Comparative Study of Oxidative Degradation of Selected Vegetable Oils during Deep Frying

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*Abstract:-***The oxidative degradation of refined sunflower, soybean, groundnut oil and pure mustard oil during deep frying at 180^{0}C were studied. The oxidative degradation of the oils was evaluated by monitoring their respective peroxide value (PV), *p*-anisidine value (*p*-AV), regression coefficient of oils and totox value (TV) for four consecutive days. Result indicate that as comparing the selected four edible oils, mustard oil shows better oxidative stability during deep frying process and soybean oil shows least oxidative stability.**

Key words: sunflower oil, soybean oil, groundnut oil, mustard oil, oxidation degradation, frying, temperature.

I. INTRODUCTION

Deep frying is one of the popular processes of food preparation. Frying temperature, time of frying, number of frying, frying oil, antioxidant and type of fryer affect the hydrolysis, oxidation and polymerization of oil during frying. Vegetable oils contain a range of components (antioxidant) such as tocopherols, phenolics, sterols, butylatedhydroxyanisole(BHA), butylated hydroxytoluene(BHT), propyl gallate (PG), and *tert*-butylhydroquinone (TBHQ) slowdown the oxidation of oil at room temperature. However, they become less effective at frying temperature due to losses through volatilization or decomposition (Boskou 1988; Choe and Lee 1998). Tyagi and Vasishtha (1996) reported the ineffectiveness of 0.01% BHA and TBHQ during deep-fat frying of potato chips in soybean oil. The presence of a high content of polyunsaturated fatty acids increases the susceptibility of oil to oxidation (Quaglia & Bucarelli, 2001). Oil resistance to oxidation in the frying process depends mainly on the fatty acid composition and antioxidant content of the oil (Rossell, 2001; Sanches-Silva *et al*., 2003; Nogala-Kalucka *et al*., 2005; Przybylski & Eskin, 2006).Sunflower and soybean oil contain more polyunsaturated fatty acids (linoleic acid) than Groundnut and mustard oil. Mustard and Groundnut oil contain more monounsaturated fatty acids (oleic acid and erucic acid resp.) and Sunflower and soybean oil.

Lipid oxidation is a major cause of food quality deterioration as during deep frying of food products, vegetable oil undergoes thermal oxidation. Oxidation of unsaturated fatty acids occurs via free radical chain reaction. Lipid hydroperoxides have been identified as primary product (ROOH). The hydroperoxide are very unstable and quickly decompose to secondary oxidation product, such as aldehyde, alcohol, ketones and epoxy compound. During deep frying process of food primary and secondary products can be absorbed into fried food. Lipid oxidation leads to change in colour, texture as well as essential nutrients and micronutrients. The aim of this study is to compare the chemical changes of sunflower,groundnut , soybean and mustard oil that occurs after exposure to prolong deep frying for four consecutive days . The oxidative degradation of the oils was evaluated by monitoring peroxide value (PV), *p* anisidine (*p*-AV), totox value.

II. MATERIALS AND METHODS

Sampling

Deep frying experiments on the vegetable oil of sunflower, Groundnut , Soybean and Mustard oil were carried out simultaneously using stainless steel frying pot of 2 lit. capacity placed 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. In total ten batches of Puri, 100 gm per batch intermittently fried for 5 min., at interval of 5 min. for period of 2 hr. per day for 4 days. The fryer was turned off at the end of the frying experiment each day 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.

Determination of Peroxide value (PV)

The Peroxide values were determined according to ISO 3960-2007. A known weight of the oil sample (5 g) was dissolved in a mixture of glacial acetic acid : chloroform (3:2, v/v, 30 ml), then freshly prepared saturated potassium iodide solution (1 ml) was added. Distilled water (30 ml) was added then titrated slowly with a sodium thiosulphate solution (0.01ml) in the presence of starch solution (1%) as an indicator. Each sample was analyzed twice.

