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Synergic effect of Citric Acid and Red Onion skin extract on the Oxidative stability of Vegetable Oil

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ABSTRACT The antioxidant potentials of citric acid and onion skin extract on the oxidative stability of vegetable oil were examined. Results from the peroxide values showed that citric acid had the best antioxidative potentials at a concentration of 0.2g/100g of vegetable oil. This was followed by the antioxidative potentials of a mixture 0.1g of citric acid and 0.1g onion skin extract in 100g of vegetable oil. 0.2g of onion skin extract in 100g of vegetable oil gave the least antioxidative potential. Using a blend of onion skin extract and citric acid gave a better antioxidative potential than using onion skin extract alone. This suggests that there has been some synergistic effect of citric acid on the onion skin extract. Such a blend could be used in place of citric acid to cut down production cost

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In the food industry, various synthetic antioxidants are often used to prevent peroxidation of the fats in foods. However, consumer concern regarding chemical food additives has prompted researchers to search for potential antioxidants from natural sources (Graw-Chin Yen and Hsin-Hsin Kao, 1993).

Edible fats and oils deteriorate rapidly in the presence of oxygen and go rancid. The rate of oxidation by air or autoxidation varies and depends on the ease of hydrogen ion abstraction from the substrate molecule. Unsaturated lipids having allylic hydrogen are more susceptible to autoxidation than saturated substances (Akaranta O and T.O Odozi, 1986).

Vegetable oils are obtained from fatty tissues of plants. They are liquids and are triglycerides – that is trimesters of glycerol (McMurray John, 1992). The structure of a triglyceride molecule has been studied (Litherfield, C., 1992). Some of the fatty acids contained in vegetable oils include: Lauric acid, Myristic acid, Stearic acid, Ricinoleic acid and Linoleic acid.

Fats and oils easily undergo deterioration as a result of poor 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.

Citric acid is commonly used in vegetable oils as a metal chelator. In other words, citric acid binds the metal ions that otherwise contribute to rancidity as they catalyse free-radical oxidation of lipids. Most formulations contain citric acid where in addition to its chelating abilities; it also acts as antioxidant synergist (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 (Robards, K et al, 2004).
Citric acid has a high antioxidant activity next to coffee among beverages
(Nicoletta et al, 2003).

Onion (Allium cepa) is a common plant in the Allium family in Nigeria. The plant is distributed across the temperate regions. They are used medicinally
for the treatment of intestinal warms, stomach ulcers, high blood pressure and malaria fever (I.J. Alinnor and Pascal Madu, 2007). Tannin is found in the protective layers of plant tissues like onion skin (Odozi, T.O et al, 1984). It is a polyhydroxyphenol of the flavonoid type. The antioxidant properties of red onion skin (allium cepa) tanning extract has been recorded (M.P. Kahkoneri et al, 1999).

In most cases, mixtures of two or more antioxidants prove more effective than the effect of one. In such cases, one antioxidant reinforces the effect of the other for maximum efficiency. For example, stability of lettuce seed oil treated with tocopherol and citric acid has been reported (Novotny, J.A et al, 2003). It was argued that the efficiency of the mixture was attributed to the ability of citric acid to regenerate any used up tocopherol.

This paper presents a report of the investigation of the effect of mixtures of citric acid and onion skin extract on the oxidative stability of vegetable oil.

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MATERIALS AND METHODS

Vegetable oil used was obtained from General International Oil Ltd., Port Harcourt. Dry onion skin was obtained from the Choba market. The onion skin was milled, weights of sample measured using a Mettler analytical Balance. Solvent extraction was carried out with the aid of a Soxhlet extraction unit using the procedure of the Association of Official Analytical Chemists (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 plant extract according to the method adopted by Blattina (Blatina, J and J. Manous, 1961). Peroxide values of oil samples were assayed using titrimetric method following the procedure of the American Oil Chemist Society (AOCS) (American Oil Chemists Society, 1960). The effect of synthetic citric acid, onion skin extract and a mixture of citric acid and onion skin extracts at various temperature ranges on the oxidative stability of vegetable oil samples were studied by titrimetric methods.

