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Synergic Effect of Citric Acid and Peanut Skin Extract on the Oxidative Stability of Vegetable Oil

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ABSTRACT: The antioxidant potentials of citric acid and peanut skin extract on the oxidative stability of vegetable oil were examined. The antioxidant potential of citric acid/peanut skin extract mixture on the oxidative stability of vegetable oils was also examined. Results showed that the citric acid had the best antioxidant potential at 0.2g/100g of vegetable oil. This was followed closely by citric acid/peanut skin extract mixture at a concentration of 0.1g citric acid and 0.1g peanut skin extract in 100g of vegetable oil. The least antioxidant potential was showed by peanut skin extract at a concentration of 0.2g/100g of vegetable oil. Results from the blend between citric acid and peanut skin extract showed there was some synergistic effect of citric acid of the peanut skin extract. Thus such a blend could be used in place of citric acid in the production process to cut down cost of production

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Peanut skins are low-value by-products of peanut processing operations, typically used as animal feed. They have been found to contain significant levels of natural antioxidants (S. F. O'Keefe and H. Wang, 2005). Peanut skin is rich in phenolic antioxidants which can be extracted and used in industrial and pharmaceutical applications thereby adding value to agricultural wastes (S.V. Nepote et al, 2004).There are three classes of phenolic acid found in peanut skin. These are caffeic acid, chlorogenic acid, ferulic and coumaric acid (Jiamnei et al, 2006). Studies have shown that peanut skin has the potential to provide an inexpensive source of phenolic antioxidant that can be used as a functional ingredient or dietary supplement e.g. catchins. Such novel use will add value to the peanut skin industry and enhance its profitability (J.S.Pruthi, 1980). Addition of natural antioxidants from peanut skin extract will provide protection against lipid oxidation being a little less efficient compared to citric acid (Hoang Van Ha, et al, 2007).

Citric acid is commonly used in vegetable oils as a metal chelator. In other words, citric acid binds the metal ions that can otherwise contribute to rancidity as they catalyze free-radical oxidation of lipids (Eastern Chemical Company, 2003). Most refiners of vegetable oils add citric acid, dissolved in either propylene glycol or water in the final stages of refining. Most formulations contain citric acid where in addition to its chelating abilities; it also acts as antioxidant synergist (Robards, K et al, 2004). Citric acid has a highly antioxidant activity next to coffee among beverages (Nicoletta Pellegrino et al, 2003).

Fats and oils are obtained from the fatty tissues of plant and animals. Animal fats and vegetable oils are the most widely occurring lipids. Animal fats like butter and lard are solids whereas vegetable oils like corn and peanut oils are liquids – their structures are closely related. Chemically, fats and oils are triacyglycerols, also called triglycerides – that is, trimesters of glycerols (McMurray John, 1992). Some of the fatty acids contained in vegetable oils include: Lauric acid,Myristic acid, Stearic acid, Oleic acid, Ricinoleic acid and Linoleic acids. Vegetable oils have a high proportion of unsaturated to saturated fatty acids than animal fats and oils as a consequence of the difference in their structures. Whereas saturated fats have a uniform shape that allows them to pack easily in a crystal lattice, the carbon-carbon double bonds in unsaturated vegetable oil introduce bends and kinks in the hydrocarbon chain, making crystal formation difficult.Fats and oils easily undergo deterioration as a result of poor processing, handling and storage methods. Two major types of deterioration were identified as that due to hydrolysis by micro-organisms and that due to atmospheric oxidation (Krishnamurthy R, 1982). The latter is a very serious problem of storage leading to a process simply described as oxidative rancidity with consequent loss in the quality of the commodity. Autoxidation involves free radical chain reactions characterized by the interaction of radicals with oxygen to yield peroxy radical, organic peroxides and a broad spectrum of stable oxygenated products. Quality changes associated with the extent of oxidation of fats and oils are measured by the peroxide value (PV). The peroxide value is a measure of the amount of peroxide formed.

The use of antioxidants, substances which prevent or inhibit oxidation has received considerable interest in the food industry for a wide range of foodstuffs are exposed to deterioration e.g. products containing fats and oils (Coombs James, 1992). Antioxidants increase the stability of foodstuffs in storage as well as increasing the retention of nutritional and flavour values by delaying rancidity

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(Chang, D.M et al, 1977). Traces of these substances when added to fats and oils during processing or while storage, retard the onset of oxidative rancidity and thus prolong the life of the product (Scott, G., 1965). This paper attempts to find out if there is any effect on the oxidative stability of vegetable oil by using a mixture of citric and peanut skin extract as antioxidants.

