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The Effect of Antioxidative Extracts on Mitigating Autoxidation of Selected Edible Oils during Deep Frying

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ABSTRACT: *The effect of extracts of pomegranate (Punica granatum L.) peel, rosemary and oregano on the oxidative stability of Coconut Oil (CO), Virgin Coconut Oil (VCO), Palm oil (PO), Sunflower Oil (SO) and Sesame Oil (SSO) during deep frying (170 ± 5 °C/10 min) was determined. These five locally available edible oils were used for frying standard size potato strips in the presence of three different antioixdative extracts namely, pomegranate pee, oregano and rosemary extracts at 2% (w/w) level. A sample of oil used for frying (10 mL) was collected into a glass vial, flushed with nitrogen and stored at -18℃ until analysis. Frying was repeated twice more with the same oil. Oil devoid of any extract was used as the control. The samples were analysed for peroxide value (PV) and thiobarbituric acid reactive substances (TBARS). Results revealed that both PV and TBARS values gradually increased with the frying cycle across all oil systems tested indicating a gradual rise of oxidation of oils with use. The order of oxidative stability of oils followed the order: SO< SSO< PO< CO< VCO. A significant ($p<0.05$) inhibition of oxidation was observed in all oil systems tested as a result of the plant extracts incorporated into oils during deep frying. The least resistance against oxidation was observed in SSO which is predominantly rich in unsaturated fatty acids while VCO exhibited the highest level of resistance. Results further revealed that the pomegranate peel powder exerted the strongest antioxidant activity compared to that of the oregano and rosemary extracts.*

Keywords: *Deep frying, edible oils, oxidation, Peroxide Value (PV), Thiobarbituric Acid Reactive Substances (TBARS).*

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INTRODUCTION

Frying is one of the most popular culinary operations practiced in both industrial and domestic food preparation procedures which develop unique sensory characteristics in the food (Leong *et al*., 2015). During repeated frying, oil undergoes a series of reactions namely hydrolysis, autoxidation, thermal oxidation, isomerisation, and polymerization (Abiona *et al*., 2011). These changes invariably bring about objectionable odours, flavours, colours, and altered texture of the fried product (Tian *et al*., 2000; Bopitiya & Madhujith, 2014). Furthermore, some of the chemical compounds generated through autoxidation, thermal oxidation and polymerization during repeated frying of oil are attributable to negative health effects (Pambou-tobi, *et al*., 2010).

Synthetic antioxidants have quite often been used in order to retard oxidative deterioration of oils and fatty products (Kahl & Kappus, 1993), however, the use of synthetic antioxidants is negatively perceived by consumers due to potential toxicity and their connotation as chemicals in food (Ramadan *et al*., 2010). Moreover, there is mounting evidence to the effect that the synthetic antioxidants bear toxic effects even at meager concentrations. As a result, a growing interest has been developing in utilizing natural antioxidative extracts as potential antioxidants. Among these, the antioxidant properties of many aromatic plants and spices have shown to be effective in retarding lipid peroxidation in oils and fatty foods (Kulisic. et al., 2003). Their antioxidant effect was due to the presence of hydroxyl groups in their chemical structure (Vekiari, et al., 1993; Shahidi, et al., 1997; Shahidi, 2000).

Numerous plant extracts such as oregano and rosemary have been used to mitigate oxidation of edible oils. The compounds responsible for antioxidative activity of rosemary are carnosol, rosmanol, rosemarinic acid, epirosmanol, isorosmanol, methyl carnosate (Shwarz & Ternes, 1992; Cuvelier et al., 1994). Oregano *(Origanum vulgare)*, a characteristic spice of the Mediterranean cuisine obtained by drying leaves and flowers for its antioxidative activity (Economou et al., 1991). Carvacrol and thymol, the two main phenolic compounds that constitute nearly 78–82% of the essential oil of oregano are principally responsible for antioxidative activity (Gordon, 1990; Adam et al., 1998). Pomegranate which has been grown in Sri Lanka since antiquity in backyards is recognized as a potential source of antioxidant for stabilizing food systems. The presence of phenolic compounds such as ellagic tannins, ellagic acids and gallic acid has been attributable to the antioxidant potential of pomegranate peel (Afaf-haniem et al., 2010; Ibrahium, 2010).

