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Studies on AV,PV,SV,EV and P-anisidine Values of different brands of Mustard Oils using Before and After Frying

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ABSTRACT: Chemical reactions such as oxidation, hydrolysis and thermal polymerization occur when cooking oil is heated during the frying process. These reactions change the physico-chemical nature of the cooking oil. The quality of oil deteriorates with increased length of frying time due to the accelerated formation of oxidized and polymerized lipid species in the frying medium. Edible vegetable oils are used in food, both in cooking and as supplements. In this studies, seven types of different brands of mustards oils collected from different places of India were analysed before and after frying using standard procedures of (AOAC) and (AOCS), the physicochemical properties such as Acid value(AV), Peroxide value(PV), Saponofication value(SV),Ester value(EV)and P-Anisidine value(P-AV) were investigated. AV was ranged between 2.98-11.94 mg KOH/g in fresh and after frying. PV was ranged between 11.46-24.98 meq/Kg in fresh and after frying. SV and EV were ranged between 169.98-184.68 and 167-192.34mg KOH/g oil in fresh and after frying oils. The P-AV was in the ranged between 1.01-2.82 in fresh and after frying oils. Furthermore, the AV and PV were to exceed the permitted value of 5.0mg KOH/g and 10 meq/Kg and deviated from the safety standards. The standard deviation was in the range between 0.29-0.49 in fresh and 0.21-0.48 in after frying oils. The standard mean error found in the range of 0.16-0.28 and 0.12-0.28 respectively

KEYWORDS: Mustard oil, Frying quality, AV,SV,EV,PV and P-anisidine Values

I. INTRODUCTION

Edible oils are derived from a wide variety of plants and plant seeds and are used in many aspects of domestic and world-wide food production. Once the oil has been extracted from a plant seed, it is refined as needed for use in foods such as salad dressings, margarine, shortenings, snack foods and frying oil. Edible oils are extracted and processed world-wide and hence are important domestic and international commodities. Edible oils are very important food for word. The human body uses oils and fats in the diet for three purposes, as an energy source, as a structural component and to make powerful biological regulators. Oils and fats also play an important role in metabolic reactions in the human body. Oils and fats contain fatty acids, which are susceptible to attack by a number of agents e.g. light, oxygen, metals, etc [1-2]. Fats and oils are parts of normal daily consumptions. As a major source of energy, fats and oils are considered as important nutrients in human diets. The edible oils are used in cooking as well as in traditional medicine for the treatment of colds, coughs, bronchitis, edema and burns, also play an important role in the body as carriers of essential fatty acids which are not synthesized in the body but are needed through the diet to maintain the integrity of cell membranes. They are also needed for the synthesis of prostaglandins which have many vital functions to perform in the body [3,4].Vegetable oils are beneficial and popular due to their cholesterol-lowering effect. In contrast to animal fats, which are predominantly saturated and hence do not react readily with other chemicals, especially oxygen, unsaturated vegetable oils are more reactive. Vegetable oils are essential in global nutrition depending on the regional conditions, a variety of oils are produced in different qualities [5].

Many researcher stated that Mustard oil is one of the vital edible oil used in India especially in northern and eastern India. Oil is produced from black mustard (Brassica nigra), brown Indian mustard (Brassica junea) and white mustard (Brassica hirta) seeds (Vaughan and Hemingway, 1959). Mustard oil is unique amongst all the fatty oils for its pungency due to the presence of allyl iso-thio-cyanate. Mustard oil contains a unique monounsaturated fatty acid, erucic acid, along with other mono and poly unsaturated fatty acids. The presence of appreciable amounts of unsaturated fatty acids and lower amounts of saturated fatty acids render mustard oil good for heart and is said to lower the risk of heart disease among Indians (Ghosh and Bhattacharjee, 2013; Khan et al., 2013).Mustard oil also contains glucosinolate which has antibacterial, anti-fungal and anti-carcinogenic properties which account for many medicinal utilities of the oil (Yadav and Kumari, 2015). Therefore there is a huge demand for mustard oil in Indian market and consequently very prone to be adulterated. The dark colour of the oil makes it more vulnerable for adulteration by any cheap oil[6-8].

