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EDIBLE QUALITY DETERIORATION OF RAW COOKING OILS IN THE PRESENCE OF METAL ION IMPURITIES OVER STORAGE EFFICIENCY

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Abstract

The stability and self life of edible oils plays key role in deciding hygienic food preparation and quality assurance of food products. Mainly internal and external factors like temperature, moisture, Oxygen, metal impurities etc. influence characteristic properties of the edible oil. The experiment was carried out to study characteristic deterioration of ground nut, soya bean and sunflower oils in the presence of inorganic metal ions such Ba^{+2}, Fe^{+3} and Mg^{+2}. Acid value, peroxide value and para-anisidine values of each oil were determined in the interval of 8days for 64 days in the presence and absence of metal ions. Ba^{+2} and Fe^{+3} ion increases the AV, PV and p-AV of oil samples gradually with respect to blank samples whereas Mg^{+2} moderately enhance the PV and p-AV of the oil samples. Ba^{+2} and Fe^{+3} record an average maximum PV of 1.4mgeq and 3.1 respectively for GNO, SO and SFO indicating that the peroxidation is not much influenced. But, the peroxidation was accelerated considerably by Mg^{+2} ions and record an average maximum PV of 14.3mgeq for oil samples GNO, SO and SFO. Ba^{+2} and Fe^{+3} ions slightly increase the p-AV for GNO, SO and SFO indicating that the secondary oxidation was controlled to a large extent. But, the secondary oxidation was accelerated considerably by the Mg^{+2} ions. An average maximum p-AV was recorded for oil samples with Mg^{+2} ions is 10.1 and contributes to characteristic deterioration of edible oils.

Key Words: Metal ions, Peroxide value, Para- anisidine value, Peroxidation, Deterioration,

INTRODUCTION

Characteristic properties of edible oils decide its hygienic utility in cooking processes and storages. Quality of edible oils or fats is based on its oxidative stability and mainly affected by processing conditions like the application of high temperature, oxidants, enzymes (such as lipoxygenase), moisture and light [1, 2]. The oxidation process destroys essential fatty acids and promotes the formation of off-flavored and potentially toxic, mutagenic, and carcinogenic new compounds like diacylglycerols, monoacylglycerols, monomers, polymers, free fatty acids, and other oxidative substances. This induces a significant loss of oil quality that promotes changes in functional, sensory properties, nutritional attributes, and safety of oils and food products [3]. The time taken for secondary products to develop from primary oxidation products (hydroperoxides),

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varies between oils [1]. Oils with significant levels of unsaturated fatty acids are generally more susceptible to the oxidation process [4].

The peroxide index is the most common parameter used to characterize oils and fats. A product with peroxide value between one and five meq/kg is classified at low oxidation state that between 5 and 10 meq / kg is classified at high oxidation state. To decide the quality of oil, the peroxide value is one of the parameter which could be determined iodometrically applying standard method [5]. Anisidine values (AnV) represent the level of non-volatile aldehydes, primarily, measuring the presence of 2-alkenals and 2,4-alkadienals generated in the fat during the decomposition of hydroperoxides [6]. A progressive increase in AnV was observed with deep-frying [7, 8], microwave [9-11] and conventional oven [12, 13] heating. The total oxidation (TOTOX) value is an extension of AnV method given as the sum of two times PV and AnV, which is an important evaluation parameter for the overall oxidation state. At low temperatures and a short storage period, the formation of oxidation compounds is slow.

