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A study on effect of antioxidants on edible oil

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Vegetable edible oil is perishable ingredients in daily consumption of food. It deteriorates rapidly under Indian climatic conditions. Ever increasing and steady demand for consumption edible oil, it becomes necessary to investigate their shelf -life. Various causes are documented for the deterioration of oil. Hence, during processing and refining of oil, it is fortified with the various synthetically prepared antioxidants. The major antioxidants added in edible oil are t–Butyl Hydro Quinone (TBHQ), Butylated hydroxy anisole (BHA) and Propyl gallate (PG). A study was planned to investigate the effect of different degree of fortification of antioxidants on shelf -life of the oil. Each sample of oil was analyzed chemically and interpreted with respect to change in their shelf -life. It showed that out of these three antioxidants, BHA was most effective and PG was found to be least effective.

Key Words : Antioxidant, Edible oil, Shelf-life

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INTRODUCTION

Indian community daily consumes edible oil of vegetable origin in their cooking. However, none of the vegetable oil has fatty acid composition in the vicinity of recommended value. Hence many oil extractors began to blend the oil to meet the fatty acid composition. The blending and refining processes tend to decrease the shelf -life of the edible oil, which can show the signs of deterioration. The climatic conditions particularly moisture and temperature are also responsible for early deterioration and rancidity. The major physical changes observed are color and aroma due to rancidity of the oil.

All naturally occurring vegetable oil contain different types of phytosterol and antioxidant which are also responsible for better shelf -life. However, the unsaturated fatty acids are oxidized due to aerial oxidation make the oil rancid can result in to free radical. The formation of free radical is dangerous to health. In order to inhibit the rate of oxidation and rancidity, the oil is fortified with the chemically synthesized antioxidant (Mattill, 1947). Such fortification may affect the shelf -life of the oil and oil can be preserved for longer duration before consumption.

A remarkable characteristic of antioxidants is their effectiveness at low concentration in the oil (Emmanuel and Mudiakeoghene, 2008). However, excess amount of antioxidants may spoil the quality of edible oil and may show adverse effect on the health. Some of the antioxidant undergo chain reaction and contribute in formation of free radicals (Valko *et al.*, 2007). The increased amount of antioxidant will show pro-oxidative effect which is known as synergism. The pro-oxidant effect is encountered with presence of trace metal and inclusion from the container storing equipment. Such metal inclusion will enhance the deterioration and affect the overall shelf -life of the oil. At high temperature and process used for the deodorization may affect the oil adversely. Certain weak organic acid and EDTA can inhibit the effect of metal presence by chelation. Thus, it is quite evident that any kind of fortification must be done with utmost care and in a scientific manner within the permissible limit. It is necessary to optimize the dosage of antioxidant treatment to oil. The optimum level depends on a substrate and type of antioxidant employed. Different types of antioxidants were used by various oil extractors to provide longer shelf -life to the oil. An attempt was made to evaluate recommend the optimize dosage of the antioxidant.

A brief market survey was conducted to establish the

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data on consumption pattern in terms of quantity and different brands of the oil. A most popular brand was selected and three different antioxidants were mixed in two different dosage. The indicator parameters for rancidity like Free fatty acid (FFA), Peroxide value (PV) and Anisidine value (AV) were analyzed for each oil sample and interpreted in terms of their shelf -life.

METHODOLOGY

A brief survey was conducted using pre-defined questionnaire in the Mumbai city amongst different families and retailers of the vegetable oil vendors. The information was collected with respect to consumption pattern, quantity of consumption in relation to family size, frequency of the purchase, brands preferred for the cooking, cost of the oil. After the survey three most popular brands were shortlisted and fortified with three different antioxidants t–Butyl HydroQuinone (TBHQ), Butylated hydroxy anisole (BHA) and Propyl gallate (PG) in two different dosages of 100mg/l and 200mg/l. Each sample was analyzed for FFA, PV and AV by the method reported in the literature (AOAC, 1984). The analysis was carried out in three replica at the end of each week and entire project were planned for eight weeks. The results were tabulated and interpreted in the light of exisiting scientific theories and supported by the literature.