Fried oil changes in the stability of the taste or quality of the oil by hydrolysis, oxidation, and polymerization. Tocopherols, essential amino acids, and fatty acids in the diet degraded during frying. Changes frying oil depends on factors like the freshness of the oil, frying conditions, the original quality of cooking oil, fried foods, types of frying, antioxidants, oxygen concentration. Frying temperature is high, the amount of fried oil, free fatty acids, polyvalent metal, and unsaturated fatty acids decrease the stability of the oil due to oxidation and the taste quality of the oil. Frying oil with high temperatures can degrade the effectiveness of antioxidants. The peroxide value is used to determine the level of oil damage. The peroxide value standard for vegetable oils that do not undergo rancidity should be well below10 meq/kg. The value of free fatty acid is often used as an indication of the general condition and the nature of the oil is safe to eat. Saponification value is a rough index of the molecular weight of the fat or oil. The smaller the saponification value higher molecular weight. It also shows the magnitude of the amount of alkali required to convert the amount of fat or oil to be soap. It can be used for checking the purity of fats or oils.[1,2]

II. RELATED WORK

Deep frying is one of the most common methods used for the preparation of food. Repeated frying causes several oxidative and thermal reactions which results in change in the physicochemical, nutritional and sensory properties of the oil [9]. During frying, due to hydrolysis, oxidation and polymerization processes the composition of oil changes which in turn changes the flavor and stability of its compounds [10]. During deep frying different reactions depend on some factors such as replenishment of fresh oil, frying condition, original quality of frying oil and decrease in their oxidative stability [11]. Atmospheric oxygen reacts instantly with lipid and other organic compounds of the oil to cause structural degradation in the oil which leads to loss of quality of food and is harmful to human health [12]. Therefore, it is essential to monitor the quality of oil to avoid the use of abused oil due to the health consequences of consuming foods fried in degraded oil, to maintain the quality of fried foods and to minimize the production costs associated with early disposal of the frying medium [13].

Lipid oxidation has a negative impact on the functionality of raw materials, sensory and nutritional quality of food, and causes economic losses [14]. 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 [15-18]. Lipid oxidation also led to a change in colour and sometimes texture, as well as the loss of essential nutrients and micronutrients. Finally, lipid oxidation can lead to the formation of potentially toxic oxidation products (oxycholesterol, malonaldehyde, endoperoxides, acrolein, polymeric peroxides) [19-20].

The consumption of repeatedly heated cooking oil is unhealthy. In the process of frying food, cooking oil is often exposed to high temperatures for long periods of time. This practice generates lipid peroxidation products that may be harmful for human health [21]. The presence of excess polar compounds in repeatedly used frying oil has been associated with increased risk of developing hypertension [22]. Consumption of repeatedly heated cooking oil might increase the risk of developing atherosclerosis. Lipid peroxidation products induce oxidative stress in endothelial cells, resulting in endothelial dysfunction that could eventually lead to the formation of atherosclerosis [23]. Consumption of repeatedly heated cooking oil is also associated with increased total serum lipid and low density lipoprotein (LDL) levels [24] .

Increase in FFA could be attributed to moisture content of the fried product that accelerates the hydrolysis of oil. It is known that water can promote the hydrolysis of triacylglycerols to form a combination of mono and diacylglycerols, glycerol and free fatty acids [25]. Moreover, the FFA content is a dynamic value because at the same time that the acids are being produced, they have sufficient vapor pressure at frying temperatures to evaporate from the surface [26]. However, FFA is not a very reliable parameter for the assessment of the degradation of frying oil, because it is difficult to differentiate FFA formed by oxidation or by hydrolysis [4]. Moreover, low molecular weight FFA may be lost through volatilization during frying [27].