The oxidative stability of oil or fat can also be determined by recording the vibrational frequency of functional groups using FTIR spectrum [14]. A secondary oxidation product of oils and fats is determined by thiobarbituric acid (TBA) test [15]. The most widely used procedure employs the oxidative capacity of lipid (Hydro) peroxides to produce iodine from potassium iodide [16, 17]. A detailed critical evaluation of methods for measurement of oxidative rancidity in vegetable oils was carried out by Marc Pignitter and Veronika Somoza [18]. Because of these compounds often contribute to rancid and unpleasant flavours, and reduce the nutritional value of fried foods [19]. Lipid oxidation has a negative impact on the functionality of raw materials, sensory and nutritional quality of food, and causes economic losses [20]. The most noticeable result of lipid oxidation is the appearance of an unpleasant flavour often referred to rancid, which modifies the sensory characteristics of the food, so its assessment by the consumer [21-24]. Lipid oxidation also led to a change in colour and sometimes texture, as well as the loss of essential nutrients and micronutrients [23]. Finally, lipid oxidation can lead to the formation of potentially toxic oxidation products (oxycholesterol, malonaldehyde, endoperoxides, acrolein, polymeric peroxides) [24, 25]. The extent of lipid oxidation depends upon the oil's internal factors not only like the degree of unsaturation and the presence of antioxidant compounds but also metals like copper and iron and the oil's external factors, such as oxygen availability and temperature. The contact of oils with oxygen gives rise to chain reactions that progress faster with higher temperatures as well as with an increased unsaturation degree of the lipids [26]. It was found that the rates of increase in peroxide value without added Fe(III) palmitate were greater than those for oils with added Fe(III) palmitate. However, the increases in *p*-anisidine value greater in oils with added Fe(III) palmitate than in oil without added Fe(III) palmitate. The results suggested that the assessment of the extent of oxidative deterioration in oils with added Fe(III) palmitate could not be evaluated using indicators of primary oxidation alone[27] The present work was concentrated on the role of metal ions in characteristic deterioration of edible oils. The experiment was focused on the raw milled edible oils such as ground nut oil, sunflower oil and soya bean oil. The quality and shelf life was decided by determining the oil factors like acid value, peroxide value and paraanisidine value.

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METHOD AND MATERIALS

Chemicals:

Acetic acid, chloroform, potassium iodide, Sodium thiosulphate, Starch powder, p-anisidine, isooctane. All chemicals are lab and analytical grade and purchased from Nice chemical supplier.

Samples:

Raw soya bean, sunflower and groundnut were collected local milling agencies by wet process around Mysore city, Karnataka, India.

Sampling:

100ml of each oil was taken in a 250 ml stoppered reagent bottle, added …mg metal salt, mixed well and allowed it for eight days with loosely connected lid. Then the acid, peroxide, and p-anisidine value were determined. The interval was continued for 64 days.

Acid Value of oil (AV):

Exactly 1±0.05 gram of peanut oil was weighed into 250ml clean conical flask. To this 25ml of neutralized ethanol was added and mixed well. The resulting solution was titrated against standard 0.1N KOH using phenolphthalein as an internal indicator to the end point colourless to pink colour. KOH solution was standardized by standard 0.1N oxalic acid solution [28].

Peroxide Value (PV):

Exactly 5gm oil was weighed into the Erlenmeyer flask with glass stopper. Acetic acid and chloroform mixture in the ratio 3:2 was added to the flask. To this 0.5 ml saturated KI solution was added, and peroxide value was determined by titrating against standard 0.01 M sodium thiosulfate solution using starch as indicator. The procedure was followed according to officially recommended method by AOCS [28].

$$PV = \frac{(S\text{-}B) \times N \times 1000}{\text{Weight of sample}}$$

B = Blank titre value. S = Sample titre value. N = Normality of sodium thiosulfate solution

p-Anisidine Value (p-AV):

The carbonyl content in oils was determined by standard method according to AOCS [28]. It measures the reactiveness of the aldehydes' carbonyl bond on the p-anisidine amine group forming a Schiff's base which absorbs at 350 nm. 2g (W) of soy bean oil was dissolved in 25 ml isooctane and absorbance A1 was measured at 350 nm against a blank isooctane. An aliquot (5 ml) of this solution, respectively 5 ml of isooctane (as blank) was transferred to each of two test tubes of 10 ml and 1ml anisidine solution (0.25% g/v glacial acetic acid) was added to each. After 10 minute the absorbance A2 was measured at 350 nm against isooctane containing p-anisidine. The p-AV is determined as;

$$p\text{-}AV = 25 \times 1.2 \times (A2\text{-}A1) / W$$ [29].