Determination of p-Anisidine value (p-AV)

p-Anisidine values were determined according to ISO 6885:2006 A test solution is prepared in isooctane. It is

reacted with an acetic acid solution of *p*-anisidine. The increase in absorbance at 350 nm is measured. This test is more sensitive to unsaturated aldehydes than to saturated aldehydes because the colored products from unsaturated aldehydes absorb more strongly at this wavelength.

Determination of Totox value (TV)

For assessing the oxidative deterioration of an oil, the total oxidation value, or 'totox value.' (TV), is calculated by the formula TV = (2 x PV) + *p*-AV. The lower the Totox value, the better the quality of oil.

Table 1: Chemical properties of sunflower, groundnut, soybean and mustard oils with frying

Type of Oil	No. of frying	Peroxide Value (PV)	Para-Anisidine Value (*p*-AV)	Totox Value
Sunflower	0	0.59	8.3	9.48
	1	1.82	19.26	22.9
	2	5.83	19.8	31.46
	3	5.52	20.3	31.34
	4	1.98	21.85	25.81
Soybean	0	0.74	6.12	7.6
	1	1.6	15.06	18.26
	2	6.2	18.61	31.01
	3	4.19	20.42	28.8
	4	2.19	22.72	27.1
Groundnut	0	0.78	5.2	6.76
	1	2.11	9.61	13.83
	2	5.16	15.81	26.13
	3	4.98	17.98	27.94
	4	3.96	18.19	26.11
Mustard	0	0.21	7.5	7.92
	1	2.66	8.85	14.17
	2	5.35	10.83	21.53
	3	3.96	12.65	20.57
	4	2.38	17.11	21.87

III. RESULT AND DISCUSSION

Hydroperoxide is the initial lipid oxidation products prepared during frying. It is determined by measuring Peroxide value (PV) of oil. The PV is expressed as milliequivalents oxygen per kg of fat/oil (Nawar, 1996).*p*-Anisidine value (*p*-AV) is a method for measuring secondary decomposition products such as aldehydes (Mariod *et al.*, 2006). Aldehydes are the carbonyl compounds formed by decomposition of hydroperoxides and can be used as markers to determine degradation of peroxidised materials produced by the heating process (Stier, 2001).

Peroxide Value (PV)

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 (O'Brien, 2004) The changes in peroxide value of different oils during frying are shown in Fig. 1 The PV increases during the first few 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 was increase from first day to the end of second day of frying (1.82 to 5.53), while it decreased slightly from the second day to third day(5.53 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 5.82) and it sharply decreases from second day to fourth day (5.82 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 7.16), while it decrease slowly after second day of frying to fourth day of frying(7.16 to 3.96). The result also show that the PV of Mustard oil increased sharply from first day to second day (2.66 to 5.96), while it decrease from second day to fourth day (5.96 to 2.38) of frying process. The result indicate that highest change in PV was observed in groundnut and than in mustard oil while, least change in PV was observed in soybean and than in sunflower oil. This may be due to presence of natural antioxidant such as tocopherols in oil and fatty acid composition.

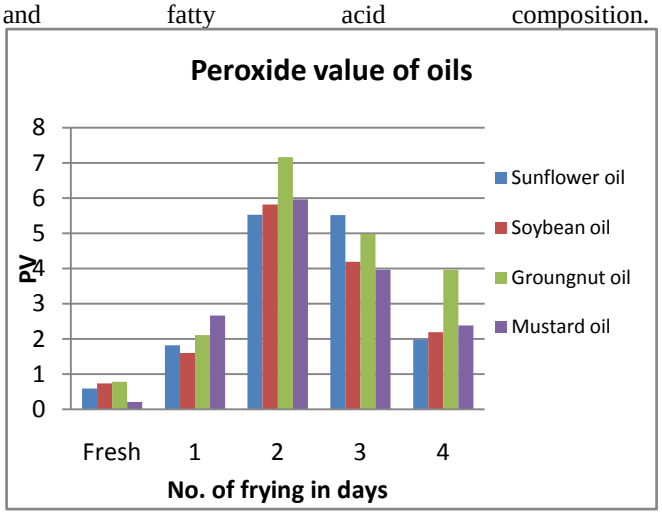

Fig.No. 1 Evalution of the Peroxide Value depending on the numbers of frying at 180^0C

p-Anisidine Value (p-AV)