MATERIALS AND METHODS

Vegetable oil used was obtained from General International Oil Ltd., Port Harcourt. The roasted peanut skin was obtained locally. The citric acid was also obtained from the market in Port Harcourt. The peanut skin was milled with the aid of a milling machine; weights of samples were obtained using a Mettler analytical balance. Solvent extraction from the peanut skin was obtained with the aid of a Soxhlet extraction unit using the procedure of the Association of Official Analytical Chemist (Official Methods of the Association of Official Analytical Chemists, 1984). The solvent extract was concentrated in a water bath and air-dried. Oil samples were treated directly with the peanut skin extract according to the method adopted by Blatina (Blatina, J and J. Manous). Peroxide values of oil samples were assayed using titrimetric method following the procedure of the American Oil Chemist Society

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The effect of synthetic citric acid, peanut skin extract and a mixture of citric acid and peanut skin extracts at various temperature ranges on the oxidative stability of vegetable oil samples were studied by titrimetric methods.

Treatment of Oil Samples with Citric Acid and Peanut Skin Extract:: Vegetable oil samples (0.5L each) were separately measured into clean, dry and labeled plastic containers. The different antioxidants were introduced into the oil samples at a concentration of 0.2g/100g of vegetable oil. Two controls were also obtained by treating one oil sample with the solvent used for obtaining extract from peanut skin (0.5ml/100g); while the second was untreated. The plastic containers were properly covered and thoroughly shaken. The treated and control samples were stored under ambient conditions.

Initial assessments of the oxidation levels of the oil samples were carried out by assay of the peroxide values. Sampling and consequent analysis were carried out on a weekly basis to monitor the changes in parameters associated with the oxidation levels of the stored vegetable oil samples.

Assay of Peroxide Values of Stored Vegetable Oil Sample : Vegetable oil sample (5.00g) was dissolved in a mixture of glacial acetic acid and chloroform (30ml), 3:2 v/v by ratio and saturated solution of potassium iodide (0.5ml) was added. The solution was allowed to stand for one minute with occasional swirling and then 30ml of water was added. The mixture obtained was titrated against 0.1M solution of sodium thiosulphate to a starch indicator end point. A blank titration (without oil sample) was also carried out.

*Calculations:*The formula below was used to calculate the peroxide values (PV): PV (Meq/Kg) = $\frac{M(S-B)100}{\text{Weight of Sample (g)}}$

Where:
S = titre value for sample
B = titre value for blank
M = Molarity of sodium thiosulphate

The relative increase in peroxide values (primary oxidation levels) of the treated and control vegetable oil samples was calculated using the formula:

% Increase in PV s

Where:
F = Final peroxide values after a given period
I = Initial peroxide value

Effect of temperature on the efficiency of peanut skin extract on the oxidative stability of vegetable oil. 100g of vegetable oil sample was treated with 0.2g of peanut skin extract and the content maintained at $60^{O}C$ in paraffin wax, using an untreated sample as control. Samples of oil were withdrawn at hourly interval, for assay of peroxide values over a period of five hours. The reaction was carried out with treated samples at different temperatures: $60^{O}C$, $80^{O}C$, $150^{O}C$ and $180^{O}C$ respectively. Peroxide values obtained at each temperature were plotted against time.

Effect of temperature on the efficiency of citric acid on the oxidative stability of vegetable oil. 100g of vegetable oil sample was treated with 0.2g of citric acid and the content maintained at a temperature of $60^{O}C$ in paraffin wax, using an untreated sample as control. Samples of oil were withdrawn at hourly interval for assay of the peroxide values over a period of five hours. The reaction was carried out with treated samples at different temperatures of $60^{O}C$, $80^{O}C$, $150^{O}C$ and $180^{O}C$ respectively. Peroxide values obtained at each temperature were plotted against time.

Comparative studies on the efficiency of citric acid and peanut skin extract on the oxidative stability of vegetable oil: Vegetable oil samples (100g) were treated with a mixture of 0.1g citric acid and 0.1g peanut skin extract and the content maintained at $60^{O}C$ in paraffin wax, using an untreated sample as control. Samples of oil were withdrawn at hourly

intervals over a period of five hours. The reaction was carried out at different temperatures of $60^{o}C$, $80^{o}C$,$150^{o}C$ and $180^{o}C$ respectively. Oxidative stability of treated oil samples was tested. Peroxide values obtained at each temperature were plotted against time.