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RESULT AND DISCUSSION

Acid value (AV)

Acid value for each experimental oil sample was determined at the interval of eight days and recorded as shown in the Table1.

Table1: Storage period against acid value in presence of salts

Oil-Salt/Days	$BaCl_2$			$FeCl_3$			$Mg(NO_3)_2$		
	GNO	SO	SFO	GNO	SO	SFO	GNO	SO	SFO
0	1.2	2.0	1.1	1.2	2.0	1.1	1.2	2.0	1.1
8	1.4	2.0	1.2	1.2	2.0	1.2	1.2	1.8	1.2
16	1.8	2.1	1.6	2.4	2.2	1.5	2.5	2.2	1.8
24	2.4	2.2	2.0	2.5	2.5	2.0	2.6	2.6	2.2
32	2.5	2.4	2.4	2.7	2.8	2.7	2.8	2.9	2.8
40	2.5	2.4	2.4	2.9	2.8	2.7	3.0	3.1	2.9
48	2.6	2.5	2.5	3.1	2.9	2.8	3.0	3.3	3
56	2.6	2.5	2.6	3.0	3.0	2.8	3.1	3.3	3
64	2.6	2.5	2.6	3.0	3.0	2.9	3.1	3.4	3.1

Table1 clearly indicates that the acid value of samples GNO, SO and SFO does not change much with storage time in the presence of $BaCl_2$ whereas in the presence of $FeCl_3$ and $Mg(NO_3)_2$ a gradual increase was observed. It is conspicuous that $BaCl_2$ is not support the hydrolysis of triglycerides to form free fatty acid. $FeSO_4$ and Mg $(NO_3)_2$ gradually increases the hydrolysis of triglycerides thereby producing increased amount of free fatty acid with storage time.

To understand the trend in the acid value with storage time, a graph of acid value versus storage time for experimental and blank oil samples was plotted as shown in the Figure1a, b. The graph clearly explains that the acid value of samples increase with storage time in general. Ba^{+2} ion hydrolysis the lipid gradually with respect to blank samples whereas Fe^{+3} and Mg^{+2} hydrolysis moderately the lipids of the oil samples. Ba^{+2} slightly increases the acid values for GNO, SO and SFO indicating that the hydrolysis is not much enhanced. But, the hydrolysis was accelerated considerably by the Fe^{+3} and Mg^{+2} ions. A maximum acid value was recorded for oil samples GNO, SO and SFO with Mg^{+2} ions and confirms that is an effective lipid hydrolyzing divalent metal ion.

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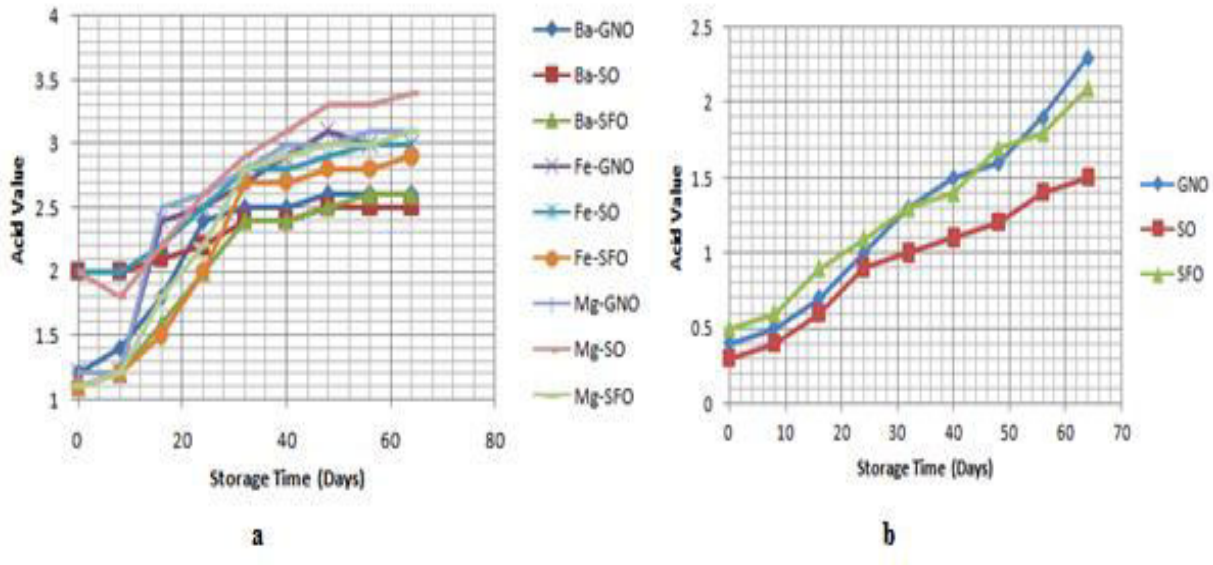