The changes in the *p*-Anisidine value of all the oils during the four consecutive day of deep frying process are shown in Fig.2. An increase in the *p*-AV of all frying oils was observed with prolonging the deep frying time. This finding could be explained by the fact that less stable primary oxidized compound (hydroperoxide) decomposed further to form aldehyde compound. Aldehyde compounds are secondary oxidized compounds which formed at frying temperature. *p*-anisidene value, therefore the level of aldehydes, increased with increasing number of frying for all four oils. The highest significant change in *p*-AV was observed in the soybean oil followed by sunflower oil, while least significant change observed in the mustard oil followed by groundnut oil. This observation could be due to presence of high concentration of polyunsaturated fatty acids (linoleic acid) that were oxidized, are present in soybean (54.2%) and sunflower (39.4) oils. From value of regression line slope (table No. 2) the rate of the decrease of oxidative stability are determined. It is decrease in the following order Mustard oil > Groundnut oil > Soybean oil > Sunflower oil. The oil rich in monounsatured fatty acids shows higher oxidative stability than the oil containing polyunsaturated fatty acids during deep frying. The mustard oil and groundnut oil showed higher oxidation stability during deep frying.

Table No. 2 Regression coefficient of oils from the linear regression of *p*-AV

Type of Oil	Rate of decrease of *p*-AV
Sunflower oil	$R^2 = 0.665$
Soybean oil	$R^2 = 0.883$
Groundnut oil	$R^2 = 0.898$
Mustard oil	$R^2 = 0.942$

