

Effect of storage duration on the acid value stability of sesamum indicum and arachis hypogaea raw oils reinforced with TBHQ and capsicum annum extracts

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Abstract:

Changes in acid values of Tertiary Butyl-HydroxyQuinone (TBHQ) and capsicum annum extract fortified oils from arachis hypogaea and sesamum indicum stored at ambient condition in the laboratory were investigated over 90 days duration. Kinetic models were applied to the data obtained. The TBHQ (synthetic anti-oxidant) gave better stability than the non-aqueous extracts of capsicum annum for the oils used. Storage stability was higher in sesamum indicum. At the end of the storage duration, acid values of sesamum indicum changed from 1.43 to 32.3127(Control), 24.8789(TBHQ) and 26.3036 (Pepper extract) showing better oxidative stability with TBHQ. Similarly, the acid value of arachis hypogaea changed from 0.71 to 20.6554(control), 14.1172(TBHQ) and 15.8775(Pepper extract) again showing a better retarding oxidation effect from TBHQ. Kinetic modeling showed better fitting with the pseudo-first order and first order models for the oils studied irrespective of anti-oxidant type. Further studies on the TBHQ/Pepper extract mix for synergistic effect would provide more options.

Keywords: oxidation, sesamum indicum, capsicum annum, arachis hypogaea, antioxidants, Tertiary ButylHydroxyquinone (TBHQ), Pepper extract

Date of Submission: 10-06-2021

Date of acceptance: 24-06-2021

I. INTRODUCTION:

Antioxidants are used as compounds to extend the induction period of oxidation or retard the oxidation rate. They scavenge free radicals like lipid alkyl radicals or lipid peroxy radicals, quench singlet oxygen, and inactivate sensitizers. (Decker 2002). Oxidative stability of oils simply means the unwillingness of lipids to undergo oxidation which begins during processing and storage (Guillen and Cabo 2002). Resistance to oxidation is expressed as the time required to reach the critical point beyond which oxidation begins, be it face-value change, organoleptic alteration or a sudden acceleration of the oxidative process (Silva et al, 2001). Oxidative stability is a quality parameter used to measure oil quality and shelf life (Hamilton 1994) since low-molecular weight off-flavor compounds are produced during oxidation. The off-flavor compounds make oil less attractive, unacceptable or unappealing to consumers as food ingredient or for industrial application. Oil oxidation destroys essential fatty acids and produces toxic compounds and oxidized polymers. Oxidation of edible oils is influenced by factors such as energy input(light or heat), composition of fatty acids, types of oxygen, and minor compounds such as thermally oxidized compounds, metals, pigments, mono- and diacylglycerols phospholipids, free fatty acids, and antioxidants. Both synthetic and natural antioxidants function as preservatives by donating electron density to fats, thus preventing their breakdown. All oils are in a state of oxidation - you cannot stop it completely - but there are ways to retard it which includes the use of antioxidants. When oil oxidizes, the breakdown products are in stages, beginning with primary products (peroxides, dienes, and free fatty acids), secondary products (carbonyls, aldehydes, trienes) and finally tertiary products (Thorat *et al.*, 2013)..

The acid value measures the fatty acids liberated by hydrolysis of glycerides when acted upon by lipolytic enzyme lipase, temperature and/or moisture. It relatively measures rancidity as free fatty acids (FFA)

are among the products of triglycerides decomposition. The value can be expressed as per cent of FFA calculated as palmitic acids, ricinoleic, oleic acid and lauric. The maximum acceptable limit of Acid Value is 4mgKOH/g oil (CODEX STAN, 1999), below which the oil is considered suitable for consumption. FFAs are not found at significant level in healthy plant cells, but FFA limits up to 15% (more in very bad cases) is present in commercial crude vegetable oils irrespective of extraction method. Synthetic antioxidants have been reported to show higher performance levels than antioxidants of natural sources, meaning that natural antioxidants show a greater reluctance to donate hydrogen atoms to prevent oxidation. Synthetic antioxidants such as TertiaryButylHydroxyQuinone (TBHQ) are generally less expensive than the natural ones, as the extraction processes of natural antioxidants from sources impacts on their prices. The type of antioxidant used depends greatly on the type of food being preserved and overall price considerations. For instance, high rancidity level food are better preserved with synthetic antioxidants since these have higher activity levels, while natural antioxidants with lower activity levels can serve for hydrogenated oils with lower rancidity levels. Acid value is one of the quality parameters commonly measured. The others include iodine value, peroxide value, ester value, saponification value, P-anisidine value, TOTOX value and so on.

