Olive Oil in Indian Kitchen: a Food for Thought, a Thought for Food

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Abstract

Background and Objective: Role of dietary fat in aetiopathogenesis of modern epidemics like CHD, Hypertension, DM and metabolic syndrome is undeniable. PUFA and MUFA- rich edible oils are in recent trend, which are replacing the Indian indigenous oils in diet claiming to be more cardio-protective. This study was taken up to evaluate the physical and chemical changes in Olive oil of cooking grade (pomace) due to duration and mode of storage, UV ray exposure and different temperatures.
Method: In this study the effect of different storage conditions, UV ray exposure and temperatures on the stability of olive oil in terms of color, odor, optical densities and generation of primary and secondary oxidation products were seen. Oxidation products were measured in terms of PV, AV, TOTOX and TBARS.
Results: There was maximum alteration in physical properties on exposure to sunlight and higher temperatures. Alteration in PV was upto 700% under sunlight, 300% in room storage condition and 100% in dark storage form. Maximum change in PV was at 60^0c and again rose to higher levels at smoke point i.e. 200^0c. The secondary oxidation product AV had very high baseline level as compared to standard oil samples and gradually decreased on storage but rose under sunlight exposure. Secondary oxidation product TBARS and TOTOX showed higher baseline level than other standard oils and rose to 100% and 200% in room temperature and sunlight exposure respectively and remained same at dark storage condition.
Conclusion: Olive oil being PUFA-rich is prone for auto- oxidation and before including the same for Indian cooking there should be proper guidelines regarding duration and condition of storage and the mode of use in cooking.
Abbreviations: PUFA- Polyunsaturated fatty acids, PV- Peroxide value, AV- Anisidine value, TBARS- Thiobarbituric acid reacting substances, TOTOX- Total oxidation value.

Key words: PUFA-rich edible oil; Olive oil; Oxidation; Peroxide value; Anisidine value; TBARS; TOTOX.

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Introduction

Role of dietary fat in aetiopathogenesis of modern epidemics like CHD, Hypertension, DM and metabolic syndrome is undeniable. PUFA and MUFA- rich edible oils are in recent trend, which are replacing the Indian indigenous oils in diet claiming to be more cardio-protective. In lieu of curbing such disorders dietary fat modification has been a measure by balancing quantity of intake of edible oils, type of oil, content of PUFA and mode of cooking. Over last century, consumption of PUFA-rich edible oils has increased drastically at an expense of indigenous fats and oils of India. Joint Food and Agriculture Organization report 2009 claims, replacing edible oils rich in saturated fatty acids with PUFA-rich edible oils will decrease the global burden of these disorders.[1] 30% of total energy is obtained from PUFA rich oils by a healthy adult in developing country whereas around 40% is obtained in western countries.[2]

Olive oil is one of the new entrants in Indian kitchens and is regarded as the healthiest oil because of its unique fatty acid profile with monounsaturated fatty acid (MUFA) (70-77%) which decreases LDL and increases HDL cholesterol and hence is cardio-protective. It is also found to be rich in phytochemicals, vitamins, antioxidants and Polyphenols like caffeic, vanillic, p-coumaric, syringic and p-hydroxy benzoic acid, 3-phenylhydroxyphenyl ethanol and 3,4-dihydroxyphenyl ethanol which impart antioxidant and anti-inflammatory property to it.[3] There are different varieties of olive oil depending upon their ways of extraction. Virgin olive oil is obtained by pure mechanical means without altering any property of the oil. Extra virgin and virgin olive oil differ by only their acidity content more than 0.8% and not more than 2% respectively.[4] Refined olive oil is obtained by refining but preserves the fatty acid structure and olive pomace oil obtained by treating the remaining pulp by solvents and physical treatments which makes pomace oil devoid of vitamin E and certain phytochemicals. Olive pomace oil is considered suitable for Indian cuisine as it is lighter and neutral tasting and claimed to be suitable for heating purposes. But the problem is same as with other newly added PUFA rich edible oils. On heating or exposure to light PUFA generates primary oxidation products like peroxides, dihydroperoxides which get readily decomposed to secondary oxidation products like

aldehydes, ketones, alcohol, hydrocarbon and esters.[5] Though amount of PUFA is less in olive oil and there is presence of antioxidants which quench the free radicals, all the cardio-protective advantages are more shared by extra virgin variety of olive oil. As Indian cooking modes are different, use of olive oil may be reconsidered.