In this backdrop, the objective of the present study was to examine the efficacy of natural antioxidative extracts obtained from rosemary, oregano and pomegranate peel to mitigate oxidation of Coconut Oil (CO), Virgin Coconut Oil (VCO), Sunflower Oil (SO), Sesame Oil (SSO) and Palm Oil (PO) during repeated frying.

MATERIALS AND METHODS

Materials

Coconut oil, virgin coconut oil and sesame oil were purchased directly from an oil mill in Pannala, Sri Lanka. Sunflower oil, palm oil and potatoes (variety Granola) were purchased from local market in Kandy, Sri Lanka. Pomegranate (Var. *Daya*) was obtained from Agriculture Research Centre, Kalpitiya, Sri Lanka. All chemicals were of analytical grade

with the highest purity available (> 99.5%) and the extracts of oregano and rosemary were acquired from Morrisons and Sons (Pvt) Ltd., Sri Lanka.

Preparation of pomegranate peel powder

Matured healthy pomegranate fruits were washed with pure water, peeled and the edible portion was carefully separated. The peels were then disintegrated into small pieces (0.5 x 0.5 x 0.5 cm), dried in a hot air oven at 40 °C for 48 hr. The dried peel pieces were ground into a fine powder and passed through a sieve (no. 24) to obtain pomegranate peel powder and stored at -18 °C until analysis.

Preparation of raw potato strips

Fresh healthy potatoes (var. Granola) were peeled off and cut into strips of uniform thickness (0.5 × 0.5 × 8.0 cm) using a mechanical cutter. The strips were kept submerged in distilled water at room temperature (26±4 °C) for 10 min and subsequently blotted dry with tissue papers.

Deep frying of potato strips

Deep fat frying was carried out in a standard size stainless steel frying pan. Raw potato strips each weighing approximately 35±0.05 g were separately introduced into CO, VCO, PO, SO and SSO containing pomegranate peel, oregano and rosemary extracts (2%, w/w) after bringing the temperature to 170±5°C. Frying was carried out for exactly 10 min with temperature maintained at 170±5°C. Oils devoid of any extract were used as the controls. The oil samples were reused twice more (three frying cycles in total) over a span of three days carrying out one frying cycle per day. Following each frying cycle, the oil was allowed to cool to 60 °C and oil samples (10.0 mL) were drawn and stored at -18 °C after flushing with nitrogen gas until analysis. All frying experiments were carried out in triplicate. The level of oxidation of frying oil following each frying cycle was assessed by determining Peroxide Value (PV) (Dámaso et al. (2001) and 2-thiobarbituric Acid Reactive Substances (TBARS) as explained by Jierong *et al.,* (2011).

Analysis of Data

Data were analysed using MS Office 2010 (Excel) and MINITAB version 16 software. All measurements were performed in triplicate and results were expressed as mean ± SD. The ANOVA tables were constructed using GLM procedure.

RESULTS AND DISCUSSION

Peroxide Value (PV) is an indicator of the extent of primary oxidative products formed in oils (Shahidi and Bhanger, 2007; Jierong*et al*., 2011 and Michotte *et al*., 2011). Figure 1 illustrates the PV and TBARS of fresh oil while PV of tested oils containing extracts and the control devoid of any extracts after each storage day is shown in Fig. 2 (a) through (e). The level of oxidation gradually increased with frying cycle for all oil systems. TBARS of frying oils tested containing antioxidative compounds and the control devoid of any additive after each frying cycle is shown in Fig. 3 (a) through (e).

