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Influence of methanol and water extracts of orange peel on stability of refined palm kernel oil

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Abstract

The antioxidative effect of methanol and water orange peel extracts on Refined Palm Kernel Oil (RPKO) stored for twelve months at room temperature (27^0C-33^0C) was determined by monitoring the colour, refractive index, free fatty acid (FFA), acid value (AV) and peroxide value (PV). The oil was dosed with different concentrations (200 ppm to 1000 ppm) of the extracts and butylatedhydroxytoluene (BHT) (Cone. 200 ppm. The colour and refractive index of RPKO containing the extracts ranged between 11.0-13.0 units and 1.458-1.460 respectively whereas the colour and refractive index of RPKO with no additive (0 ppm) and 200 ppm BHT were 10.0 units and 1.460 accordingly. Free fathy acid (FFA) and acid value (AV) of RPKO containing methanol and water orange peel extracts were lower than RPKO containing 200 ppm BHT and they were significantly different at $P<0.05$ from RPKO that contained no additive (0 ppm). PV of RPKO containing additives were slightly lower than PV of RPKO that contained no additive but they were not significantly different at $P<0.05$.The methanol and water orange peel extracts are more effective in combating hydrolytic rancidity than oxidative rancidity of RPKO. The methanol and water orange peel extracts have better antioxidant activity than butylatedhydroxytoluene

Keywords: Orange peel extracts; Butylatedhydroxytoluene; Refined palm kernel oil; Stability; Quality characteristics

Introduction

Fats and oils are important part of human diets and over 90% of lipid production is used as food or ingredient in food production (More, 1990). Lipids contain higher energy than other classes of food (carbohydrates and protein). Generally, fats and oils are sources of essential fatty acids that are of great importance to several metabolic functions in the body. It equally serves as transport medium for fat soluble vitamins (A, D, E and K) which are necessary for proper maintenance of health in both human and animal bodies (Salma and Tranveer, 2005). Hydrolysis is caused by chemical action prompted by factors such as heat or presence of water or enzymatic lipase while oxidation is mainly concerned with the unsaturated fatty acids resulting to characteristic unfavourable off-flavours and odour of lipids which invariably reduces the nutritional quality of foods (Gunstone and Norris, 1983; Navar, 1996; Madhavi *et al*. 1996; Hamilton *et al.*, 1997).

Refined palm kernel oil is an edible oil obtained from kernels or seeds of African oil palm (Elaeis guineensis). The oil palm kernel contained about 45-50% oil content (Anomymous, 2011). The crude oil is extracted mechanically by pressing or chemically by using solvent (hexane) after processing the kernels in such away that its surface area have increased (Bernardini, 1973). Thereafter, the crude oil is refined either by chemical or physical processes involving degumming, neutralization, bleaching and deodourization (Ihekoronye and Ngoddy, 1985; Arawande and Seyifunmi, 2010). Refined palm kernel oil is one of the cheapest vegetable oils in Nigeria and due to its cheapness, it is widely consumed by poor Nigerians. In most cases, it is bought in larger quantity when it is abundantly available due to its low buying price at this time.The oil is stored and sold when the selling price has gone up after six months or more. And during the storage period a lot of unpalatable organoleptic changes would have taken place which posess health risk to the consumers of such oil. Hence the need to prevent oil rancidity by adding antioxidants becomes inevitable.

The uses of synthentic chemical substances in combating or delaying oil rancidity have been reported (Carrasquero *et al.* 1998; Enrol *et al.* 2004). Such chemical substances are butylatedhydroxytoluene (BHT), butylatedhydroxyanisole (BHA), propylgallate (PG), tertiary butylatedhydroquinone (TBHQ) and citric acid. Although they are found effective at very low concentrations but they are not safe owing to their toxicity, carcinogenicity and mutagenicity (Maleck, 2002; Murkovic, 2003; Rehab, 2010).This now necessitates

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provoking interest in searching for safer means of natural antioxidants of plant origin that will have the same or higher potency with the synthetic antioxidants in preventing both oxidative and hydrolytic rancidity of edible oils. The use of various plant extracts as antioxidants or preservative has been documented and reported by researchers (Frankel, 1996; Wanasundara and Shahidi, 1998; Farag *et al*. 2003; Farag *et al.* 2006; Arawande and Abitogun, 2009).