PUFA and antioxidants though have potential to quench the free radicals and prevent oxidation injury; they themselves are chemically unstable, highly thermo-labile and get auto-oxidised on storage or exposure to high temperature and UV light and thus behave as pro-oxidants in *vivo* as well as *ex vivo*.[5]

PUFA is subjected to oxidation during refining of oils, during transport and storage before reaching the consumers and also by modes of oil storage by the consumers. In Indian context, mostly food is cooked by boiling, sautéing, frying, roasting or baking processes, where hardly there's a scope for using the edible oils in its raw form, Hence the oils are exposed to different high temperatures, mostly beyond their smoke points.

Hence with the objective of studying the effect of different physical factors such as duration of storage, temperature, light and UV exposure on olive oil this study was taken up after obtaining clearance from Institutional ethical committee.

Materials and Methods

This study was done in the department of Biochemistry of Kalinga Institute of Medical Sciences, Bhubaneswar, Odisha over a period of two months. Pomace olive oil was procured from the local market. To observe for the effect of storage, oil was poured into amber colored bottle and stored in dark, an aliquot was kept at room temperature and another aliquot was kept under direct sunlight everyday at least for 6 hours. Samples were assayed from day 0 to every fortnightly for 2 months. Physical properties like color, odor, optical density and degree of unsaturation were seen. Primary oxidation products were studied in terms of Peroxide value (PV) and the secondary oxidation products as p-Anisidine value (AV) and MDA (Malondialdehyde). Total oxidation value (TOTOX) was calculated too. Effect of temperature was analyzed by subjecting the oil to temperatures of 37^0c, 60^0c, 70^0c, 100^0c and 200^0c and maintaining that temperature in a water bath for 15min and analyzed for primary and secondary oxidation products after cooling.

Iodine number: It was used to determine the degree of unsaturation. Oil sample was treated with an excess of the Hanuš solution (IBr) in glacial acetic acid. Unreacted iodine monobromide is then allowed to react with potassium iodide, converting it to iodine, whose concentration is determined by titration with sodium thiosulfate.

Optical density: Optical density was measured at 420 nm in spectrophotometer (Systronic 2202 double beam).

Smoke point: It is the temperature at which, under defined conditions, enough volatile compounds emerge from the oil that a bluish smoke becomes clearly visible. It is the temperature at which the oil is decomposed and produces harmful products. The smoke point for oil increases as the free fatty acid content decreases and degree of refinement increases. The different oil samples were heated till they began to smoke and then with thermometer the temperature was recorded.

To measure primary oxidation products, **Peroxide value (PV)** was measured by AOCS standard method[6,7] and as a measure of secondary oxidation products **Thiobarbituric acid reactive substances (TBARS)**[8,9] and **Anisidine value (AV)**[10,11,12] was measured by Ke et al and AOCS (American Oil Chemist Society) official methods respectively.

Peroxide value (PV): It is defined as the amount of peroxide oxygen per 1 Kg of fat or oil. It is expressed in meq/Kg. Peroxide value is determined by measuring the amount of iodine formed by the reaction of the peroxides from oils with the iodide ion. The iodine liberated is then titrated with sodium thiosulphate. The indicator used in this reaction is a starch solution that forms a blue to black solution with iodine and is colourless where iodine is titrated.

Anisidine value (AV): The amount of aldehydes in edible oils is determined by reaction in an acetic acid solution of aldehyde compounds in oil and p-anisidine and then measuring the absorbance at 350nm.

The oxidative status of a fat should be evaluated considering both its primary and secondary oxidation. In fact it may so happen that a fat that has initially a high peroxide value, kept in stock for a long time in absence of oxygen, endures a secondary oxidative process that determines the decrease of peroxide value but the increase of Anisidine value. So analyzing only peroxide value can sometimes give false idea on the quality of oil. Therefore if both PV and AV values are analyzed together it will give a better idea on the quality of oxidation of edible oils.

These 2 values are combined into the TOTOX (Total oxidation value) number:

TOTOX value = AV + (2 x PV)

MDA

It is one of the several low-molecular-weight end products formed via the decomposition of certain primary and secondary lipid peroxidation products. It gives the measure of secondary oxidation products generated from the fats/oils.

At the end of 60 days statistical analyses were done by Microsoft Excel.

Result and Observation

In the beginning of the study on 'Day 0' the physical characteristics as well as chemical properties were studied. Smoke point of olive oil was found to be 200^0c. Iodine number was measured to be 90-95. It is lesser than other oil samples like blended oil (220^0c), clarified butter (Deshi ghee) (254^0c), rice bran oil (254^0c). Iodine number was measured to be 90-95 that shows it to have

moderate degree of PUFA. Sunflower oil has iodine value of 125-145 and coconut oil has iodine value of 7-12.