Treatment of Oil Samples with Extract: Vegetable oil samples (0.5L each) were separately measured into clean, dried and labeled plastic containers. Onion skin extract was introduced into the samples at a concentration of 0.2g/100g. The extract was to serve as natural antioxidant. Two controls were also obtained by treating one oil sample with the solvent used for the extraction from the plant (0.5ml/100g) while the second was untreated. The plastic containers were firmly covered and shaken to mix the extract and vegetable oil. 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 subsequent analysis were carried out on a weekly basis to monitor the changes in parameters associated with the oxidation levels of the stored vegetable oils.

Assay of Peroxide Values (PV): Vegetable oil sample (5.0g) 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 of sample
B = Titre of blank
M = Molarity of sodium thiosulphate

Oxidation At 60°C In The Presence Of Onion Skin Extract: Vegetable oil sample (100g) was treated with onion skin extract (0.2g) and the contents maintained at $60^{O}C$ in paraffin wax, using an untreated oil 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 so obtained at each temperature were plotted against time.

Effect of temperature on the efficiency of synthetic citric acid on the oxidative stability of vegetable oil.: Vegetable oil sample (100g) was treated with citric acid (0.2g) and the contents maintained at $60^{O}C$ in paraffin wax, using an untreated oil 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 onion 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 onion skin extract in a reaction vessel at different temperatures of $60^{O}C$, $80^{O}C$, 150oC and $180^{O}C$ respectively. Oxidative stability of treated oil samples was tested. Peroxide values obtained at each temperature were plotted against time.

Extracts tested for their antioxidative potentials were first compared for their ability to protect the vegetable oil against extensive oxidation under ambient conditions. This was achieved by comparing the relative increase in the peroxide values (primary oxidation levels) of the treated and controlled vegetable oil samples. The percentage increase in peroxide value (PV) was monitored during the period of the experiment using

the formula:% Increase in PV =100(F-1)1

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

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 had the lowest peroxide values. The sample treated with a mixture of citric acid and onion skin extract followed in the antioxidant activity and the least with the highest peroxide values were the samples treated with onion skin 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. Also at 180^{o}C, the peroxide values of some of the vegetable oils rose to a maximum at the third and declined rapidly as 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 onion 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 onion 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 onion
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)	erimental condition
0	2.80	Vegetable oil	3.60	Vegetable oil
1	4.00	0.2g citric acid	4.40	0.1g onion
2	4.80	Temperature of	5.00	skin extract +
3	4	60^{o}C	6.80	o.1g citric acid
4	5		7.60	Temperature
5	5.5		7.60	of 60^{o}C.

Table 2: Peroxide values of citric acid and onion skin extract at 80^{o}C.

Time (hour)	Peroxide values (Meq/100	erimental condition	Peroxide values (Meq/100g)	erimental condition
0	13.00	Vegetable oil	5.20	Vegetable oil
1	14.00	without	5.20	0.2g onion
2	16.00	antioxidant.	7.60	skin extract.

3	16.60	Temperature of	8.20	Temperature
4	18.00	80^{o}C.	11.60	of 80^{o}C.
5	18.60		16.60	

Time (hour)	Peroxide values (Meq/100g)	Experimental condition	Peroxide values (Meq/100g)	Experimental condition
0	6.20	Vegetable oil	6.20	Vegetable oil
1	6.60	0.2g citric acid	7.00	0.1g onion
2	7.20	Temperature of	7.40	skin extract +
3	7.20	80^{o}C	7.80	0.1g citric acid
4	7.8		8.20	Temperature
5	8.40		8.80	of 80^{o}C

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

Time (hour)	Peroxide values (Meq/100g)	Experimental condition	Peroxide values (Meq/100g)	erimental condition
0	15	Vegetable oil	8.00	Vegetable oil
1	16	without	16.00	0.2g onion
2	17	antioxidant.	16.20	skin extract.
3	17	Temperature of	18.80	Temperature
4	20	150^{o}C.	19.40	of 150^{o}C.
5	25		19.60	

Time (hour)	Peroxide values (Meq/100g)	erimental condition	Peroxide values (Meq/100g)	erimental condition
0	6.80	Vegetable oil	7.20	Vegetable oil
1	12.60	0.2g citric acid	14.00	0.1g onion
2	14.40	Temperature of	15.20	skin extract +
3	14.60	150^{o}C.	17.60	0.1g citric acid
4	31.60		20.00	Temperature
5	24.20		20.40	of 150^{o}C.

