IODINE VALUE AND FREE FATTY ACID : AN INDEX OF EDIBLE OIL OXIDATION

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Abstract:

Edible oils play an important role in the body as carriers of essential fatty acids (EFA). Oil oxidation is an undesirable series of chemical reactions involving oxygen that degrades the quality of an oil. Researchers have found a relative loss of the C18:2 fatty acid and a decrease in the iodine value (IV) of oil after heating due to more intensive thermo-oxidative transformations that occur compared to heated oil containing food. The decrease in the iodine value can be attributed to the destruction of double bonds by oxidation, scission, and polymerization. IV is not a measure of quality but is an indicator of oil composition . Present paper is an attempt to discuss importance of iodine value and free fatty acid value for monitoring oxidative rancidity of an oil

Keywards: Free fatty acid, iodine value, peroxide value, free radical,

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1.Introduction

Oils have always been an integral part of human foods, being essential for health. Industrially, they play an important role in the development of different areas of chemical products, pharmaceutical, cosmetics, paints and most importantly, food (Atef, 2010). Edible oils play an important role in the body as carriers of essential fatty acids (EFA). Oils are naturally occurring esters of long straight-chain carboxylic acids. They belong to the saponifiable group (contain an ester groups) of lipids. Lipids are biologically produced materials that are relatively insoluble in water but soluble in polar and non-polar organic solvents. Edible oils are constituted of triacylglycerol molecules, mainly formed by unsaturated (oleic, linoleic, linolenic acids etc.) and saturated fatty acids (myristic, palmitic, stearic acids etc.) esterified to Glycerol units (Andersson et al., 2010).

Oil oxidation is an undesirable series of chemical reactions involving oxygen that degrades the quality of an oil. Oxidation eventually produces rancidity in oil, with accompanying off flavours and smells Oxidation is a complex series of reactions which on oxidation produces a series of breakdown products in stages, starting with primary oxidation products (peroxides, dienes, free fatty acids), then secondary products (carbonyls, aldehydes, trienes) and finally tertiary products.

Oxidation progresses at different rates depending on the following factors .

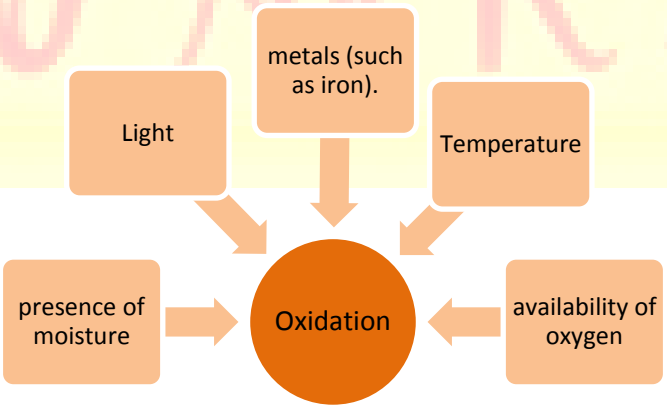

Fig: 1

The type of oil also influences the rate of oxidation Autoxidation is the most common process leading to oxidative deterioration and is defined as the spontaneous reaction of atmospheric oxygen with lipids. The process can be accelerated at higher temperatures and is known as thermal oxidation (usually associated with deep frying) resulting in increases in free fatty acid and polar matter contents, foaming, color, and viscosity. The available methods to monitor lipid oxidation in foods can be classified into five groups which is based on determination of different content(Fig:2)