RESULTS AND DISCUSSION

There was general increase in peroxide value of control and treated samples (Tables 1 – 4). However when results were considered on the basis of relative increase in peroxide values of the vegetable oil samples with period of storage, the samples treated with citric acid and peanut skin extract followed in the antioxidant activity and the least with the highest peroxide values were the samples treated with peanut extract alone.

Two temperatures ranges were used for the experiments. The low temperature range of $60^{o}C$ and $80^{o}C$ and high temperature range of $150^{o}C$ and $180^{o}C$. Results show that at low temperatures, the peroxide values of all oil samples vary with temperature during the period under test. However, at high temperatures, the peroxide values of all oil samples increase rapidly a s shown in Fig. 4.

The results show a correlation between the efficiency of the antioxidants and the temperature which they are used. The relative stability of the peroxide values at lower temperatures is indicative of the efficiency of the citric acid and peanut skin extract when used as antioxidants for vegetable oil at low temperatures. On the other hand, the high peroxide values at high temperatures indicate the inefficiency of the antioxidants at such temperatures. The rapid decline in peroxide values at $180^{o}C$ could be attributed to the decomposition of the hydroperoxide formed during the primary stages of autoxidation.

Table 1: Peroxide values of citric acid and peanut skin extract at $60^{o}C$

Time (hour)	Peroxide values (Meq/100g)	erimental condition	Peroxide values (Meq/100g)	erimental condition
0	13.00	Vegetable oil	6.00	Vegetable oil
1	14.00	without	8.80	0.2g peanut
2	15.80	antioxidant.	12.40	skin extract.
3	16.20	Temperature of	12.40	Temperature
4	17.60	$60^{o}C$.	12.60	of $60^{o}C$.
5	18.20		23.00	

Time (hour)	Peroxide values (Meq/100g)	Experimental condition	Peroxide values (Meq/100g)	Experimental condition
0	2.80	Vegetable oil	5.60	Vegetable oil
1	4.00	0.2g citric acid	8.60	0.1g peanut
2	4.80	Temperature of	10.60	skin extract +
3	4.80	$60^{o}C$	11.20	o.1g citric acid
4	5.20		12.00	Temperature
5	5.60		13.00	of $60^{o}C$

Table 2 Peroxide values of citric acid and peanut skin extract at $80^{o}C$

Time (hour)	Peroxide values (Meq/100g)	Experimental condition	Peroxide values (Meq/100g)	Experimental condition
0	13.00	Vegetable oil	7.00	Vegetable oil
1	14.00	without	9.00	0.2g peanut
2	16.00	antioxidant.	9.00	skin extract.
3	16.60	Temperature of	10.40	Temperature
4	18.00	$80^{o}C$.	13.80	of $80^{o}C$.
5	18.60		29.80	

Time (hour)	Peroxide values (Meq/100g)	Experimental condition	Peroxide values (Meq/100g)	Experimental condition
0	6.20	Vegetable oil	6.40	Vegetable oil
1	6.60	0.2g citric acid	8.80	0.1g peanut
2	7.20	Temperature of	11.00	skin extract +
3	7.20	80^{o}C.	11.20	0.1g citric acid
4	7.80		12.80	Temperature
5	8.40		14.00	of 80^{o}C.

Table 3: Peroxide values of citric acid and peanut skin extract at 150^{o}C

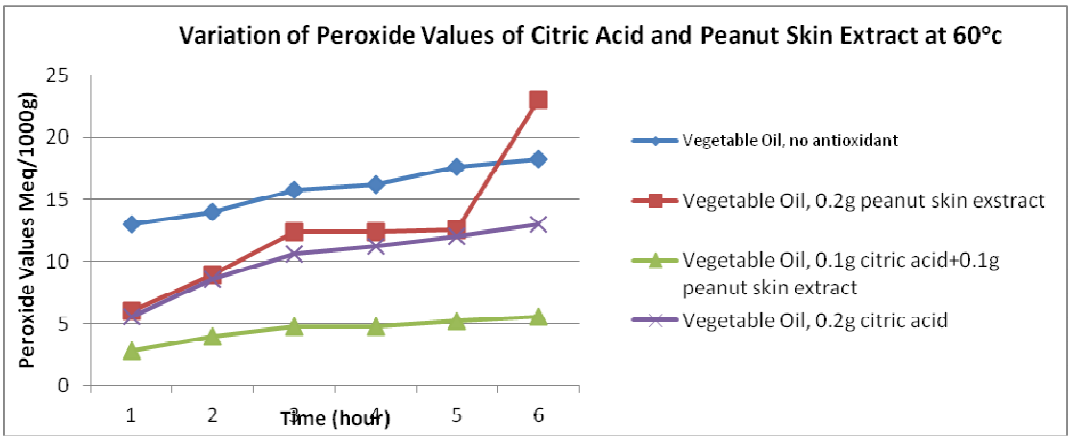
Time (hour)	Peroxide values (Meq/100g)	Experimental condition	Peroxide values (Meq/100g)	Experimental condition
0	11.00	Vegetable oil	11.00	Vegetable oil
1	16.00	without	16.20	0.2g peanut
2	17.60	antioxidant.	16.20	skin extract.
3	17.80	Temperature of	19.20	Temperature
4	20.60	150^{o}C.	20.20	of 150^{o}C.
5	25.00		20.20	