Capsicum annum is rich in ascorbic acid and their attractive red color is due to several carotenoid pigments which includes β -carotene with pro-vitamin A activity and oxygenated carotenoids such as capsantine, capsorubin, and cryptocapsin, which are exclusive to these fruits and have proven to be effective at scavenging free radicals [Deepa et al, 2006]. Peppers also contain large quantities of neutral phenolic compounds or flavonoids called quercetin, luteolin, and capsaicinoids [Hasler, 1998]. Sesamum Indicum and Arachis hypogea are some of the major local sources of vegetable oils in Nigeria. They account for about 20% of all expensive vegetable oils in the markets only behind palm olein, palm kernel oil (PKO) and palm oil in terms of availability. These oils are however affected by high storage room temperatures in the Nigeria guinea and Sahel savannah and hence the need to stabilize to increase shelf-life. N-hexane extracts of the dry capsicum annum was compared with TBHQ in stabilizing the stored oils from at ambient condition.

II. MATERIALS AND METHODS:

Materials:

Raw dried sample of capsicum annum, arachis hypogea and sesamum indicum were obtained from local market in Enugu, Nigeria. The samples respectively sorted out with chaffs and other extraneous contaminants removed before washing with water and drying at 50°C. The washed dried samples were milled to very fine powder of uniform size. All reagents and chemicals used for this work were either obtained from Sigma-Aldrich chem. Co (St. Louis, MO, USA) or Fischer Scientific (Oakville, ON, Canada). All the chemicals were of analytical grade.

Sample Preparation

Oil from the samples (arachis hypogea, sesamum indicum, and capsicum annum) was extracted by using N-Hexane in a soxhlet extractor / apparatus. 100 g of finely divided sample was measured into a soxhlet apparatus connected to a weighed 1L flat bottomed flask containing 400 ml n-Hexane. The solvent was continuously heated at 40 to 60°C extracting the lipids from the samples. After 16 h of extraction the N-hexane was evaporated by rotary evaporation. The flask containing the crude oil was then dried to constant weight at 105°C in the laboratory oven for 2 h. The raw oils obtained were now stored at 10°C in refrigerator in tight closed plastic bottles for further studies (Adegbe et al., 2016).

Acid Value- the AOAC 969.17 method was adopted (AOAC, 1990).

1g of the raw oils were separately weighed into 250ml conical flasks. Isopropyl alcohol (5ml) was then added to the flask and thoroughly mixed before three drops of phenolphthalein indicator was added and titrated against 0.1N KOH to the persistence of a faint pink colour for a duration of 30s. The titre value of the KOH, Vb, used was recorded and acid value was calculated as:

$$A.V \left(\frac{mg \text{ KOH}}{g \text{ oil}} \right) = \left(\frac{\text{Titre Value}(V_b) \times \text{Molar Conc.} \times \text{Molar mass}(KOH)}{\text{weight of sample}} \right) \\ = \left(\frac{V_b \times \text{Molar Conc.}(KOH) \times 56.1}{\text{weight of sample}(W)} \right) \quad (1)$$

Storage duration

The oil samples without antioxidants (S.O.C and G.O.C) as controls and with anti-oxidants (S.O.P, S.O.T, G.O.P and G.O.T) were formulated (200 g oil in 500-ml glass beaker). In this study, 200 ppm of TBHQ and capsicum annum extract (Akhtar, et al., 2014; Choe and Min, 2006) was used to formulate the vegetable

oils as per FDA norms (Codex 1995). The raw oils from *Sesamum indicum* (SO) and *Arachis hypogea* (GO) and their mixture with 200 ppm of TBHQ (SOT, GOT) and 200ppm capsicum annum extract (SOP, GOP) were stored at room temperature which varied within 24 – 31°C in the laboratory for 90 days. A portion was withdrawn to determine the oxidative stability using the acid value at interval of 10 days.

Oxidative stability

The Acid values were measured in days over a period of 3 months. Oxidative stability was measured as deviation from samples without anti-oxidants.

$$\text{Oxidative Stability}(\%) = \left(\frac{A.V_c - A.V_x}{A.V_c} \right) \times 100 \quad (2)$$

Where $A.V_c$ = Acid value of oil sample without anti-oxidant (S.O.C or G.O.C)

$A.V_x$ = Acid value of samples with anti-oxidants (SOP, SOT, GOP, GOT)

Oxidative instability

Oxidative instability was measured as deviation from standard value of freshly prepared oil sample.

$$\text{Oxidative instability} = \left(\frac{AV_x - AV_i}{AV_i} \right) \times 100 \quad (3)$$

Where AV_x = Acid Value of oil samples (SOC, SOP, SOT, GOC, GOP, GOT), AV_i = Acid Value of freshly extracted oil sample. (Sesame oil = 1.43, Groundnut oil = 0.71)

Kinetic data analysis.