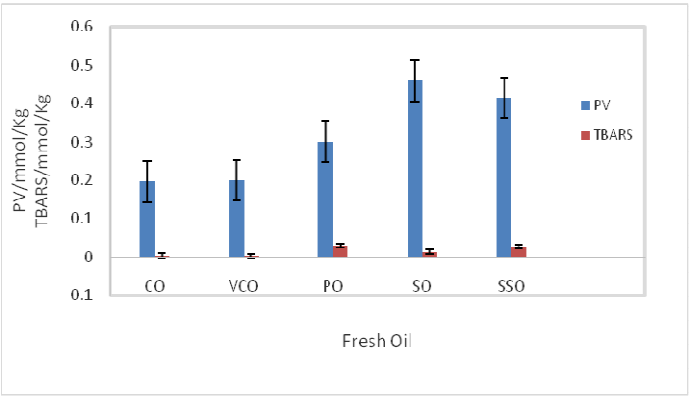
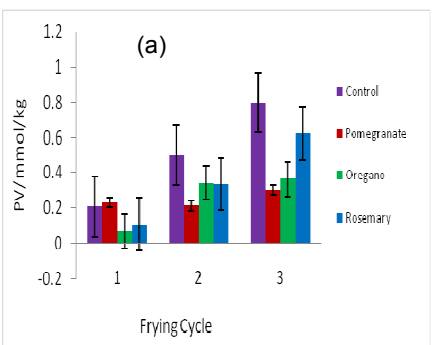
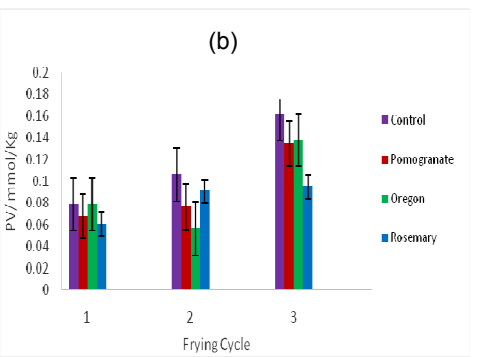


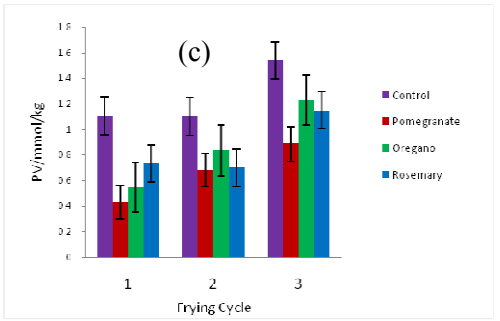
Fig. 1. Peroxide value (PV) and Thiobarbituric reactive substances (TBARS) of five fresh oils used for the study.

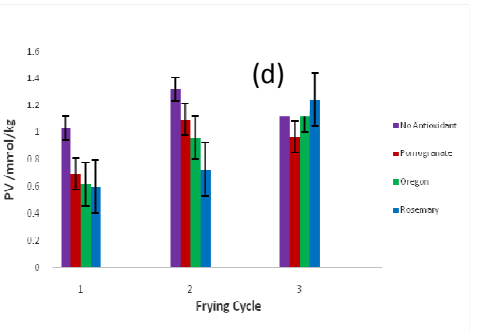
Results revealed that both PV values gradually increased with frying cycle in all oil systems tested indicating a gradual oxidation of oils with time. A significant ($p<0.05$) inhibition of oxidation due to incorporation of additives was observed in all oil systems. Significantly ($P<0.05$) high level of oxidation was observed in sunflower which is predominantly rich in unsaturated fatty acids than the saturated oils (virgin coconut oil, coconut oil). The PV ranged from 1.10 mmol/kg to 1.58 mmol/kg in SO devoid of any additive and this was reduced to 0.4 mmol/kg to 0.9 mmol/kg with the addition of pomegranate peel powder. Virgin coconut oil exhibited the highest level of resistance towards oxidation compared to other four oils. Also it is clear that according to the observations obtained by fresh oil samples, frying accelerates oxidation. The PV of fresh oil was significantly ($p<0.05$) lower than that of the first frying cycle for all oils. Relatively low PV observed in the samples stabilized with pomegranate peel extract than Oregano and Rosemary is indicative of effectiveness of the peel extracts in the mitigating oxidation of oils.