OBSERVATIONS AND ASSESSMENT

The entire project was aimed at the shelf -life of the vegetable oil since most of the edible oils are perishable and develop certain toxins during storage for longer time. The hectic life style of the urban city makes the family to purchase larger family pack of the oil which may last for at least eight weeks. Such purchases are cost effective also. However, detailed door-to-door survey reveals that majority of consumer purchase five liter jar and average storage time is eight week. Most of the consumers buy different brands of edible oil. Brands are selected primarily based on cost and occasionally because of their health benefits. However, no consumer was aware of shelf -life of the oil. Following table indicates the popular brands of vegetable edible oil consumed in the Mumbai city. It is seen that sunflower brand oil is most popular amongst them. The probable reason may be the better sales strategy and role of media. Although refined palm oil is not consumed by the individual family but almost all the bulk buyers give preference to palm oil because of better shelf -life of products.

Consumption of different brands of oil	
Types of oil	n=100
Groundnut oil	20
Refined groundnut oil	10
Sunflower oil	53
Coconut oil	10
Refined palm oil	-
Soybean oil	2
Refined cottonseed oil	-
Vanaspati oil	-
Sesame oil	5

Table 1 : Effect of antioxidants on physical and chemical parameters of refined palm oil

Week	Dosage (mg/l)	TBHQ			BHA			PG		
		FFA	PV	AV	FFA	PV	AV	FFA	PV	AV
Initial		0.14	4.8	13.7	0.14	4.8	13.7	0.04	4.8	13.7
1st	100	0.14	4.8	13.7	0.14	4.8	13.7	0.04	4.8	13.7
	200	0.15	4.8	13.7	0.14	4.8	13.7	0.04	4.8	13.7
2nd	100	0.16	5.9	13.7	0.14	4.8	13.7	0.06	5.0	13.7
	200	0.16	5.9	13.7	0.14	4.8	13.7	0.06	5.0	13.7
3rd	100	0.16	6.4	13.7	0.14	4.8	13.7	0.07	5.5	14.0
	200	0.16	6.4	13.7	0.14	4.8	13.7	0.07	5.5	14.0
4th	100	0.16	6.4	14.5	0.14	4.8	13.7	0.09	5.8	14.0
	200	0.16	6.4	14.5	0.14	4.8	13.7	0.09	5.8	14.0
5th	100	0.17	7.9	14.5	0.14	4.8	13.7	0.09	6.1	14.3
	200	0.17	7.9	14.5	0.14	4.8	13.7	0.10	6.1	14.3
6th	100	0.17	7.9	14.5	0.14	4.8	13.7	0.10	7.7	14.3
	200	0.17	9.2	14.5	0.14	4.8	13.7	0.10	7.7	14.3
7th	100	0.18	9.2	14.5	0.15	4.8	13.7	0.12	8.4	14.5
	200	0.19	8.1	14.5	0.15	5.0	13.7	0.12	8.4	14.5
8th	100	0.20	8.8	14.9	0.15	5.0	14.0	0.14	9.9	14.6
	200	0.24	8.8	14.9	0.15	5.0	14.0	0.14	9.9	14.6

Different cooking oils stay fresh for different amounts of time. The oil container should be tightly covered and stored in the dark away from the heat. The lower exposure to atmospheric conditions may have decreased rate of deterioration.