Changes in lipids quality was measured by the appearance or disappearance of quality variables, symbolized by A (AV, AnV, PV and FFA) from the rate equation (Piedrahita et al, 2015) as shown in eqn (4)

$$r_A = -\frac{dA}{dt} = K[A]^m \quad (4)$$

For a zero order Kinetic model, $m=0$. The equation becomes

$$r_A = -\frac{dA}{dt} = K[A]^0 = K$$

For parameters that are increasing or appearing, the negative sign (-) associated with disappearance is replaced with positive sign (+) so that the equation becomes

$$r_A = +\frac{dA}{dt} = K[A]^0 = K$$

$$A_1 - A_0 = Kt \quad (5)$$

A plot of $A_1 - A_0$ against t was performed with Slope, K = rate constant of oxidation of oil and Intercept = 0.

First Order Kinetic Model $\ln\left(\frac{A_1}{A_0}\right) = Kt$ (6).

$\ln(A_1/A_0)$ vs t was plotted. Slope = K = rate constant of first order oxidation, intercept = 0

Second Order Kinetic Model

$$\frac{1}{A_1} - \frac{1}{A_0} = Kt. \quad (7)$$

A plot of $(1/A_1 - 1/A_0)$ vs t was used obtained with slope (K) = 2nd order rate constant and intercept = 0.

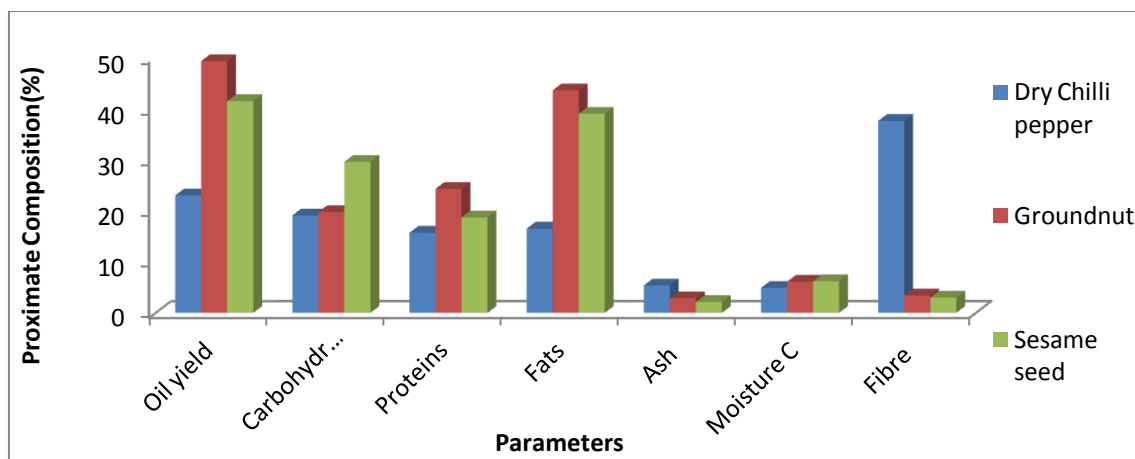
III. RESULT AND DISCUSSION:

Proximate Analysis

The result of proximate analysis of the samples is shown in Table 1. The carbohydrates content was higher in pepper than the sesame seeds and groundnut seeds. Between the sesame and groundnut, values obtained for fats, proteins, ash and fibre contents were higher in groundnut than in sesame seeds as shown in Table 1 and Figure 1. The crude oil content of the groundnut also called peanut was found to be within the range reported by Shad et al (2012) for four varieties of peanuts (45.09 – 51.63%) but higher than that reported by Fasoyiro et al., (2006) and comparable to those reported by Asibu et al., (2008). The moisture content of the powdered pepper was 9.70% as shown in Table 1. which was higher than value reported for powder of hot pepper seeds of 4.48 g/100g (Zou et al, 2015) and Al-Jasass & Al-Jasser (2012), who reported a value of 4.68 and 4.36 g/100 g for black pepper seeds (*Piper nigrum*) and mustard seeds (*Sinapis alba*). Ash content obtained was higher than 4.94g and 4.88g reported by Zou (2015) and Embaby and Mukhtar (2011). Values obtained for crude fat and crude protein contents were lower than 23.65 and 21.29 g/100 g, respectively reported by Zou et al (2015). . These values were also lower than those found by Embaby & Mokhtar (2011), who obtained values of 19.57 and 19.28 g/100 g for hot pepper seeds.