Figure: 1 a) Plot of AV versus storage time of samples b) Plot of AV versus storage time of blanks

Peroxide Value (PV)

Peroxide value for each experimental oil sample was determined at the interval of eight days and recorded as shown in the Table2.

Table2: Storage period against peroxide value in presence of salts

Oil-Salt/Days	$BaCl_2$			$FeCl_3$			$Mg(NO_3)_2$		
	GNO	SO	SFO	GNO	SO	SFO	GNO	SO	SFO
0	0.4	0.3	0.5	0.4	0.4	0.5	0.4	0.4	0.6
8	1.2	0.9	1.1	1.2	0.9	1.3	5.2	2.2	3.1
16	1.4	0.9	1.1	1.5	1.0	1.7	6.0	3.4	3.5
24	1.4	1.1	1.2	1.8	1.3	1.9	7.2	4.2	4.5
32	1.4	1.2	1.3	2.1	1.5	2.4	9.3	8.4	9.3
40	1.4	1.1	1.1	2.3	2.2	2.5	9.6	8.9	9.3
48	1.4	1.3	1.2	2.6	2.4	2.7	10.0	9.7	9.6
56	1.3	1.3	1.2	2.7	2.5	3.0	13.6	12.3	13.2
64	1.4	1.4	1.3	2.9	2.7	3.1	15.2	13.2	14.6

Table2 clearly indicates that the peroxide value of samples GNO, SO and SFO does not change much with storage time in the presence of $BaCl_2$ whereas in the presence of $FeCl_3$ and $Mg(NO_3)_2$ a gradual increase was observed. It is conspicuous that $BaCl_2$ is not support the peroxidation of triglycerides to form free fatty acid. $FeCl_3$ and Mg $(NO_3)_2$ gradually increases the peroxidation of triglycerides thereby showing increased peroxide value of oil samples with storage time.

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To correlate the trends in the peroxide value with storage time, a graph of peroxide value versus storage time for experimental and blank oil samples was plotted as shown in the Figure2a, b. The graph clearly explains that the peroxide value of samples increase with storage time in general. Divalent Ba^{+2} ion increases the PV of lipid gradually with respect to blank samples whereas Fe^{+3} and Mg^{+2} moderately enhance the peroxidation of lipids of the oil samples. Ba^{+2} slightly increase the PV for GNO, SO and SFO indicating that the peroxidation is not much increased. But, the peroxidation was accelerated considerably by the Fe^{+3} and largely by Mg^{+2} ions. A maximum PV was recorded for oil samples GNO, SO and SFO with Mg^{+2} ions and confirms that it is an effective divalent metal ion to enhance lipid peroxidation.