Most vegetable oils oxidize over time and eventually become rancid. When oil becomes rancid the aroma and flavor gradually changes over time. Rancid oils have a sharp, bitter, unpleasant aroma different from the aroma of the same oil when it is fresh. Oxidation of fats is known as rancidity and is caused by a biochemical reaction between fats and oxygen. The long-chain fatty acids are degraded and short-chain compounds. The reaction product is butyric acid, which causes the typical rancid taste. Rancidification is the decomposition of fats, oils and other lipids by hydrolysis or oxidation, or both. These chemical processes can generate highly reactive molecules in rancid foods and oils, which are responsible for producing unpleasant and noxious odors and flavors. These chemical processes may also destroy nutrients in food. Under some conditions, rancidity, and the destruction of vitamins, occurs very quickly.

Rancidification can be decreased, by storing oils in a cool, dark place with little exposure to oxygen or free radicals. Rancid fats have been implicated in increased rates of heart disease, atherosclerosis and are carcienogenic. Antioxidants are added to edible oil in order to retard the development of rancidity due to oxidation. Natural anti-oxidants include flavonoids, polyphenols, ascorbic acid (vitamin C) and tocopherols (vitamin E) (Kamal-Eldin and Appelqvist, 1996). Synthetic antioxidants include t–Butyl HydroQuinone (TBHQ), butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), Propyl Gallate (PG) and ethoxyquin.

An antioxidant is a molecule capable of inhibiting the oxidation of other molecules. Oxidation is a chemical reaction that transfers electrons from a substance to an oxidizing agent. Oxidation reactions can produce free radicals (Gillian *et al.*, 2008). In turn, these radicals can start chain reactions. The reason for better shelf -life is due to fatty acid composition with higher percentage of saturated fatty acid of the palm oil. Some of the fatty acid component from the extracted oil decomposes due to moisture, higher temperature, auto aerial oxidation and the lack of antioxidant component in the extracted oil. The use of synthetic antioxidants can play major role in enhancing the shelf -life of the edible oil. Many chemically synthesized antioxidants can be added during extraction to increase the shelf -life of the oil. TBHQ, BHA and PG are commonly added antioxidants for the purpose. As a part of investigation and effectiveness of these three antioxidants, experiments were planned. In order to establish the optimum dosage of the antioxidant two different dosages of 100mg/l and 200mg/l was tried.

The parameters like Free fatty acid (FFA), Peroxide Value (PV) and Anisidine value (AV) were determined using method reported in the literature. The peroxide value of an oil or fat is used as a measurement of the extent to which rancidity reactions have occurred during storage. Other methods are available but peroxide value is the most widely used. The rancidity of oil is directly related to these parameters. Increase in these values is indicative about the rate of deterioration. Three popular brands of edible oil were selected for

Table 2 : Effect of antioxidants on physical and chemical parameters of refined groundnut oil

Week	Dosage (mg/l)	TBHQ			BHA			PG		
		FFA	PV	AV	FFA	PV	AV	FFA	PV	AV
Initial		0.06	0.6	11.0	0.06	0.6	11.0	0.06	0.6	11.0
1st	100	0.06	0.6	11.0	0.06	0.6	11.0	0.06	0.6	11.0
	200	0.06	0.6	11.0	0.06	0.6	11.0	0.06	0.6	11.0
2nd	100	0.06	0.6	11.0	0.06	0.6	11.0	0.06	0.6	11.0
	200	0.06	0.6	11.0	0.06	0.6	11.0	0.06	0.6	11.0
3rd	100	0.06	0.6	11.4	0.06	0.6	11.0	0.07	0.8	11.4
	200	0.06	0.6	11.4	0.06	0.6	11.0	0.07	0.8	11.4
4th	100	0.07	0.7	11.4	0.06	0.6	11.0	0.08	0.8	11.7
	200	0.07	0.7	11.4	0.06	0.6	11.0	0.08	0.8	11.7
5th	100	0.07	0.8	11.4	0.06	0.7	11.0	0.09	0.9	11.7
	200	0.07	0.8	11.4	0.06	0.7	11.0	0.09	0.9	11.7
6th	100	0.08	0.9	11.9	0.06	0.7	11.1	0.10	1.0	12.1
	200	0.08	0.9	11.9	0.06	0.7	11.1	0.10	1.0	12.1
7th	100	0.09	0.9	11.9	0.07	0.7	11.1	0.13	1.2	12.4
	200	0.09	0.9	11.9	0.07	0.7	11.1	0.13	1.2	12.4
8th	100	0.10	1.0	12.5	0.07	0.7	11.1	0.17	1.5	12.9
	200	0.10	1.0	12.5	0.07	0.7	11.1	0.17	1.5	12.9