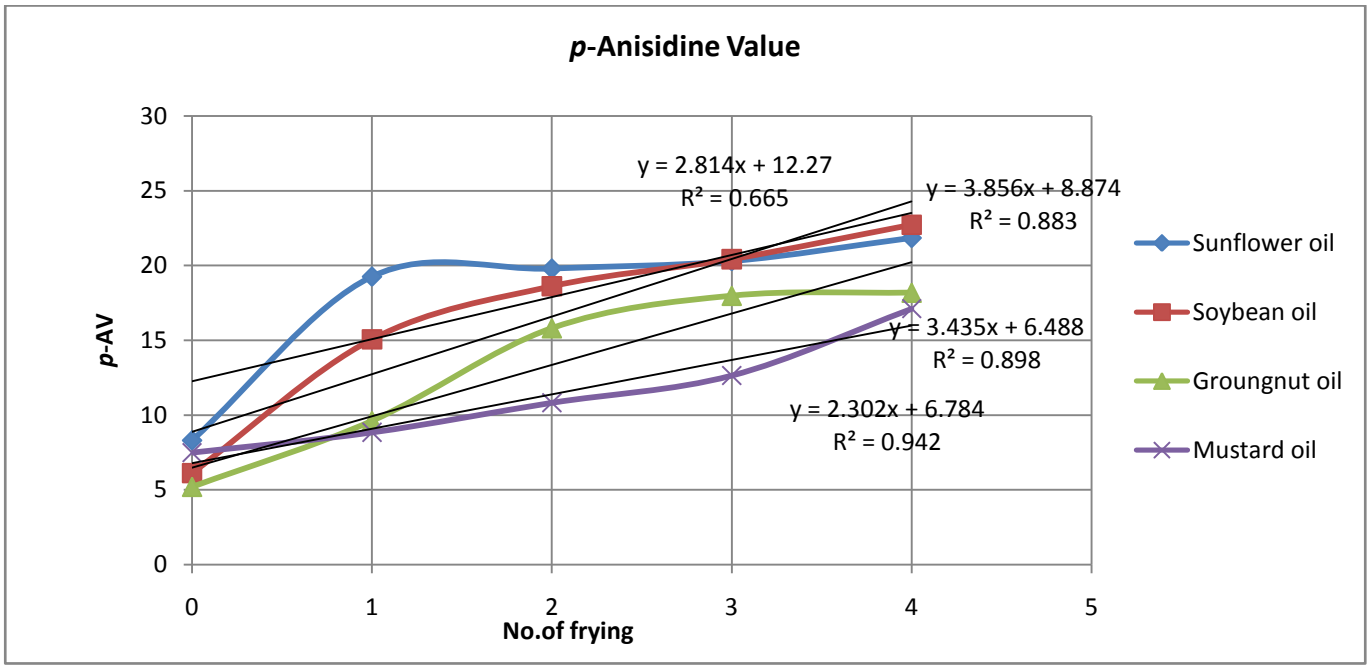

Fig.No. 2 Evalution of the *p*-Anisidine Value depending on the numbers of frying at 180^0C

Totox value (TV)

The Totox value is a measure of the total oxidation, including primary and secondary oxidation products. It is a combination of PV and *p*-AV. Totox value measures both hydroperoxides and their breakdown products, and provides a better estimation of the progressive oxidative deterioration of oils. The result obtained from TV determination is shown in Table No. 1. After the fourth day of frying, the TV of all the frying oils was increased. As shown in table no. 1, the highest and lowest TV were seen in soybean oil and mustard oil respectively, indicating that soybean oil shows lowest oxidative stability and mustard oil shows highest oxidative stability as compared to other oils. This observation could be explained by the high and low concentration of poly and monounsaturated fatty acids and presence of natural antioxidants in oils. Although, soybean oil had highest amount of linoleic acid than other and mustard oil had highest erucic acid than other oils were studying in this paper. Thus the frying oil containing higher amount of linoleic acid was shown to be less stability during deep frying process. This observation is in agreement with Wai et al 2009 who have reported that lower the totox value, the better the quality of the oil.

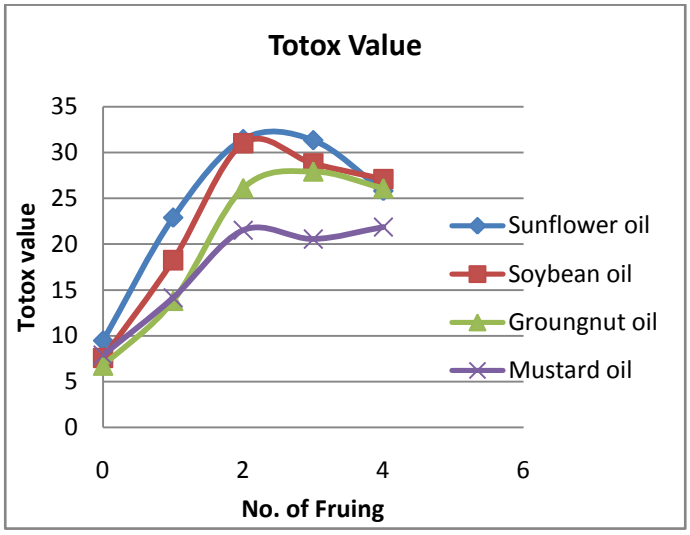

Fig.No. 3 Totoxo value provide evaluation of progressive oxidative deterioration of oils depending on the numbers of frying at 180^0C

IV. CONCLUSION

The result of this study indicated that during deep frying of sunflower, soybean, groundnut and mustard oil, highest change in PV was observed in Groundnut oil while, least change in PV was observe in soybean oil. The highest significant change in *p*-AV was observed in the soybean oil, while least significant change observes in the mustard oil. The highest and lowest TV was seen in soybean oil and mustard oil respectively. This may be due to presence of high concentration of polyunsaturated fatty acids that were oxidized are present in soybean and sunflower oils while mustard and groundnut oils contain more monounsaturated fatty acids. The oil rich in monounsaturated fatty acids shows higher oxidative stability than the oil containing polyunsaturated fatty acids during deep frying. Soybean oil shows lowest oxidative stability and mustard oil shows highest oxidative stability during deep frying as compare to other oils.

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