Table 1. Proximate analysis of samples.

Parameters	Capsicum annum (%)	Arachis hypogea (%)	Sesamum indicum (%)
Oil yield (%)	23	49.32	41.48
Carbohydrates	19.1	19.73±0.3	29.6±0.05
Proteins	15.7	24.3±0.06	18.7 ±0.16
Fats	16.5	43.6±	39±0.1
Ash Content	5.38	2.86±0.15	2.13±0.20
Moisture content	4.9	6.1±0.04	6.2±0.24
Fibre Content	37.6	3.4±0.3	2.98±0.3

**Figure 1:** proximate composition profile of the samples.

The differences in ash, crude fat and crude protein contents of various pepper seeds is related to their individual genetic background and environmental factors. Chemical composition of plant is influenced by soil, climate and plant factors (Koyuncu *et al.*, 2014). The same plant species might show different response to uptake of nutrients from the soil even when they were grown in the same conditions (Yildiz *et al.*, 2014; Zou *et al.*, 2015).

The high proximate value of carbohydrates correlates with the results obtained by Shah, 2013 (25.0%) and Nzikou *et al.*, 2009 (23.4%). This value is more than half of the RDA by FAO/WHO of 55%. Thus a diet of sesamum indicum seeds and another food with mild carbohydrate can serve as a good source the daily required carbohydrate intake. The significant values of protein and fats/oil in *Sesamum indicum* seeds are in line with the findings of Anilakumar *et al.*, 2010, (18.3% and 43.3%), Nzikou *et al.*, 2009 (20% and 48.5%) and Dashak *et al.*, 1993 (20.8±0.14% and 34.6±0.11%), respectively. Thus, *Sesamum indicum* seeds are excellent sources of plant proteins, which are in high demand in human and animal nutrition

The proximate profile of the dried capsicum annum used is shown in table 1. The fibre content was highest in the pepper than the oil bearing seeds (sesamum indicum and arachis hypogea). It is also used as a natural flavourant and colorant in food industry (Vinaya *et al.*, 2009) as well as raw material for the pharmaceutical industry. It is mainly cultivated for three constituents of fruits *viz.*, capsaicin, capsanthin and oleoresin (Amusa *et al.*, 2004). Protein (%), Oil yield (%), fats (%), and fiber (%) contents were higher in peanuts than in sesame. Carbohydrates content (%) was however significantly higher in sesamum indicum seed as shown in Table 1. The results should not be generalized as they do not include the seasonal or locality factors. The differences are, however, sufficiently great to enable some general conclusions. Variation in the oil yield (%) may be due to differences in variety of plants, extraction method, the harvesting time of seeds, cultivation climate and ripening stage of seeds (Nzikou, 2009).

Table 2: Physico-chemical characterization of the oils.

Parameter	Arachis Hypogea oil	Sesamum indicum oil
Acid value (mg KOH/kg)	0.71	1.43
Saponification (mg KOH/kg)	184.11	189.81
Peroxide value (meq O ₂ / kg)	1.57	1.73
Iodine value (mg I ₂ /g)	94.23	108.7
Molecular weight (g/mol)	917.67	910.69
Flash point (°C)	318.00	308.00
Fire point (°C)	373.00	370.00
Smoke point (°C)	164	179
Cloud point (°C)	17	16
Pour point (°C)	14.50	12.50

Refractive index @ 29 ⁰ C	1.4645	1.4658
Moisture (%)	0.022	0.026
Density (g/ml)	0.894	0.898
Kinematic viscosity @ 40 ⁰ c (mm ² s ⁻¹)	45.29	41.57