The aim of present study was to evaluate the effect of frying on the chemical properties such as acid value (AV),peroxide value (PV), ester value (EV), saponification value (SV)and P-anisidine values of some edible cooking oils were measured before and after frying and to assess whether these oils could be re-used or not.

III. METHODOLOGY

All the chemicals reagents and glassware used in this analytical work are analytical grade. Edible oil samples Kacchi ghanni Mustard (Pantanjali)(kgmp) , Kacchi ghanni mustard (emami)(kgme), pure kacchi ghanni mustard (fortune)(pkgmf), refined mustard (Dhaara)(rmd), Premium mustard kacchighaani(RRO Mustdil)(pmkgrm),

Kacchighaani mustard oil (Nature fresh)(kgmnf) and Kacchighaani mustard oil (Mahakosh)(kgmm) oils were purchased from some food super markets in Jalgaon city of Maharashtra, India and home kitchen uses. In this study, cooking oil samples of different types of oil were subjected to controlled heating and frying in the laboratory. The acid value, peroxide value, saponification value, ester value and P-anisidine value of edible oil before and after frying were measured according to the AOCS and AOAC [27-30].

2.1 Method for Determination of Acid Value.

Five grams of each cooled oil sample was weighed in 250mL of conical flasks and 50 mL of freshly neutralized ethyl alcohol (ethanol) was added to the samples and then shaken well to dissolve sample. The sample solution was boiled for about five minutes and cooled and then 1mL of phenolphthalein indicator was added to the sample solution. The sample solution was titrated with 0.1N sodium hydroxide solution until permanent pink light color appeared. The acid value was estimated using the following equation:

$$\text{Acid value} = 56.1 \times V \times 100/W \quad \text{---------- (1)}$$

Where W is weight of oil that equals 5 grams, V is titer value of 0.1N NaOH [27,30].

2.2 Method for Determination of Saponification Value.

Two grams of each oil sample was weighed in 250mL Erlenmeyer flasks; then 25mL of alcoholic potassium hydroxide solution was added into the flasks. The blank determination was conducted along with the sample. The samples flask and the blank flask were connected with air condensers and boiled gently in the water bath, steadily until the saponification was completed, indicated by absence of oily matter and the appearance of clear solution. Clarity was achieved in half hour boiling. After the flask and the condenser cooled, inside of the condensers was washed down with about 10mL of ethanol and then 1mL of phenolphthalein indicators was added to the solution. Excess potassium hydroxide was titrated with 0.5N hydrochloric acid until cloudy solution was formed. The saponification value was estimated using the following equation:

$$\text{Saponification value} = 56.1 \times (b - a) \times N/W, \quad \text{---------- (2)}$$

Where W is weight of sample that equals 2 grams, b is blank titer value, a is sample titer value, and N is 0.5 normality of HCl [28, 30].

2.3 Method for Determination of Peroxide Value.

Five grams of each oil sample was weighed in 250mL of conical flask; then, 30mL of acetic acid and chloroform solvent mixture (3:2) was added to each oil sample and swirled to dissolve. Then, 1mL of potassium iodide solution was added to the solution. The solution was kept for 1min in dark room with occasional shaking and then 30mL of distilled water was added. Slowly, titrate liberated iodine in 0.01N sodium thiosulphate solution until vigorously shaking yellow color was gone and after that 1mL of starch solution indicator was added and we continued titration by vigorous shaking to release all I2 from CH3Cl layer until blue color disappeared.

The peroxide value was estimated using the following equation:

Peroxide value = □ × □ × 100/W, ---------- (4)

Where V is volume of sodium thiosulphate, N is normality used for titer and W is weight of the sample [29-30].