investigation. Each sample was fortified with two different dosages and stored for eight weeks. Every sample was analyzed at the end of specified time and their FFA, PV and AV were calculated. The results are tabulated in the table. The changes in the values are also graphically represented to understand the time wise deterioration.

Vegetable oils differ in the type of fats they contain and the rate in which they oxidize and deteriorate. Oils that are highly saturated like coconut oil (85% SFA) and palm oil (50 % SFA) have a stable shelf -life. Oils that are rich in essential fatty acids and other polyunsaturated fats are the most nourishing for our skin, but are the most fragile of the oils (Chem Man *et al.*, 1999). Their shelf -life is shorter than oils that contain saturated and monounsaturated fats.

Refined palm oil contains essential fatty acid in the proportion SFA: MUFA : PUFA= 50: 37: 35. It has higher percentage of SFA suggest that it is more stable against oxidative rancidity (Matthaus, 2007). Also, naturally present antioxidants in the palm oil is the another cause for better shelf -life. The freshly extracted oil from palm fruit has dark color but after refinement color becomes lighter and also improves the aroma of the oil. It has long shelf -life and food deep fried in palm oil has better shelf -life.

It can be seen from Table 1, that refined palm oil fortified with TBHQ has FFA value of 0.14 and at the end of 8th week it reaches the maximum value of 0.24. Similarly, the peroxide value rises from 4.8 almost double the value of 9.2. The increase in FFA and PV suggest that palm oil began to decompose. Anisidine value is closely related to color of the oil. On decomposition of oil, the color becomes darker and AV is increased. The AV rises of approximately 9 per cent from 13.7 to 14.9 suggest that oil has changed the color very little and become darker with little aroma. However, there is no significant change due to higher dose of 200mg/l. The effect of BHA is quite evident since these parameter values remain nearly same with marginal rise on storage for eight week. Against that PG has very poor effect on the shelf -life of the oil since the changes in the FFA and PV is quite prominent. Even color of the oil becomes much dark with objectionable limits of the color of edible oil (Ubiquinones *et al.*, 2000).

Refined groundnut oil has very good lipid profile. It has saturated, monounsaturated and polyunsaturated (SFA : MUFA : PUFA= 18 : 49 : 33) fats in healthy proportions. It is one of the stable cooking oils; having a better shelf -life. Shelf life of peanut oil is about six months in ordinary conditions. When preserved in an airtight container in cool, dry, dark and moisture-free environment its quality may remain good for up to nine months. Its shelf may be extended for more than 12 months with the addition of anti-oxidants (Chu and Hsu, 1999) like vitamin E. The results and observation on this fortification is summarized in Table 2.

A simultaneous experiment on refined groundnut oil was planned with antioxidants in the same dosage. The values of FFA and PV have increased within eight weeks and suggest that groundnut oil has started degradation. The marginal increase in the AV indicates that oil show increase in the color with slight noxious smell. The antioxidant TBHQ (Almedia, 2011) and PG

Table 3 : Effect of antioxidants on physical and chemical parameters of refined sunflower oil