Effect of Storage duration on the Acid Values

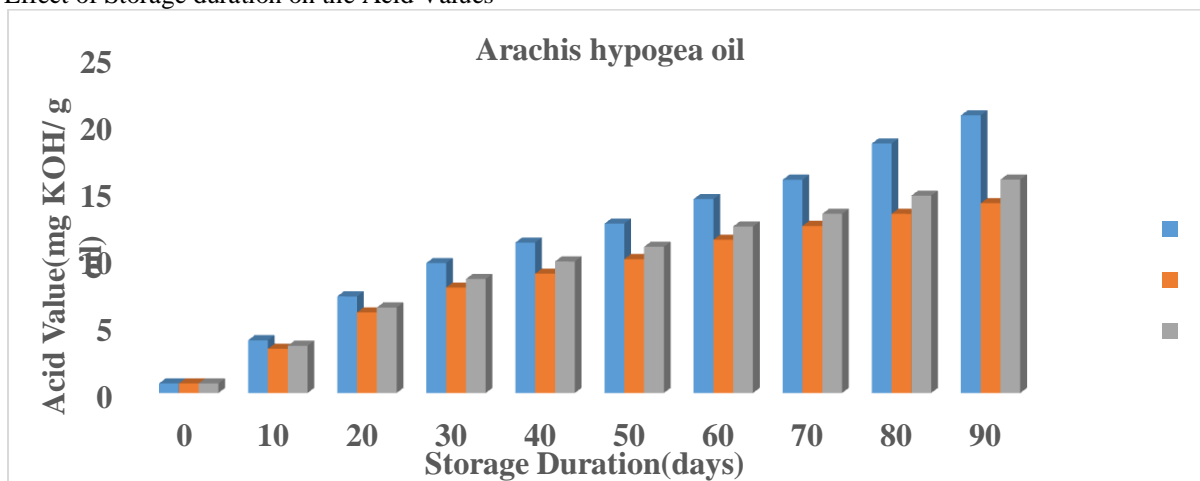


Figure 2: effect of antioxidants an storage duration on acid value of arahis hypogea

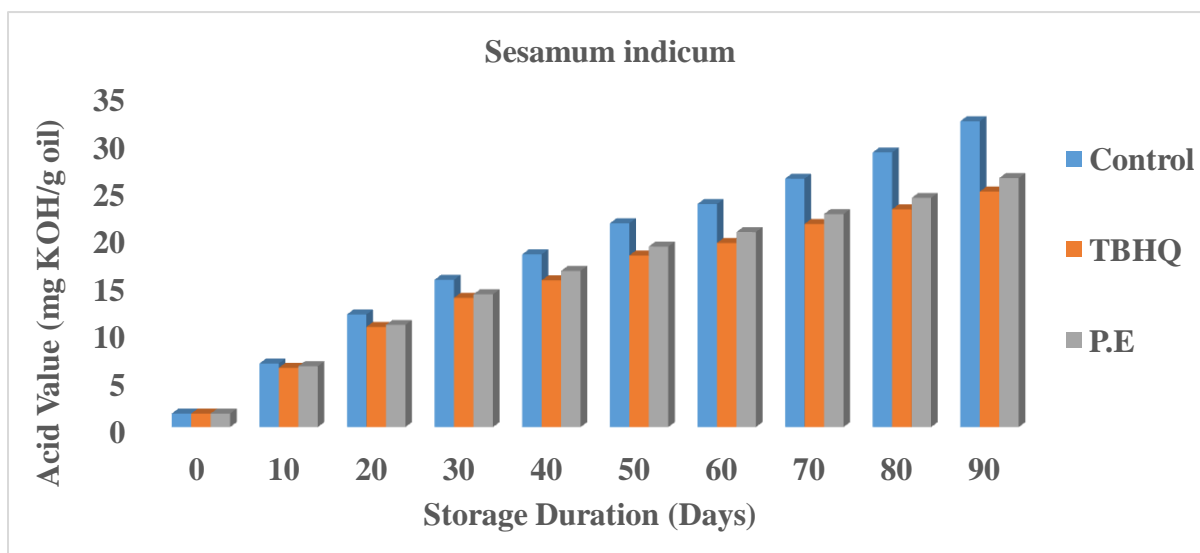


Figure 3: effect of antioxidants and storage duration on the acid value of Sesamum indicum oil.

Figure 2 and 3 shows an increase in the acid value (Av) of the oils with increase in storage duration irrespective of antioxidant type used. Samples without antioxidants (Control) witnessed a highest increase in antioxidants. The A.v indicates the amount of carbonyl compounds, primarily 2-alkenals (Golmakani etal, 2018). The increase in A.v with storage indicates the degradation /deterioration of the oils by hydrolytic scission (Ghosh etal, 2014). As lipids rancidify or undergo oxidative deterioration, triglycerides are converted into fatty acids and glycerol causing an increase in acid number. This means that the higher the acid value, the lower the oil quality, the more the corrosion of machine components, the more the tear and wear, the higher the cost for machines operation, the lower the stability. Lower acid value for the TBHQ fortified samples means effective inhibition of the hydrolytic scission of the C = C bonds implying better/higher quality oil and better resistance to oxidation/spoilage as seen in figures 2 and 3.