Storage in Dark: Table 1 shows the different properties of the oil that was kept as the main stock in dark and cold condition. There was no visible colour change of the oil but smell became mildly rancid at the end of 45 days. Optical density reduced by 0.072 units by end of 60 days. As a measure of primary oxidation products it increased by only 2 units (100%) at the end of 60 days. As a measure of secondary oxidation product AV was initially quite high (33.85) which reduced to almost half by the end of 60 days yet the value is high as compared to other oils.[13] Ideal AV value should be less than 10. MDA was initially high which reduced by half on 15th day but gradually again raised to little more than the initial value at 60th day. TOTOX value also reduced from initial value yet remained high at the end of 60th day.

Storage in room temperature: Table 2 shows Effect of storage at room temperature. Room temperature varied from $23-28^0$c and only indirect light exposure was there. There was mild color change towards 45th day, which became overtly yellowish by 60th day and mild rancid smell was there by 45th day. Optical density of the oil

sample changed from 0.359 on 'Day 0' to 0.214 on 'Day 60'. Primary oxidation product (PV) increased gradually from 2 meq/kg to 8 meq/kg. AV value reduced till 45th day to again increase gradually till 60th day. MDA value reduced initially but again increased almost double the initial value by 60th day. TOTOX value decreased till 30th day but again increased to same as 'Day 0' value.

Storage under sunlight: Table-3 shows effect of direct sunlight on olive oil. Under direct sunlight exposure there was visible deterioration of the color of the oil and odor also changed to rancid by 45th day. PV value constantly increased and reached up to 16meq/ kg. AV value decreased initially but by 60th day it became more than (700%) of Day 0 AV values. MDA values increased constantly.

Table 4 shows alteration of physical and chemical properties at different temperatures. The color changed from greenish yellow to dark yellow with increase of temperature and OD diminished. With increased temperature though smell altered, it was not rancid. PV increased till 60^0c, decreased up to 100^0 c and again raised at 200^0c. MDA decreased till 70^0c and then gradually increased up to 200^0c and exceeded the value at 37^0c.

Table 1: Effect of Duration of Storage in Dark for Olive Oil

Days	Color	OD	Odor	PV (meq/Kg)	AV	MDA (nmol/ml)	TOTOX
0	Greenish Yellow	0.359	Distinctive	2	33.85	2.02	37.85
15	Greenish Yellow	0.348	Distinctive	2	15.13	1.06	19.13
30	Greenish Yellow	0.324	Distinctive	2	16.47	1.42	20.47
45	Greenish Yellow	0.294	Mild rancid	2	16.98	1.97	20.98
60	Greenish Yellow	0.287	Mild rancid	4	17.42	2.24	25.42

Table 2: Effect of Storage at Room Temperature

Days	Color	OD	Odor	PV (meq/Kg)	AV	MDA (nmol/ml)	TOTOX
0	Greenish Yellow	0.359	Distinctive	2	33.85	2.02	37.85
15	Greenish Yellow	0.336	Distinctive	4	15.42	1.67	23.42
30	Greenish Yellow	0.304	Distinctive	4	13.86	2.98	21.86
45	Greenish Yellow	0.219	Mild rancid	6	18.26	3.32	30.26
60	Yellowish	0.214	Mild rancid	8	20.18	3.89	36.18

Table 3: Effect of Sunlight Exposure on olive oil

Days	Colour	OD	Odour	PV (meq/Kg)	AV	MDA (nmol/ml)	TOTOX
0	GreenishYellow	0.359	Distinctive	2	33.85	2.02	37.85
15	Yellowish	0.261	Altered smell	8	26.2	2.73	42.2
30	Deep yellow	0.235	Mildly rancid	10	28.13	3.32	48.13
45	Yellowish brown	0.104	Rancid	16	36.98	4.28	68.98
60	Brownish	0.098	Rancid	12	38.24	6.54	62.24

Table 4: Effect of Temperature on physical and chemical characteristics of olive oil

Temperature (^{0}C)	Colour	OD	Odour	PV (meq/Kg)	MDA (nmol/ml)
37	Greenish Yellow	0.359	Distinctive	2	0.077
60	Yellowish	0.314	Smell retained	6	0.061
70	Brownish	0.339	Smell retained	4	0.062
100	Brownish	0.297	Altered smell	2	0.064
200	Brownish	0.255	Altered smell but not rancid	4	0.083