Week	Dosage (mg/l)	TBHQ			BHA			PG		
		FFA	PV	AV	FFA	PV	AV	FFA	PV	AV
Initial		0.04	0.3	14.0	0.04	0.3	14.0	0.04	0.3	14.0
1st	100	0.04	0.3	14.0	0.04	0.3	14.0	0.04	0.3	14.0
	200	0.04	0.3	14.0	0.04	0.3	14.0	0.04	0.3	14.0
2nd	100	0.04	0.3	14.0	0.04	0.3	14.0	0.04	0.3	14.0
	200	0.04	0.3	14.0	0.04	0.3	14.0	0.04	0.3	14.0
3rd	100	0.04	0.3	14.0	0.04	0.3	14.0	0.05	0.5	14.6
	200	0.04	0.3	14.0	0.04	0.3	14.0	0.05	0.5	14.6
4th	100	0.06	0.4	14.5	0.04	0.4	14.1	0.06	07	14.9
	200	0.06	0.4	14.5	0.04	0.4	14.1	0.06	0.7	14.9
5th	100	0.06	0.4	14.5	0.04	0.4	14.1	0.07	0.7	14.9
	200	0.06	0.4	14.5	0.04	0.4	14.1	0.07	0.7	14.9
6th	100	0.08	0.5	14.5	0.04	0.4	14.1	0.09	0.9	15.5
	200	0.08	0.5	14.5	0.05	0.4	14.1	0.09	0.9	15.5
7th	100	0.09	0.5	14.9	0.05	0.4	14.2	0.11	1.2	15.9
	200	0.09	0.5	14.9	0.05	0.4	14.2	0.11	1.2	15.9
8th	100	0.11	0.6	14.9	0.06	0.6	14.2	0.14	1.6	16.2
	200	0.11	0.6	14.9	0.06	0.6	14.2	0.14	1.6	16.2

has poor impact on the shelf -life but BHA has inhibits the aerial oxidation and minimizes the rancidity rate. The higher dose of antioxidant (Sies, 1993 and 1997) does not show any change in the values and it may be optimize to 100mg/l.

Refined sunflower oil :

Contains essential fatty acid in the proportion SFA : MUFA : PUFA= 12 : 21: 67. It has higher percentage of PUFA suggest that it is less stable against oxidative rancidity. However, it has better content of natural antioxidant. The freshly extracted oil from plant has light color pleasant aroma of the oil. It has shelf -life of maximum 6 months and food prepared in sunflower oil develops smell on storage. Hence, it is necessary to add synthetically prepared antioxidant (Imlay, 2003).

The most popular brand sunflower oil was tested with the same three antioxidants in the similar dosages. The analytical results of FFA show increased value within eight week span of storage. There many reasons for increased value of FFA and suggest that sunflower oil gets degraded rapidly. The high content of PUFA is advantageous to health but shelf -life of the oil is lowered rapidly. It gets oxidize faster and becomes rancid with bad aroma. The peroxide value supports the observation and indicative of poor shelf -life oil. The study also indicates that antioxidant propyl gallate has minimum impact on sunflower oil since degradation of sunflower oil began within 4th week of storage. Even increased dose of PG does not have better shelf -life impact.

The color, texture and clarity of the product may change with age. But when the fats begin to go rancid, the oil goes bad and an unpleasant odour and taste develops. Practicing proper hygiene and food safety discipline will help prevent food borne illness. The best way to store oils are in their original air tight containers in a cool dark place like the pantry, away from the stove or other appliances (German, 1999). Shelf life of oil can be increased if they are refrigerated. They may become cloudy and solidify in the fridge.

Conclusion :

In nutshell, the addition of synthetically prepared antioxidant has a positive reaction and do inhibit the oxidative rancidity. The degree of inhibition is dependent on native fatty acid composition of individual oil and percentage of phytosterol within the oil. All the three antioxidant has favorable impact on the shelf -life of the refined palm oil, refined groundnut oil and sunflower oil. However, the antioxidant BHA has better impact while PG does not show any appreciable impact on these oils. The study also suggests that higher dose of antioxidant do not exhibit favorable control in the degradation process and dose of 100mg/L can be optimized. It is recommended that proper storage condition with refrigeration can further enhance the shelf -life of these oils.

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