Sweet orange peel is basically one of the agricultural wastes that hardly can any Nigerian eats it, though the peel has been reported that it contains a lot of phytochemicals such as ascorbic acid, flavonoids and vitamin A which are of immense importance to healthy living (Anonymous, 2011).Most of these natural antioxidants found in plants are always coloured or pigmented (carotenoids, chlorophyll, etc) (Oboh and Rocha, 2006); therefore the yellow colour in ripped orange peel suggests that it will be rich in phytochemical antioxidants that can be extracted by suitable solvents. The aim of this work is to investigate the effect of methanol and water extracts of ripped orange peel at varying concentrations (200 ppm – 1000 ppm) on the colour, refractive index, free fatty acid, acid value and peroxide value of refined palm kernel oil stored in white transparent plastic containers and to compare their antioxidative effect with that of butylatedhydroxytoluene (BHT).

Materials and methods

Sources of materials

Orange fruits were purchased from a local farmer at Utelu camp, Iyere, Owo, Ondo-State, Nigeria. The refined palm kernel oil was obtained before being fortified with vitamin A at JOF Ideal Family Farms Limited, Owo, Ondo-State, Nigeria.

Preparation and extraction of orange peel

Orange fruits were peeled with hands and knife, rinsed with water, chopped into smaller pieces for easy sun drying. The dried peel was ground using electric blending machine and it was sieved with 40mm mesh size. The sample was packed into a black polyethene bag prior to extraction.

Twenty gram of the sample was weighed into two cleaned and dried reagent bottles; and 200mL of each solvent (methanol and water) was separately added to each bottle and left for 72 hours during which it was intermittently shaken on a shaking orbit machine. The mixture was filtered through a 0.45µm Nylon membrane filter. The extracts were evaporated to dryness under reduced pressure at 40^{o}C by a rotary evaporator (Amir *et al*. 2005; Arawande and Komolafe, 2010).

Addition of additives to refined palm kernel oil

Methanol and water extracts of orange peel at concentrations of 200 ppm (0.02g per 100ml oil) to 1000 ppm (0.10g per 100ml oil) were separately added to Refined palm kernel oil (RPKO) contained in white transparent plastic bottles of equal capacity and they were thoroughly shaken for proper mixing. RPKO containing 200 ppm BHT (0.02g per 100ml oil) and that which contained no additive (0 ppm (control)) were also set- up. Each container was appropriately labeled and stored in an open place at room temperature ranging from 27^{o}C to 33^{o}C.

Physical and chemical analysis

The colour of the oil sample was determined as described by AOCS 2004 using Lovibond Tintometer (Model 520). The refractive index was also determined using Abbe's Refractometer at 40^{o}C (AOCS, 2004). Thereafter, the free fatty acid (FFA), acid value (AV) and peroxide value (PV) of each oil sample were monitored monthly using standard method of analysis (AOCS, 2004) for a period of twelve months.

Statistical analysis

The results (except colour and refractive index) were compared by one-way analysis of variance (one-way ANOVA) to test for significant difference. Means of the group were compared using Duncan Multiple Range Test (DMRT) (SAS, 2002).

Results and discussion

Table I reveals changes in colour and refractive index of refined palm kernel oil stored with varying concentration of methanol and water orange peel extracts and 200 ppm BHT. Colour and refractive index are very important physical characteristics for the assessment of edible oils. The addition of additives (methanol orange peel extract (MOPE) and water orange peel extract (WOPE) increased the colour units of refined palm kernel oil (RPKO) by 1 to 3 units when compared with the colour of RPKO that contained no additive (0 ppm). RPKO containing 200 ppm to 1000 ppm MOPE and WOPE had colour units ranged from 11.0 to 13.0 units whereas RPKO containing 200 ppm BHT and the control (0 ppm) had colour of 10.0 units. The lower the colour unit, the more acceptable and attractive the oil becomes. RPKO containing both extracts had colour unit slightly higher than the control but still with acceptable limit (15.0 units maximum) recommended by Standards Organization of Nigeria for refined palm kernel oil (Anomymous, 2000). The addition of WOPE and MOPE at varying concentrations to RPKO did not reflect that the oil was adulterated because the refractive index of those oil samples had approximately the same value (1.458-1.460) with the control (0 ppm) and RPKO containing 200 ppm BHT (1.460).