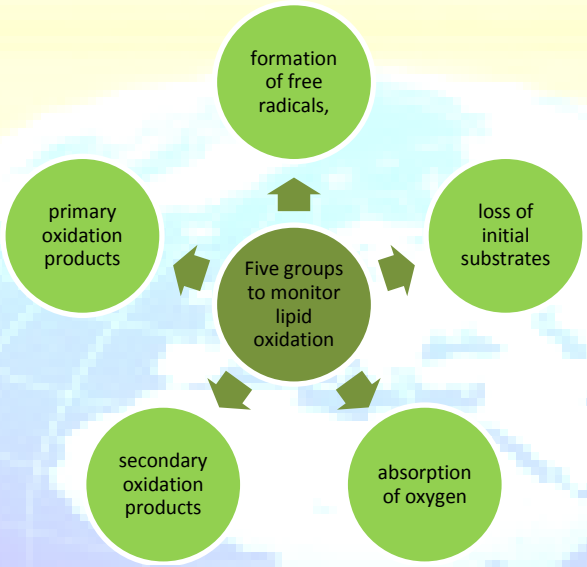

Fig :2

A number of physical and chemical tests as density, viscosity, refractive index, free fatty acid ,acid number, iodine number, peroxide value including instrumental analyses, have been employed in laboratories and the industry for measurement of various lipid oxidation parameters. These include the weight-gain and headspace oxygen uptake method for oxygen absorption; chromatographic analysis for changes in reactants, Fourier transform infrared (FTIR) method for peroxide value; spectrometry for conjugated dienes and trienes, 2-thiobarbituric acid (TBA) value, p-anisidine value (p-AnV), and carbonyl value; Rancimat and Oxidative Stability Instrument (OSI) method for oil stability index; and electron spin resonance (ESR) spectrometric assay for free-radical type and concentration. Other techniques based on different principles, such as differential scanning calorimetry (DSC) and nuclear magnetic resonance (NMR), have also been used for measuring lipid oxidation.

The IV ("iodine adsorption value" or "iodine number" or "iodine index") measures the number of reactive double bonds present in an oil. Iodine numbers are often used to determine the amount of unsaturation in fatty acids. A higher IV number indicates more double bonds in the sample and therefore that greater care will be needed to slow down oxidation. IV is not a measure of quality but is an indicator of oil composition. The higher the iodine number, the more C=C bonds are present in the fat.[1] It can be seen from the table 1 that coconut oil is very saturated, which means it is good for making soap. On the other hand, linseed oil is highly unsaturated, which makes it a drying oil, well suited for making oil paints.

Name of oil	Iodine value
Coconut	8-10
Beef tallow	30 - 45
Palm oil	37 - 54
Lard	45 - 70
Olive oil	75 - 95
Peanut oil	85 - 100
Cottonseed oil	100 - 117
Corn oil	115 - 130
Fish oils	120 - 180
Soybean oil	125 - 140
Safflower oil	130 - 140
Linseed oil	155 - 205

Table 1 Iodine value of some vegetable oils

The quantity of substance used in the determination should be such that at least 70% of the iodine added is not absorbed. Unless otherwise specified in the monograph, the quantity of

the substance indicated in the following Table 2 should be used for the determination, depending on the expected iodine value:

Iodine value	Quantity of substance in g
less than 20	1.0
20 - 60	0.5 - 0.25
60 - 100	0.25 - 0.15
more than 100	0.15 - 0.10

Table 2

The amount of iodine absorbed in percentage is the measure of unsaturation in the oil. No oil has zero iodine value and oils are classified as drying, semi drying and non drying on the basis of iodine value. Oleic acid containing 1 double bond absorbs 90% of iodine, linoleic acid (2 double bonds) absorbs 181% iodine and linolenic acid (3 double bonds) absorbs 274% iodine. Non drying oils have 1 double bond and absorbs iodine below 90%. Semi drying oils contain some proportion of double bonds and have iodine value below 140.

In general, deep-fat frying decreases the content of unsaturated fatty acids in frying fat and oil. The decrease in the iodine value can be attributed to the destruction of double bonds by oxidation, scission, and polymerization. According to previous studies (Orthoefer *et al*., 1996; Tyagi and Vasishtha, 1996; Choe and Min, 2007) the heat treatment causes the oxidative rancidity resulting in an increase in the free fatty acids. This is why heated and unheated fats and oils should be monitored by means of analysis e.g., the FAC and IV indicating the degradation of the FAs.

The iodine value (IV) gives a measure of the average *degree of unsaturation* of a lipid: the higher the iodine value, the greater the number of C=C double bonds. By definition the iodine value is expressed as the grams of iodine absorbed per 100g of lipid. Iodine value (I.V.) is directly proportional to the degree of unsaturation (No of double bonds.) and inversely

proportional to the melting point (M.P.) of lipid. An increase in I.V.indicates high susceptibility of lipid to oxidative rancidity due to high degree of unsaturation (Table: 3)