Effect of duration on the Storage Stability

Values were not obtained for control since it was the reference point from where other samples with antioxidants were measured as shown in equation (2).

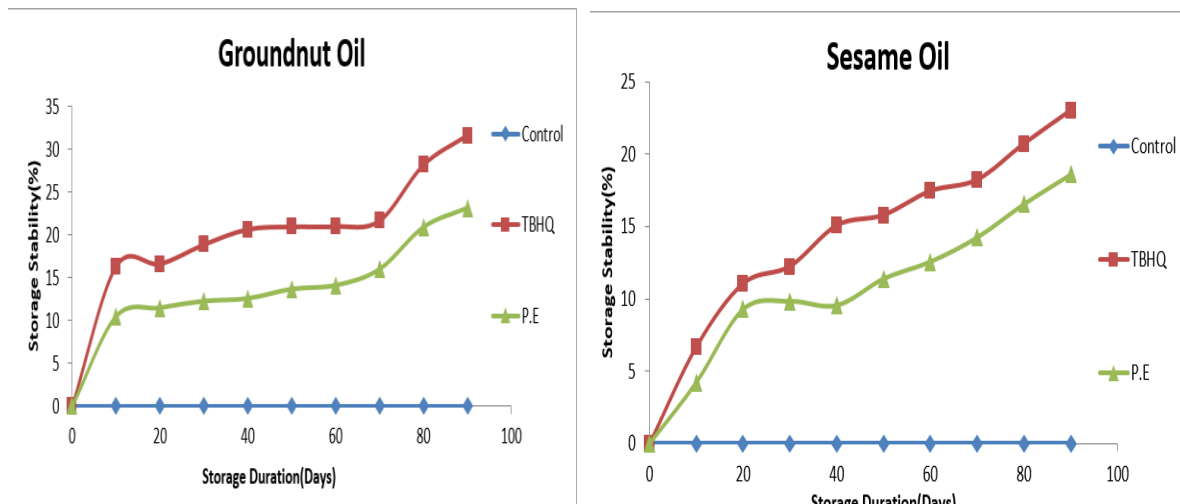


Figure 4 Storage stability of Arachis Hypogaea oil and Sesamum Indicum oil.

Figure 4 shows better resistance to oxidation for oil samples containing TBHQ. However, the difference in stability between TBHQ and pepper samples tended to widen with increase storage duration with the TBHQ showing better resistance. This is due to the ease with which TBHQ, a synthetic antioxidant readily donates hydrogen to scavenge free radicals such as lipid alkyl radicals or lipid peroxy radicals, control transition metals, quench singlet oxygen, and inactivate sensitizers. TBHQ readily donate hydrogen atoms to free radicals and convert them to more stable non-radical products (Decker 2002). The Capsicum extract rich in natural antioxidants shows relative reluctance to donate hydrogen.

Effect of duration on the Storage instability

As expected, samples without antioxidants (Control) suffered more instability as shown in figure 5 with the arachis hypogea (groundnut) more affected than the sesamum indicum (Sesame) oil. This is probably due to the abundance of inherent natural anti-oxidants in sesamum indicum such as Vitamins E, Sesamol, phytosterols, sesaminol and lignans.