Figure I. depicts free fatty acid (FFA) of RPKO stored with methanol orange peel (MOP) extract and butylatedhydroxytoluene (BHT) for twelve months. It was observed that RPKO containing 200 ppm to 1000 ppm MOP extract had lower FFA values than oil sample containing 200 ppm BHT in the first nine months of storage. As the concentration of the extract increases, the FFA of RPKO gradually decreases. The FFA of oil containing MOP extract and 200 ppm BHT was lower than FFA of oil which contained no additive (0 ppm (control)). Figure II. reveals free fatty acid (FFA) of RPKO stored with water orange peel (WOP) extract and butylatedhydroxytoluene (BHT) for twelve months. The FFA of oil sample which contained WOP extract and 200 ppm BHT was lower than FFA of oil sample that contained no additive. In the first nine months of storage,

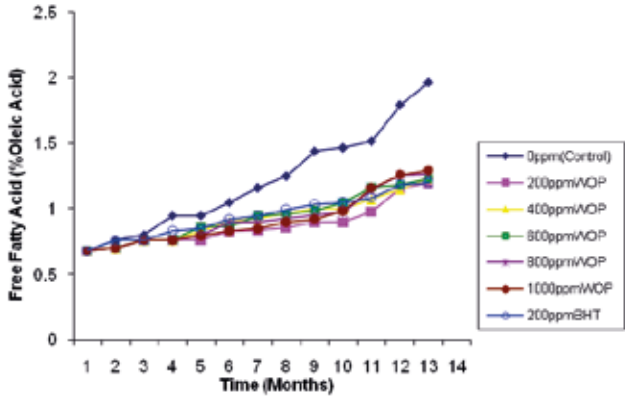

Figure2: Free Fatty Acid of Refined Palm Kernel Oil stored with Water Orange Peel (WOP) Extract and BHT for twelve months

Table I: Changes in colour and refractive index of refined palm kernel oil stored with varying concentration of methanol and water orange peel extracts and 200 ppm BHT.

Concentration of Additive	Colour(Units) in 1 inch cell	Refractive Index at 40°C
0 ppm (No additive)	1R+5Y=10.0	1.460
200 ppm MOPE	1R+6Y=11.0	1.459
400 ppm MOPE	1.2R+6Y=12.0	1.460
600 ppm MOPE	1.2R+7Y=13.0	1.460
800 ppm MOPE	1R+6Y=11.0	1.460
1000 ppm MOPE	1.1R+7Y=12.5	1.460
200 ppm WOPE	1R+6Y=11.0	1.460
400 ppm WOPE	1.1R+6Y=11.5	1.460
600 ppm WOPE	1.2R+7Y=13.0	1.460
800 ppm WOPE	1.2R+7Y=13.0	1.458
1000 ppm WOPE	1.1R+7Y=12.5	1.459
200 ppm BHT	1R+5Y=10.0	1.460

MOPE= Methanol Orange Peel Extract; WOPE= Water Orange Peel Extract, BHT= Butylated hydroxyl toluene
R = Red Slide; Y = Yellow Slide

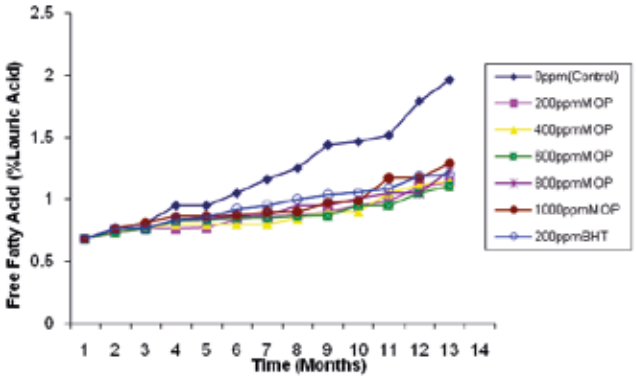

Figure1: Free Fatty Acid of Refined Palm Kernel Oil stored with Methanol Orange Peel (MOP) Extract and BHT for twelve months

the FFA of oil containing WOP extract was lower than the FFA of oil containing 200 ppm BHT. The FFA of the oil sample containing WOP extract slightly decreased as the concentration of WOP extract increased in the oil. Hence increase in the extract concentration in the oil reduces the rate at which the oil undergoes hydrolytic rancidity.

The acid value (AV) of refined palm kernel oil stored with methanol orange peel (MOP) extract and BHT for twelve months is revealed in Figure 3. The trend observed resemble that of Figure III. above. It was clearly observed that in the first nine months of storage, all the varying concentrations of MOP extract were effective in lowering the acid value of refined palm kernel oil than 200 ppm BHT. The capability of MOP extract to reduce acid value of RPKO slightly increased as the concentration of the extract increased. Figure IV.