	Saturated (SFA)				Mono saturated (MUFA)		Polyunsaturated (PUFA)			Iodine Value (IV)
Oil/ fat	Lauric C12:0	Myristic C14:0	Palmitic C18:0	Stearic C18:0	Oleic C18:1	Rincinoleic C18:1	Linoleic (ω6) C18:2	Linolenic (ω3) C18:3	Eleaosteric C18:3	
No of double bond	0	0	0	0	1	1	2	3	3	
Coconut	44	18	11	6	7	-	2	-	-	8-10
Corn	-	-	13	4	29	-	54	-	-	115-130
Soybean	-	-	11	4	25	-	51	9	-	125-140
Safflower	-	-	8	3	13	-	75	1	-	130-140
Sunflower	-	-	11	6	29	-	52	2	-	125-136
Linseed	-	-	6	4	22	-	16	52	-	155-205
Caster	-	-	12	1	7	87	3	-	-	81-91
Tung	-	-	4	1	8	-	4	3	80	160-175

Table : 3 Fatty acid composition and Iodine value of some oils

2.Methodology

2.1 Iodometric Titration

One of the most commonly used methods for determining the iodine value of lipids is "Hanus method". This particular analysis is an example of iodometry. The lipid to be analyzed is weighed and dissolved in a suitable organic solvent, to which a known excess of iodine chloride is added. Some of the IBr reacts with the double bonds in the unsaturated lipids, while the rest remains:

$$R\text{-}CH{=}CH\text{-}R + IBr_{excess} \rightarrow R\text{-}CHI\text{-}CHBr\text{-}R + IBr_{remaining}$$

The amount of IBr that has reacted is determined by measuring the amount of IBr remaining after the reaction has gone to completion ($IBr_{reacted} = IBr_{excess} - IBr_{remaining}$). The amount of IBr remaining is determined by adding excess potassium iodide to the solution to liberate iodine, and then titrating with a sodium thiosulfate ($Na_2S_2O_3$) solution in the presence of starch to determine the concentration of iodine released:

$$IBr_{remaining} + 2KI \rightarrow KBr + KI + I_2$$

$$I_2 + \text{starch} + 2Na_2S_2O_3\ (\text{blue}) \rightarrow 2NaI + \text{starch} + Na_2S_4O_6\ (\text{colorless})$$

Iodine value was calculated as follow

$$\text{Iodine value} = \frac{12.69 \times (B\text{-}S)\ N}{W}$$

B= Vol. of 0.1 N $Na_2S_2O_3$ solution needed for Blank

S =Vol. of 0.1 N $Na_2S_2O_3$ solution. needed for samples

N = Normality of Standard $Na_2S_2O_3$

w= Weight in gm of the oil

2.2 FTIR Spectroscopy

The primary spectra in infrared for absorption of the bond between carbonyl (1740cm-1) and the double bond carbon -carbon bond (1651cm-1) a quick determination of the iodine value is possible, characterized by the content of unsaturated fatty acids in oil (Hendi *et al*). The strong overlapping effects and differences in intensities reduce the use of band at 1654cm-1. The identification of fatty acid is done on the basis of absorption of the carbonyl group (1745cm-1)

Conclusion

Iodine value is intended as a measure of unsaturation and at times it is used as quick alternative to oxidation test of edible oils. Iodine value indicates drying quality of oil, the drying oil having higher iodine values. Oxidative and chemical changes in oil during storage and deep frying or heating at higher temperature are charcterized by decrease in the total unsaturation of the oil and an increase in free fatty acid contents

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Dr. Geeta Verma (*nee* Singh) received M.Sc (Organic Chemistry) from Lucknow University, U .P and completed her research work on the topic "Synthesis of Novel Peptides of Biological Significance" (having GH releasing and immunosuppressant activity) from Central Drug Research Institute Lucknow, U.P and got Ph .D degree from Dr. R. M .L. Avadh University, Faizabad, U.P & M.A.(Eng) from Barkatullah Univeristy, Bhopal , M.P. Currently, She is working as an Assistant Professor in the Department of Chemistry in Chandra Shekhar Azad Govt Post Graduate Nodal College, Sehore, M. P. India. She has completed Minor research project sanctioned by UGC ,CRO Bhopal and got Best paper award by International Academy of Science Engineering and Technology (IASET) in Sep 2015 edition for MRP work. Her major areas of interests are Peptide Chemistry , Green chemistry and Food Chemistry including Astrology, Spirituality, Vastu Shastra, English Literatures Social & Family related issues *etc*. She has publications in following Journals

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- *Naveen shoadh sansar*
- *International Journal of Research in Applied Natural and Social Science (IMPACT) ,*
- *International Journal of Applied and Natural Science (IASET)*
- *one Indian Patent.*