2.4 Method for determination of ester value:

The ester value is the ‘mg’ of KOH required to react with glycerol/ glycerin after saponify 1 g of oil sample. Ester value is calculated by the following relation [28,30]

$$\text{Ester Value} = \text{Saponification Value (SV)} - \text{Acid Value (AV)}$$

2.5 Method foe determination of P-anisidine value (P-AV)[31]

The p-anisidine value was obtained using a spectrophotometer (UV 1700, Shimadzu Corporation) according to the AOCS method Cd 18-90 (AOCS, 1989d).The carbonyl content in oils was determined by standard method according to AOCS. 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 Mustard oil was dissolved in 25 ml isooctane and absorbance A1 was measured at 350nm against a blank isooctane. An aliquot (5ml) of this solution, respectively 5 ml of isooctane (as blank) was transferred to each of two test tubes of 10ml 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;

$$\text{P-AV} = 25 \times 1.2 \times (A2-A1) / W.$$

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IV. EXPERIMENTAL RESULTS

Table 1. Chemical characteristics of different brands of Mustard oil before and after frying

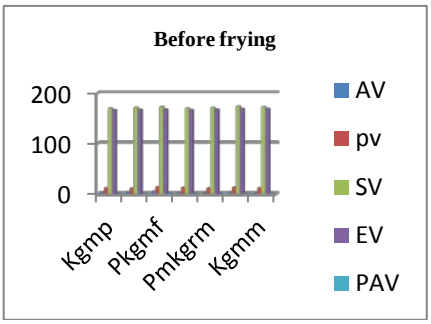
Sr. no	Name of oil	Before frying					After frying				
		AV, mg KOH / g oil	PV, Meq/ Kg	SV, mg KOH / g oil	EV, mg KOH /g oil	P-anisidine	AV, mg KOH / g oil	PV, Meq/Kg	SV, mg KOH / g oil	EV, mg KOH /g oil	P-anisidine
1	Kgmp	3.66	12.32	170.12	166.46	1.01	7.98	22.54	184.24	176.26	1.92
2	Kgme	4.23	11.46	171.87	167.64	1.21	9.23	24.28	183.68	174.45	2.54
3	Pkgmf	5.12	13.92	173.14	168.02	1.31	10.34	24.98	185.92	175.58	2.12
4	Rmd	2.98	12.98	169.98	167	1.21	11.21	23.56	181.98	170.77	1.62
5	Pmkgrm	3.28	11.68	171.37	168.09	1.01	10.97	22.88	183.48	172.51	1.90
6	Kgmnf	4.26	13.12	173.82	169.56	1.82	11.56	23.12	182.56	171	2.75
7	Kgmm	3.24	12.35	172.78	169.54	1.71	11.94	23.38	184.68	172.74	2.82
8	Total	26.77	87.83	1203.08	1176.31	9.28	73.23	164.74	1286.54	1213.31	15.67
9	Mean	3.82	12.55	171.87	168.04	1.33	10.46	23.53	183.79	173.33	2.24
10	SD	0.29	0.36	0.28	0.49	0.47	0.35	0.36	0.48	0.42	0.21
11	CV	7.55	2.87	0.17	0.29	35.27	3.38	1.54	0.26	0.24	9.32
12	SEM	0.17	0.21	0.16	0.28	0.27	0.2	0.21	0.28	0.24	0.12

(AV-Acid value, BF-Before frying, AF-After frying, PV-Peroxide value, SV-Saponofication value, EV-Ester value, P-AV-P-anisidine value SD-standard deviation, CV-coefficient of variation, SEM-standard error)

Table 2.Test results before and after frying and codex standards

Sr.no	Test	Before frying	After frying	Codex Alimentarius commission standard
1	Acid value	2.98-5.12mg KOH/g	7.98-11.94	5.0 mg KOH/g
2	Peroxide value	11.46-13.92 MeqO2/Kg	22.54 to 24.98 MeqO2/Kg	10.0 MeqO2/Kg
3	P-anisidine value	1.01-1.82	1.62-2.82	20 MeqO2/Kg

The data obtained from the experimental measurements and accuracy of different parameters for different varieties of oils have been analysed and the Statistical parameter like standard deviation, coefficient of variance and standard mean error were calculated for AV,IV,SV,EV and P-AV for different brands of oils before and after frying. All the experiment was carried out in triplicate and the results are presented as the Mean, S.D., CV and SEM. Accuracy and descriptive Statistics of different oils from different parts of India as shown in figure1to3.