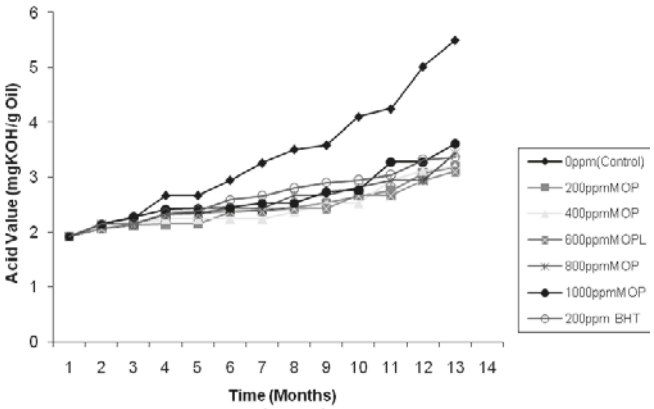

Figure3: Refined Palm Kernel Oil stored with Methanol Orange Peel (MOP) Extract and BHT for twelve months

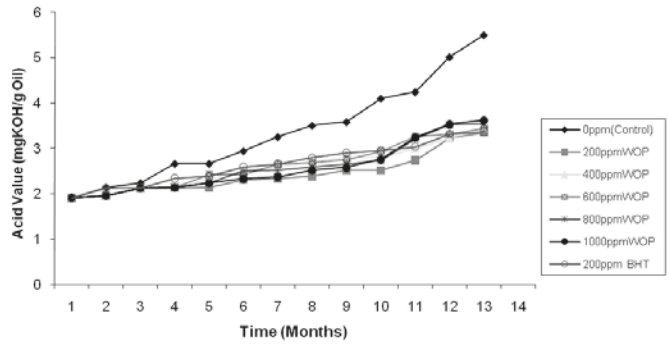

Figure 4: Acid Value of Refined Palm Kernel Oil stored with Water Orange Peel (WOP) and BHT for twelve months

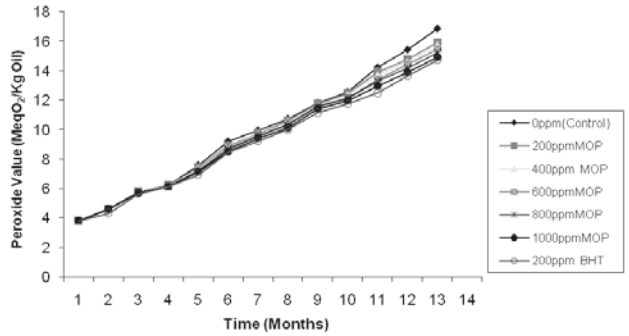

Figure5: Peroxide Value of Refined Palm Kernel Oil stored with Methanol Orange Peel (MOP) Extract and BHT for twelve months

depicts acid value of refined palm kernel oil stored with water orange peel (WOP) extract and BHT for twelve months. Throughout the twelve months of storage the acid value of RPKO that contained no additive was higher than oil samples that contained additives (extracts and BHT). As the concentration of WOP extract increased in the oil sample, the acid value of the oil decreased remarkably. In the first nine months of storage, orange peel extracts were more effective than 200 ppm BHT in reducing the acid value of RPKO.

Figure V. reveals the peroxide value (PV) of refined palm kernel oil stored with methanol orange peel (MOP) extract

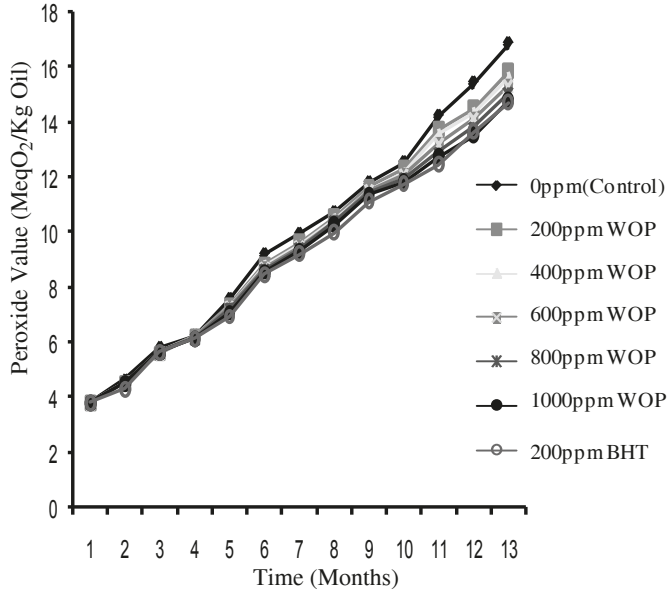

Figure 6: Peroxide Value of Refined Palm Kernel Oil stored with Water Orange Peel (WOP) Extract and BHT for twelve months