2-Thiobabituric Reactive Substances (TBARS) provide a measure of the formation of secondary oxidative products mainly carbonyls which contribute to the development of off flavour in oxidized oils (Shahidi and Bhanger, 2007). TBARS of all three oils increased gradually with frying cycle and the oils containing antioxidant extracts showed the highest resistance towards generation of malondialdehyde (secondary lipid oxidation product). TBARS of frying oils tested containing antioxidative compounds and the control devoid of any additive after each frying cycle is shown in Fig.3 (f) through (i).









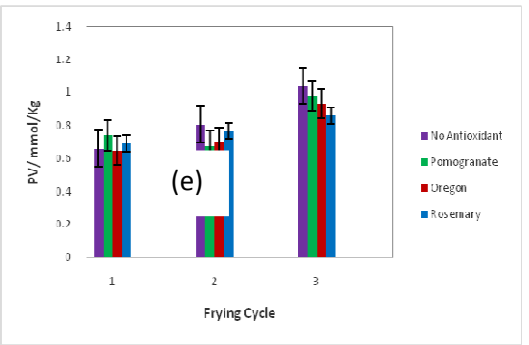
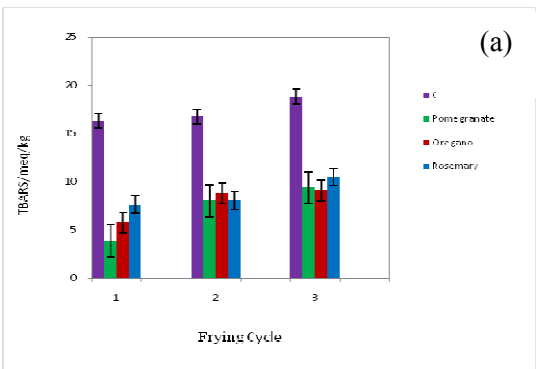
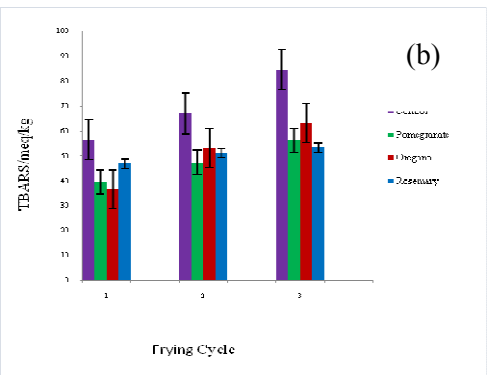


Fig. 2. Peroxide Value (PV) of (a) coconut oil (b) virgin coconut oil (c) sunflower oil (d) palm oil and (e) sesame oil in the presence of three antioxidative extracts following each frying cycle.





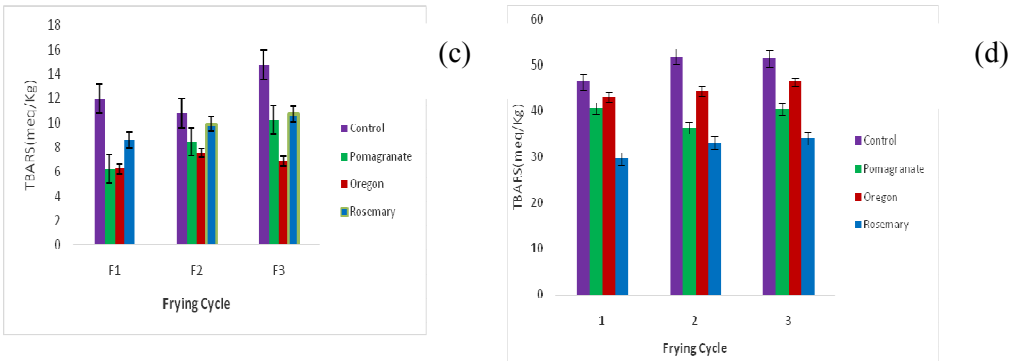


Fig. 3. Thiobabituric reactive substances (TBARS) of (a) coconut oil (b) virgin coconut oil (c) sunflower oil (d) palm oil and (e) sesame oil in the presence of three antioxidative extracts following each frying cycle.