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

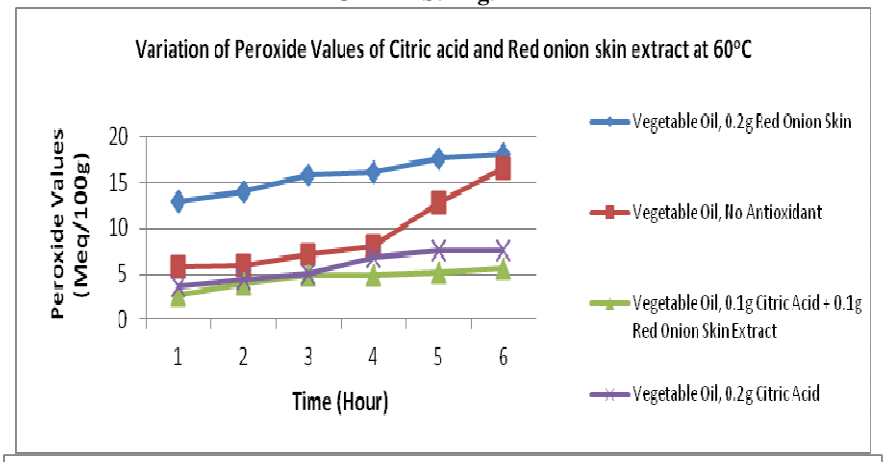
Time (hour)	Peroxide values (Meq/100g)	Experimental condition	Peroxide values (Meq/100g)	xperimental condition
0	11.00	Vegetable oil	7.80	Vegetable oil
1	11.60	without	10.00	0.2g peanut
2	16.40	antioxidant.	12.60	skin extract.
3	24.80	Temperature of	21.60	Temperature
4	45.60	180^{o}C.	25.40	of 180^{o}C.
5	60.80		25.80	

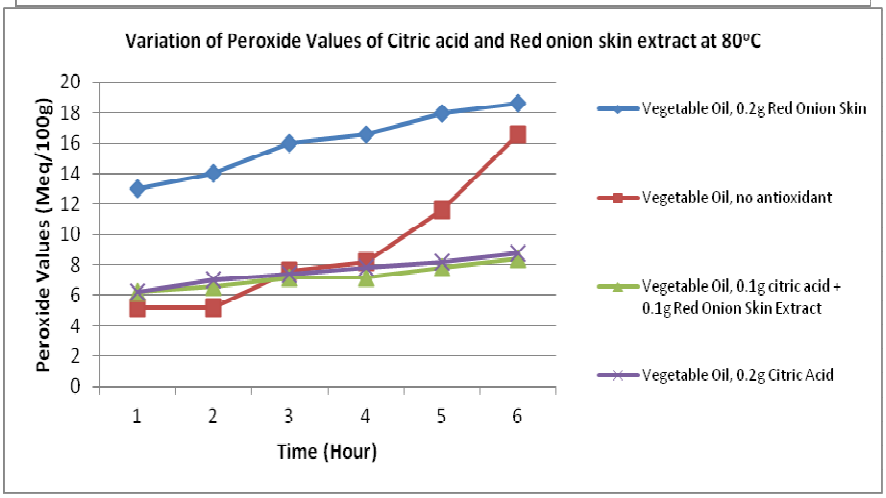
Time (hour)	Peroxide values (Meq/100g)	Experimental condition	Peroxide values (Meq/100g)	Experimental condition