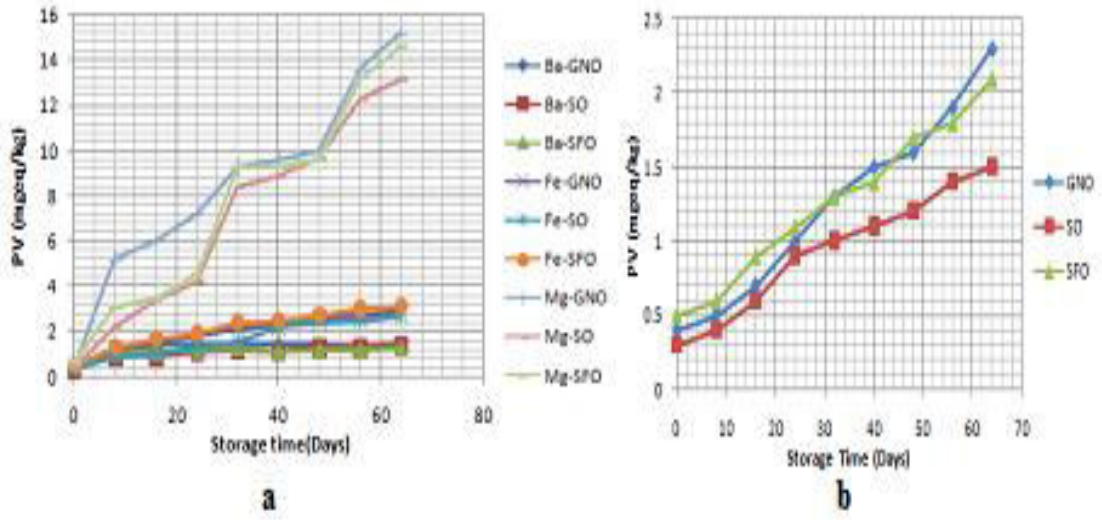

Figure: 2 a) Plot of PV versus storage time of samples b) Plot of PV versus storage time of blanks

p-Anisidine Value(p-AV)

p-AV for each experimental oil sample was determined at the interval of eight days and recorded as shown in the Table3.

Table3: Storage period against p-anisidine value in presence of salts

Oil-Salt/Days	$BaCl_2$			$FeCl_3$			$Mg(NO_3)_2$		
	GNO	SO	SFO	GNO	SO	SFO	GNO	SO	SFO
0	0.2	0.3	0.1	0.3	0.1	0.4	0.2	0.1	0.3
8	0.5	0.5	0.3	0.6	0.4	0.6	2.2	1.7	2.1
16	0.7	0.7	0.6	0.8	0.6	0.7	3.3	2.8	3.5
24	1.0	0.9	0.9	1.3	1.1	1.0	4.2	3.6	4.3
32	1.3	1.1	1.2	1.5	1.4	1.3	6.1	4.4	5.9
40	1.5	1.4	1.3	1.8	1.7	1.5	7.6	5.6	6.7
48	1.8	1.7	1.6	2.3	2.0	1.9	8.0	7.1	8.1
56	2.1	2.3	2.0	2.3	2.2	2.3	9.4	8.4	9.1

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64	2.4	2.5	2.2	2.5	2.6	2.7	10.2	9.8	10.1

Table3 clearly indicates that the p-AV of samples GNO, SO and SFO does not change much with storage time in the presence of $BaCl_2$ whereas in the presence of $FeSO_4$ and Mg $(NO_3)_2$ a gradual increase was observed. It is conspicuous that $BaCl_2$ is not support the hydrolysis of triglycerides to form free fatty acid. $FeCl_3$ and Mg $(NO_3)_2$ gradually increases the hydrolysis of triglycerides thereby producing increased amount of free fatty acid with storage time.

To understand the trend in the p-AV with storage time, a graph of p-AV versus storage time for experimental and blank oil samples was plotted as shown in the Figure3a, b. The graph clearly explains that the p-AV of samples increase with storage time in general. It is noticed that Ba^{+2} and Fe^{+3} ions are not much increased the p-AV of the oil samples to that of blank samples whereas Mg^{+2} recorded conspicuously higher p-AV for the oil samples. Ba^{+2} and Fe^{+3} ions slightly increase the p-AV for GNO, SO and SFO indicating that the secondary oxidation was controlled to a large extent. But, the secondary oxidation was accelerated considerably by the Mg^{+2} ions. A maximum p-AV was recorded for oil samples GNO, SO and SFO with Mg^{+2} ions and confirms that it is responsible for characteristic deterioration of edible oils.