Discussion

Olive oil has been used in the Mediterranean basin and ancient Greek in cooking, cosmetics, pharmaceuticals, lighting lamps, in soaps and Engineering and showed evidence of extracting oil from olive since 6000BC.[14] Recently due to its high MUFA (70%) and PUFA content particularly Linoleic acid (30%) it is considered as a functional food for better cardiovascular health by maintaining LDL and HDL cholesterol levels, fasting TG ,blood sugar levels and having antithrombotic, anti-inflammatory and with antihypertensive effects.[13] With increase in awareness of numerous health benefits, olive oil market in India has been expanding rapidly with an average import of about 14,000 MT (Metric Tonne) in 2013 with an expected rise upto 42,000 MT by 2025 or more. To cope up with this rising demand, cultivation of olive oil are now under pilot project started by ROCL (Rajasthan olive cultivation limited) but availability of seeds, appropriate temperature for growth are important pre requisites which needs a huge investment behind this project. Even the olive oil producing countries have hiked up the prices of olive oil by almost 40% .So no doubt the growing olive oil demand in Indian market will definitely put pressure on our economic aspect as edible oils contribute significantly to our GDP.

Olive oil is available in different varieties; extra virgin, virgin and pomace olive oil. Extra virgin olive oil is prepared by mechanical means with no chemical treatment. It contains a natural organic compound called oleocanthal which is responsible for anti-inflammatory and anti-oxidant properties.[13] It is also good source of vitamin E, antioxidant squalene and oleic acid.

Major problem with use of olive oil is that at high temperatures and oxygen exposure, there occurs a substantial loss of antioxidants, like oleocanthal which is destroyed even after mild heating and there is development of rancidity and increase in free fatty acids. In our study we have observed maximum increase in primary and secondary oxidation products in pomace olive oil when stored under sunlight with constant increase in PV, AV and TBARS values, rancidity was observed within 45th days of storage (Table 1). Least change was seen when stored in dark bottles in cupboard. This suggests that storage of oil plays a crucial role in maintaining the shelf life of oil and hence should be stored in dark at cool places and once the bottle is opened it should be used quickly in fresh state.

When exposed to various temperatures there are marked changes in physical and chemical properties with change in color and odour at around 100^0C, which is much below the frying temperature. PV initially increased but later at 100^0C it decreased which may be because of formation of secondary oxidation products which increases at higher temperatures. This finding is in accordance with the study done by BL Halverson et al where they suggested that hydroperoxides are unstable to heat so they decompose to more stable secondary oxidation products.[15] Initially MDA as the marker of secondary oxidation was found to be higher which may be due to formation of oxidation products during transportation or due to refining of pomace oil. Later at 70^0C it decreases which may be due to formation of volatile products. It then increases at higher temperatures due to conversion of primary to secondary oxidation products.[16] But according to the study done by Y Allouche et al antioxidant present in olives are sufficient enough in resisting oxidation due to heat and suggested that if it is added to other oils, olive oil becomes more stable.[17]

As regards the effect of heat, duration of storage and UV exposure on MUFA no concrete literature were available.

These findings suggest that use of olive oil in Indian cooking is quite limited as hardly there is intake of raw oil mostly the modes of cooking being sautéing, frying, shallow frying or steaming. Though extra virgin olive oil is rich in antioxidants and anti inflammatory products, it can only be used raw for its better benefits. Pomace olive oil obtained by refining shares the disadvantage of producing oxidation products which may in long run lead to chronic inflammatory diseases. So completely replacing our indigenous oils and introducing new oil in Indian market which cannot be used variedly in our Indian context can how far be acceptable and useful have doubts.

Keeping in view of the above findings and discussion certain questions arise:

1. Should we promote expensive edible oil while less costlier options (as the blend of oils are already in use in traditional cooking based on different geographical regions and socio-cultural variation) available?
2. In order to use olive oil and to derive the claimed benefits maximally should we change our pattern of cooking in India?

3. Should we promote olive oil whose cost is not going to change much even after its cultivation is domesticated ()?

4. In the name of PUFA –rich oils are we incurring more hazards for health?

Conclusion

A thorough study on all the indigenous oils of India should be done versus Olive oil for different effect of physical factors like heat, sunlight exposure and storage on them. Various blending of olive oils should also be studied so that the beneficial effects of olive oil may be protected. In vivo effects of olive oil consumption may be studied in animals and human beings. From this study we conclude that due to production of huge amount of oxidation products olive oil use may best be avoided all modes of Indian methods of cooking. It can be used in the raw form only if it is used within a month or so and stored in a cool and dark place. If a cheaper and healthier alternative of olive oil could be available, which is being already cultivated in India, then it may help in the growth of GDP of the nation, improvement in farmer's financial condition and more independence in the global market.

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