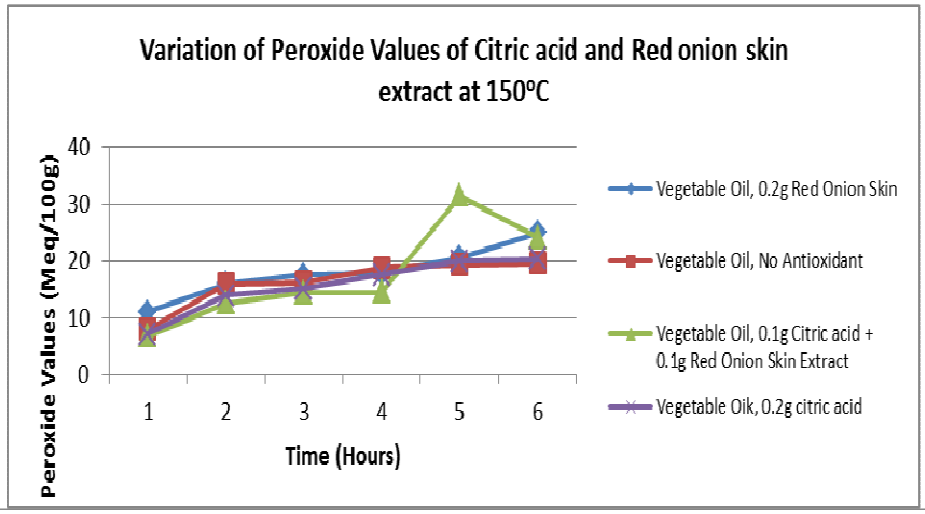
0	7.20	Vegetable oil	10.60	Vegetable oil
1	8.40	0.2g citric acid	16.40	0.1g onion
2	16.40	Temperature of	16.60	skin extract +
3	29.60	180 ^{o}C.	17.20	0.1g citric acid
4	18.40		19.60	Temperature
5	16.80		20.00	of 180 ^{o}C.

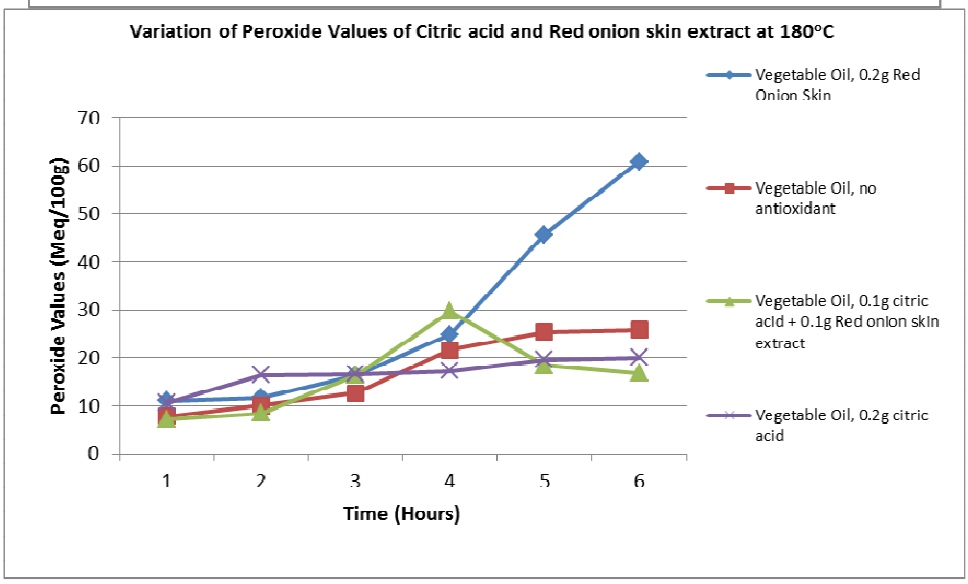
Conclusion: Results from the above studies show that citric acid and onion skin extract serve as antioxidants for the oxidative stability of vegetable oil. Citric acid is more efficient than onion skin extract. However, a mixture of citric acid and onion skin extract gave a better result than using onion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

GRAPHS: Fig. 1–4









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