TBARS in the oil samples increased gradually with frying. TBARS content in all oils containing different antioxidative extracts were significantly ($p<0.05$) lower than that of the control. It is obvious that the secondary oxidative products as measured by TBARS increased with frying cycle indicating oxidative degradation of oils.

Based on PV and TBARS values, the stability of oils increased in the order: sunflower oil < Sesame oil < palm oil < coconut oil < virgin coconut oil. The oils containing antioxidative extracts showed the highest resistance towards generation of oxidative products compared to the control devoid of antioxidative additives. Both primary and secondary oxidative product generation was significantly higher ($p<0.05$) in sunflower oil compared to all the oils tested while VCO generated the lowest oxidative products in VCO (PV range 0.007-0.16 mmol/kg, TBAR range 12.00 – 15.00 meq/kg).

According to the Table 1, a significant ($p<0.05$) percentage drop of PV and TBARS of edible oils containing three different additives compared to the corresponding oil devoid of any additive could be seen in all oil systems containing different additives thus showed a high oxidative stability as measured by PV and TBARS. The pomegranate peel extracts exhibited the highest resistance towards generation of oxidative products. Also the results revealed that the fatty acid composition mainly affects both PV and TBARS, a significantly ($p<0.05$) higher level of oxidation can be seen in unsaturated oils (SO, SSO and PO) than that of the saturated oils (VCO, CO). Sunflower oil exhibited the highest oxidation among the all five oil systems.

Table 01. Percentage drop of PV and TBARS of edible oils containing three different additives compared to the corresponding oil devoid of any additive following each frying cycle

Oil	Type of Antioxidant	Frying cycle 1		2		3	
		% drop					
		PV	TBARS	PV	TBARS	PV	TBARS
CO	Rosemary	47.68	53.41	32.74	51.89	44.20	44.20
	Oregano	68.04	64.75	31.33	47.42	51.65	51.89
	Pomegranate	13.58	76.28	57.56	52.07	50.12	53.41
VCO	Rosemary	23.21	28.10	8.17	53.51	41.19	27.59
	Oregano	0.51	47.79	30.41	30,00	30.66	53.51
	Pomegranate	14.28	48.18	21.80	47.79	17.02	30.84
SO	Rosemary	33.60	33.41	36.31	25.11	25.66	36.81
	Oregano	50.87	29.36	24.22	20.92	20.52	29.68
	Pomegranate	61.15	29.98	38.26	35.36	42.65	16.94
SSO	Rosemary	-4.82	44.35	4.79	12.58	17.03	18.9
	Oregano	1.72	-7.23	13.20	-12.16	10.27	12.75
	Pomegranate	-12.11	36.39	16.48	29.73	5.63	29.93
PO	Rosemary	41.93	36.06	44.82	36.05	0.35	33.59
	Oregano	40.36	7.15	27.42	14.55	7.24	9.76
	Pomegranate	32.9	12.58	17.08	29.80	22.52	21.36

CONCLUSION

Based on the PV and TBARS values which indicate the generation of primary and secondary oxidative products, the oxidative stability during frying showed the order of SO>SSO>PO>CO>VCO. These results illustrate that the antioxidative extracts such as pomegranate peel powder, rosemary and oregano extracts exhibit strong antoxidative activity in preventing oxidation of all five edible oils tested and thereby mitigating the generation of both primary and secondary oxidative products. Pomegranate peel extract has been effective in mitigating oxidation of all oils tested than the rosemary and oregano.

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