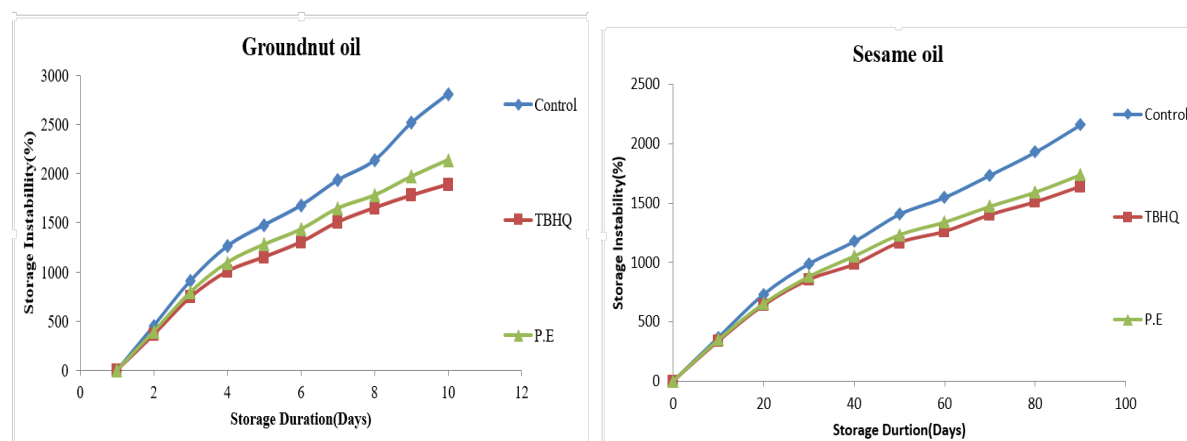


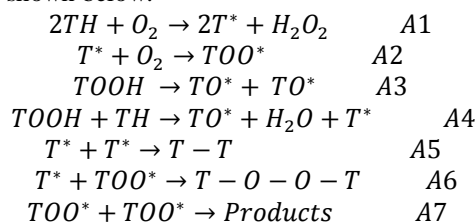
Figure 5: Storage instability of Groundnut oil and Sesame oil

Figure 5 also shows an increase in instability with increase in storage duration. Since antioxidants donate hydrogen to inhibit oxidation of oils, they are being oxidized and hence are reducing agents. A threshold is reached (induction period or end of shelf life) when all the antioxidants get oxidized and the oil begins to deteriorate with the buildup of free radical species. This is why oils without inherent antioxidants such as arachis hypogea showed more readiness to deteriorate with storage duration as seen in their relative instability when compare with sesamum indicum.

Effect of antioxidants:

Samples without antioxidants had higher regression values (R^2) than samples with antioxidants. The presence of antioxidants retarded the oxidation of the oils. The autoxidation by free radical chain is inhibited by either the chain-breaking inhibitors (or antioxidants, DH) or preventive inhibitors (Yanishlieva-Maslarova,

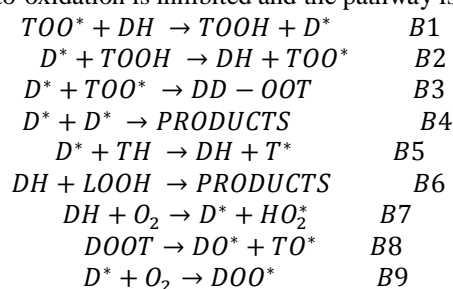
2001; Yanishlieva-Maslarova and Marinova, 2007). When antioxidants are introduced, there is a change in the kinetic process and mechanism as shown below.



Mechanism A: Auto-Oxidation of control (samples without antioxidants)

As shown in Mechanism A, TH is the oxidizing lipid substrate, and TOO^* is the peroxy radical. The hydro peroxides, $TOOH$, which are tasteless and odourless are the primary products of oxidation. They initiate oxidative chains through decomposition to free radicals (A3 and A4). Due to further oxidation and cleavage of the hydro peroxides molecules, low molecular weight products of rancidity such as ketones, aldehydes, acid, alcohols, furans, lactones esters are formed (Yanishlieva and Marinova, 2007).

In the presence of antioxidants, auto-oxidation is inhibited and the pathway is as shown in Mechanism B.



Mechanism B: Inhibited Autoxidation

Introducing the antioxidant, DH, into the oxidizing system changes the mechanism and kinetics of the process (Denisov and Khudyakov, 1987). Comparing this with non-inhibited oxidation process as shown in mechanism 1, the system being oxidized contains no short-lived radicals T^* and the termination proceeds according to A7 (Mechanism A) and/or B1 and B2 (Mechanism B).

As shown in figure 4 the regression R^2 values shows that the sesame indicum oil is more likely to store longer than the arachis hypogea oil. This is due to numerous inherent natural anti-oxidants such as Vitamins E, Sesamol, phytosterols, sesaminol and lignans in sesame indicum oil.