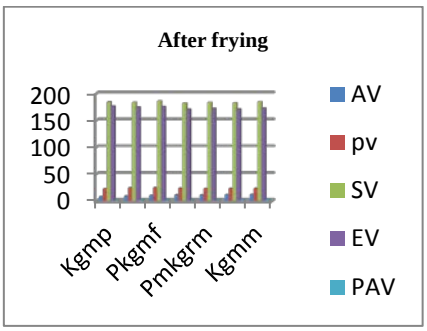


Figure1 and 2 shows the graphical representation of different brands of mustards oils of AV,PV,SV,EV and P-anisidine value before and after frying from different parts of India.

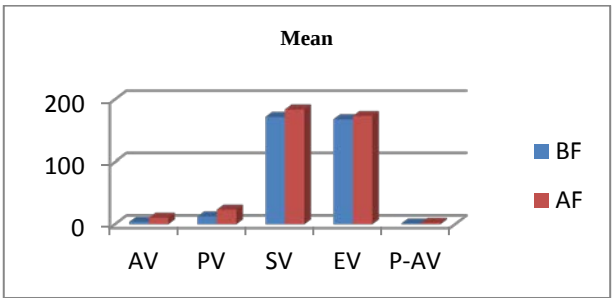


Figure 3.represents mean of AV,PV,SV, EV and P-anisidine value of different brands of mustard oils from different parts of India

V. RESULT AND DISCUSSION

Physicochemical characteristics of kgmp,kgme,pkgmf,rmd,pmkgrm,kgmnf and kgmmof different brands of mustard oils samples before frying and after frying have been extensively investigated. The experimental data of AV,PV,SV,EV and P-AV of different mustard oils are illustrated in Tables 1-2 and figures 1-3. It can be seen from the tables 1-2 and figure 1-3 that, AV of different mustard oils are in the range of 2.98-11.94,in case of fresh oils it is 2.98-5.12 while after frying it is 7.98-11.94 which are exceeding the codex standards .In case of PV, It is in the range of 11.46-24.98 whereas in fresh oils in the range betwwen11.46-13.92 and after frying it is in between 22.54-24.98 which are exceeding the codex standards causing secondary oxidation in the oil samples after frying. SV and EV of the respective mustard oil samples were found in the range between 169.98-184.68 and 167-192.34.In case of fresh oils it is 169.98-173.82 and 167-169.56 while in case of after frying it is in the range of 181.98-184.68 and 169.12-192.34.The P-AV ,1.01-1.82 in fresh oils and 1.62-2.82in after frying. Generally, the obtained data indicated that the AV and PV were increased after frying of all the mustard oils samples may attribute to the complete inhibition of enzymes activity and causing undesirable odor of oil sample after frying. These results might be due to the effect of high frying temperature causing destruction of some glycerides. The standard deviation was in the range between 0.29-0.49in fresh and 0.21-0.48in after frying oils. The standard mean error found in the range of 0.16-0.28 and0.12-0.28 respectively.

VI. CONCLUSION

In this study, the experimental results of different brands of mustard oils from different places of India used before and after frying analysis met the FSSAI specifications in terms of acid, peroxide, saponofication, ester and P-anisidine values. Frying process has affected chemical properties of edible vegetable oils. AV,PV,SV,EV and P-AV value showed an increased in after frying. It is clear from the obtained results that, the acid and peroxide values of edible oil increased after frying compared with that before frying which might be due to the effect of high frying temperature causing destruction of some glycerides and deviates the safety standards. The use of same oil for frying many times is a general practice mostly in commercial and sometimes in domestic cooking processes. This practice generates lipid per oxidation products that may be harmful to human health. The level of awareness of the general public in India regarding the usage of repeatedly heated cooking oil needs to be increased.

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