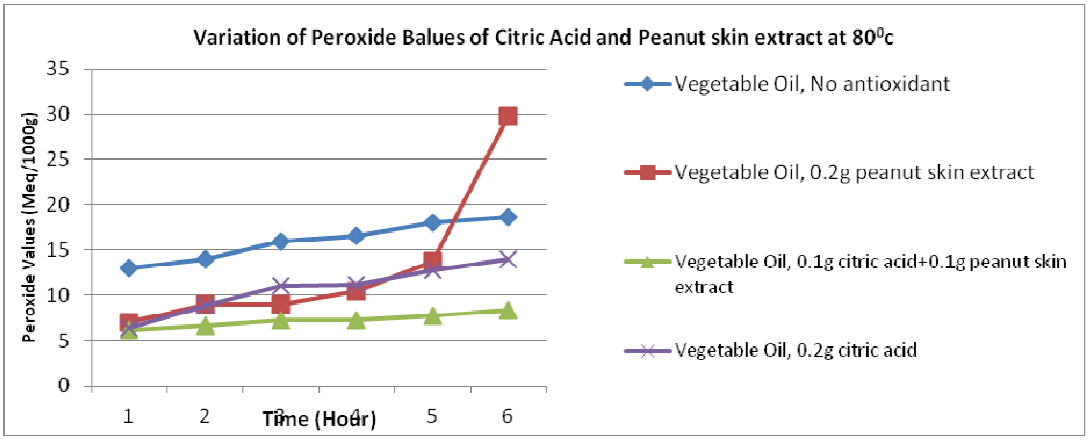
Time (hour)	Peroxide values (Meq/100g)	Experimental condition	Peroxide values (Meq/100g)	Experimental condition
0	6.80	Vegetable oil	7.80	Vegetable oil
1	12.60	0.2g citric acid	15.20	0.1g peanut
2	14.40	Temperature of	21.80	skin extract +
3	14.60	150^{o}C.	22.00	0.1g citric acid
4	31.60		39.40	Temperature
5	24.20		25.60	of 150^{o}C.

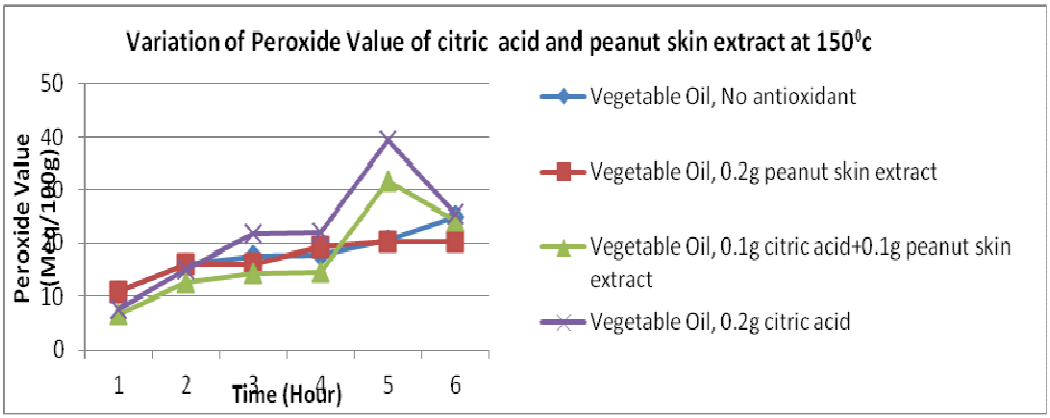
Table 4: Peroxide values of citric acid and peanut skin extract at 180^{o}C