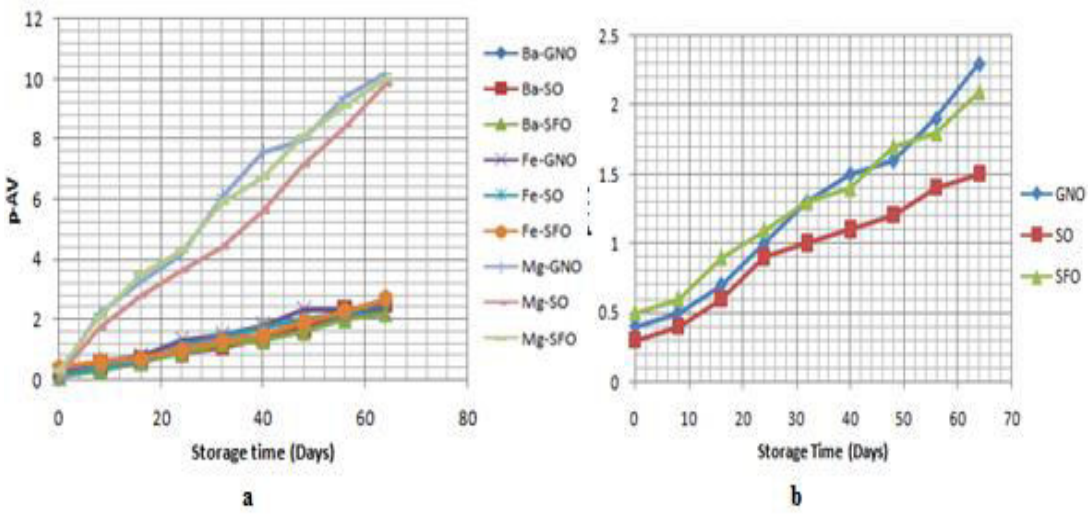

Figure: 3 a) Plot of p-AV versus storage time of samples b) Plot of p-AV versus storage time of blanks

CONCLUSION

Quality of edible oil plays vital role in deciding hygienic food preparation and quality assurance of food products. There are many internal and external factors influence characteristic properties of the edible oil in usage. Most commonly available or used oils are ground nut oil, soya bean oil, sunflower oil, olive oil, sesame oil etc. Self life is very important in usage of edible oils in the usage for a definite period as it undergo auto oxidation to for hydro peroxide and secondary oxidized products like carboxylic acids, ketones, aldehydes, etc. leading to rancidity. The pro-

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oxidation of GNO, SO and SFO oils in the presence of Ba, Fe and Mg metal ions was studied at storage temperature. Ba^{+2} and Fe^{+3} ion increases the AV, PV and p-AV of oil samples gradually with respect to blank samples whereas Mg^{+2} moderately enhance the PV and p-AV of the oil samples. Ba^{+2} and Fe^{+3} record an average maximum PV of 1.4 and 3.1 respectively for GNO, SO and SFO indicating that the peroxidation is not much influenced. But, the peroxidation was accelerated considerably by Mg^{+2} ions and record an average maximum PV of 14.3 for recorded for oil samples GNO, SO and SFO. Ba^{+2} and Fe^{+3} ions slightly increase the p-AV for GNO, SO and SFO indicating that the secondary oxidation was controlled to a large extent. But, the secondary oxidation was accelerated considerably by the Mg^{+2} ions. An average maximum p-AV was recorded for oil samples GNO, SO and SFO with Mg^{+2} ions is 10.1 and contributes to characteristic deterioration of edible oils.

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CONFLICT OF INTEREST

Authors declared no interest of conflict

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