and butylatedhydroxytoluene (BHT) for twelve months. The trend observed was in agreement with the observations reported by Amir *et al*. 2005 for the plot of peroxide value of soybean oil mixed with pistachio hull extract; Zalejiska-Fiolka 2001 for the plot of peroxide value of oxidation process of edible oils mixed with garlic extract and Maskan and Karatas 1998 for the plot of peroxide value of pistachio nut. All the additives slightly lowered peroxide value of RPKO. MOP extract at all the varying concentrations were not as effective as 200 ppm BHT in lowering peroxide value of refined palm kernel oil. Peroxide value of refined palm kernel oil stored with water orange peel (WOP) extract and butylatedhydroxytoluene (BHT) for twelve months is shown in Figure 6. RPKO mixed with 200 ppm -1000 ppm WOP extract had higher peroxide value than oil sample mixed with 200 ppm BHT. Generally, the peroxide value of refined palm kernel oil gradually decreased as the concentration of MOP and WOP extracts increased in the oil sample for the twelve months of storage.

Table II reveals the mean values of FFA, AV and PV of refined palm kernel oil stored with varying concentrations of methanol and water orange peel extract and 200 ppm BHT for a period of twelve months. The addition of methanol and water extracts of orange peel to RPKO resulted in lowering FFA and AV of oil sample than 200 ppm BHT. Free fatty acid and acid value of any lipid are measure of hydrolytic rancidity (Cocks and Rede, 1966, Ihekoronye and Ngoddy, 1985; Farag *et al*. 2003; Farag *et al*. 2006; Rehab 2010). The higher the value of FFA and AV of any lipid, the higher the degree of hydrolytic rancidity that set-in (Ihekoronye and Ngoddy, 1985; Arawande and Amoo, 2009). The FFA and

AV of RPKO containing all varying concentrations of both MOP and WOP extracts were not significantly different at P<0.05 when compared with 200 ppm BHT but it was significantly different at P<0.05 in comparison with the was higher than that of 200 ppm BHT. But the antioxidant activity of both extracts against oxidative rancidity in RPKO was relatively lower than 200 ppm BHT.

Table II: Mean value of some selected quality properties of refined palm kernel oil stored with varying concentration of methanol and water orange peel extract and 200 ppm BHT over a period of twelve months

Concentration of Additive	*Free Fatty Acid (FFA) (% Lauric acid)	*Acid Value (AV) (mg KOH/g Oil)	*Peroxide Value\ (PV) (meq O2/Kg Oil)
0 ppm (No additive)	1.214±0.401b	3.368±1.107b	9.913±14.183b
200 ppm MOPE	0.873±0.140a	2.445±0.391a	9.683±3.961ab
400 ppm MOPE	0.873±0.143a	2.445±0.400a	9.589±3.896ab
600 ppm MOPE	0.871±0.119a	2.439±0.333a	9.483±3.813a
800 ppm MOPE	0.911±0.148a	2.552±0.413b	9.411±3.746a
1000 ppm MOPE	0.942±0.175a	2.638±0.488a	9.277±3.638a
200 ppm WOPE	0.871±0.159a	2.439±0.444a	9.595±3.937ab
400 ppm WOPE	0.922±0.171a	2.581±0.477a	9.483±3.844a
600 ppm WOPE	0.936±0.184a	2.621±0.515a	9.401±3.756a
800 ppm WOPE	0.925±0.195a	2.592±0.546a	9.300±3.661a
1000 ppm WOPE	0.916±0.204a	2.567±0.570a	9.199±3.572a
200 ppm BHT	0.948±0.164a	2.654±0.458a	9.100±3.564a

NOTE: Within each column, mean values followed by the same superscript are not significantly different at P ‹ 0.05 level according to Duncan Multiple Range Test (DMRT).

*Mean Value of Quality Properties ± Standard Deviation.

MOPE= Methanol Orange Peel Extract; WOPE= Water Orange Peel Extract, BHT= Butylated hydroxyl toluene

control which contained no additive. The Peroxide Values of RPKO containing methanol and water orange peel extracts at varying concentration were slightly higher than RPKO that contained 200 ppm BHT. The PV of RPKO containing additives was significantly different at P<0.05 from PV of RPKO which contained no additive. The peroxide value of oil samples decreased gradually as the concentration of additives increased. Peroxide value is a measure of oxidative rancidity of oils and the lower the PV value the better is the oil quality (Ihekoronye and Ngoddy, 1985; Rossel, 1994, Amir *et.at*, 2005) Water and methanol orange peel extracts are not as effective as 200 ppm BHT in combating oxidative rancidity of RPKO.

Conclusion

Both methanol and water extracts of orange peel had pronounced antioxidant activity against hydrolytic and oxidative rancidity of refined palm kernel oil stored in white transparent plastic bottles. The antioxidant activity of both extracts against hydrolytic rancidity in refined palm kernel oil

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