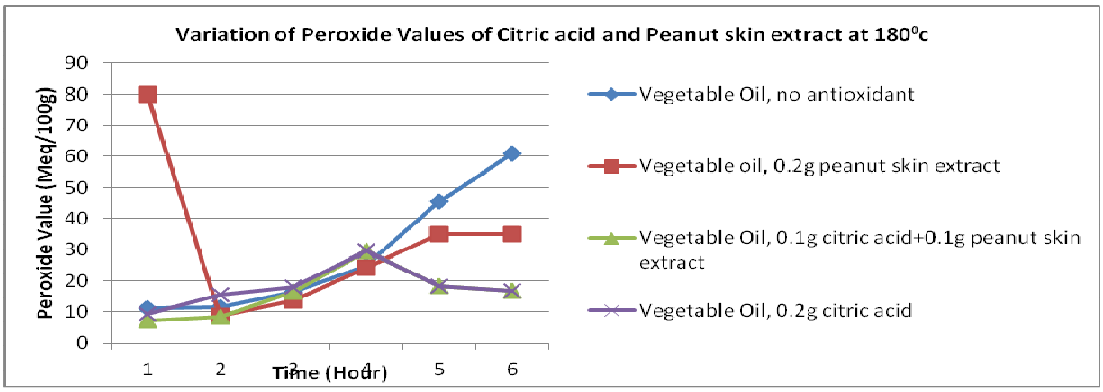
Time (hour)	Peroxide values (Meq/100g)	Experimental condition	Peroxide values (Meq/100g)	Experimental condition
0	11.00	Vegetable oil	8.00	Vegetable oil
1	11.60	without	8.60	0.2g peanut
2	16.40	antioxidant.	13.60	skin extract.
3	24.80	Temperature of	24.20	Temperature
4	45.60	180^{o}C.	35.00	of 180^{o}C.
5	60.80		35.00	

Time (hour)	Peroxide values (Meq/100g)	Experimental condition	Peroxide values (Meq/100g)	Experimental condition
0	7.20	Vegetable oil	9.20	Vegetable oil
1	8.40	0.2g citric acid	15.40	0.1g peanut
2	16.40	Temperature of	18.00	skin extract +
3	29.60	$180^{o}C$.	29.60	0.1g citric acid
4	18.40		18.40	Temperature
5	16.80		16.80	of $180^{o}C$.









Conclusion: Results from the above studies show that citric acid and peanut skin extract serve as antioxidants for the oxidative stability of vegetable oil. Citric acid is more efficient than peanut skin extract. However, a mixture of citric acid and peanut skin extract gave a better result than using peanut skin extract alone. The peroxide values of citric acid/peanut skin extract are comparable to those of citric acid. This suggests that there has been synergistic effect of citric acid on peanut skin extract. Therefore, it is better to blend the peanut skin extract with citric acid than to use the peanut skin extract alone. This mixture can therefore be used in place of citric acid. This will go a long way to reduce production cost as the citric acid is more expensive than peanut skin extract which can be got at very little or no cost. This will add value to the peanut industry.

REFERENCES

American Oil Chemists Society (1960) Official methods of analysis of fats and oils
.

Blatina, J. and J. Manous (1961). Tcocopherol as antioxidant in food; J.
Sci. Agric. 12 150

Chang, D. M; S. Gromelski; R. Rupp and J. Mulvaney (1977). J. Polm.
Chem. 45, 571

Coombs James (1992). Dictionary of Biotechnology, Stockton Press, New York, 2nd ed. P 29

Chemical Company (2003). Tenox CA-50 Food – Grade Antioxidant: citric acid and vegetable oil
s

6.Hoang Van Ha, Jan Pokorn and Detoshi Sakurai (2007). Peanut skin
Antioxidants; Journal of Food Lipids, 14, 3 pp298-314

7. Jiamnei Yu; Mohamed Amehda and Jian Dai (2006). Journal of Food
Composition and analysis, vol 19, pp 364-371

J.S. Pruthi (1980). Food Chemistry Antioxidants and bioactive agents, Session 67B, p23

Krishnamurthy, R. (1982). Deterioration of Fats and Oils. Bailey's industrial Oil and fats products, Wiley International Science 4th ed. Chap 5 11

John (1992). Organic Chemistry; Brooks/Cole Publishing Co. California, 3rd ed. P 1092

. Nicoletta Pellegrino; Mauro Serafini; Barbara Colouls and Daniele Del

Rio (2003). J. Nutr. 133 2812 – 2819

Robards, K et al (2004). J. Agric. Food Chem. 52, 962 – 971

. G. (1965). Atmospheric oxidation and Antioxidants. Elsevier, Amsterdam

S.F O'Keefe and H. Wang (2005). Effects of peanut skin extract on quality and storage of beef products; Meat Science 73, 2 pp 278-286

15. SV. Nepote; M.G Mestrallet and N.R. Grosso (2004). Journal of Food
Science, Blackwell Energy 69(7), 295-300