Pérez Camino, W. Moreda, A. Cer, (1996). Determination of diacylglycerol isomers in vegetable oils by solid-phase extraction followed by gas chromatography on a polar phase, Journal of Chromatography A 721: 305-307.

[17]. Sadoudi R, Ammouche A and Ali Ahmed D, (2014). Thermal oxidative alteration of sunflower oil, African Journal of Food Science, 8(3):116-121

[18]. Barthel, G., Grosch, W., (1974). Peroxide value determination: comparison of some methods. Journal of Americun oil chem. soc., 51: 540-544.

[19]. Lapointe A, Couillard C, Lemieux S.(2006). Effects of dietary factors on oxidation of low-density lipoprotein particles.Journal of Nutritional Biochemistry.17(10): 645-58.

[20]. Mariod, A., Matthaus, B., Eichner, K. & Hussein, I.H. (2006). Frying quality and oxidative stability of two unconventional oils. Journal of the American Oil Chemists' Society 83, 529- 538

[21]. Dobarganes, M.C. and Márquez-Ruiz, G. (2003). Oxidized fats in foods. Curr.Opin. Clin. Nutr. Metabol. Care, 6:157–63.

[22]. S.Garby., H. Harhar., B.Kartah. I.Chafchauni. Z. Sibawayh and Z. Charrouf. (2013), Chemical Cheracterixation and oxidative stability of two monovarietal virgin olive oils grown in morocco. Journal of materials and environmental science. 4(6): 935-942.

[23]. Bhundit Innawong, parameswarakumar, Mallikarjunan, (2004).The determinations of frying oil quality using Fourier transform infrared attenuated total reflectance. Lebensm. Wiss U. Technol., 37: 23-28

[24]. Pragasam A, Vinayak M.Naik, Preeti N. Tallur.(2015). Assessment of physic-chemical characteristic deterioration of lipids by FTIR spectra for successively used soy bean and sunflower oils in frying spice food stuffs. Journal of applied chemistry, 8(3): 47-51.