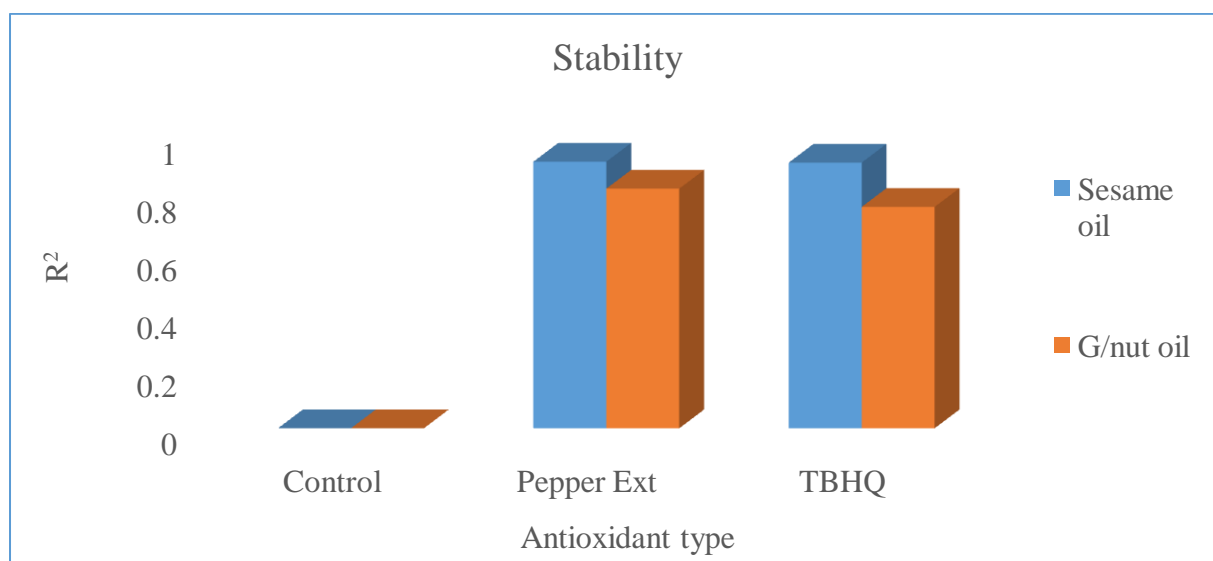


Figure 6: Effect of antioxidant on the rate of oxidative stability w.r.t regression value.

Again, it was observed that samples with capsicum extracts showed better stability during storage than samples with TBHQ. This is probably due to the numerous inherent natural antioxidants in capsicum annum as observed from the regression value. Capsicum annum is rich in antioxidants such as capsanthin, violaxanthin, luteolin, lutein and quercetin.

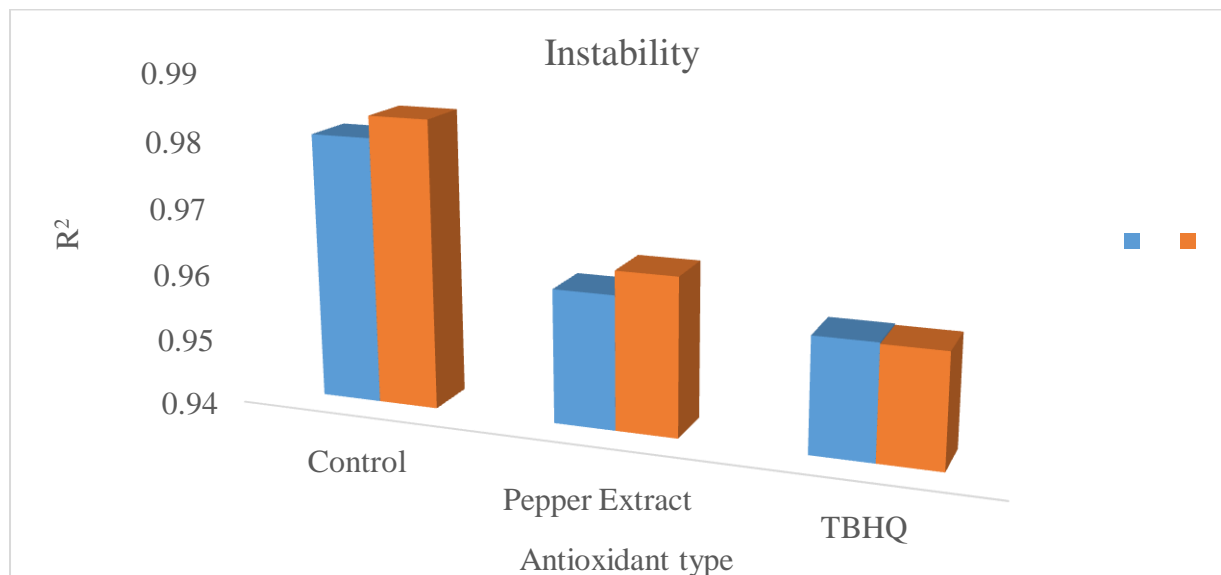


Figure 7: Effect of antioxidant on the rate of oxidative instability w.r.t regression value.

From the instability profile as shown in table 7, higher regression values signifies high rate of instability and value obtained for *Arachis hypogea* using equation (3) showed higher rate of oxidative deterioration (instability) as seen in figure 7. The regression values for samples with TBHQ were smaller than those with *capsicum annuum* (pepper extract) which were in turn smaller than those without antioxidants (control). The order shows the unwillingness to undergo deterioration and hence is the order of stability.

Kinetic Modelling:

Table 3: summary of oxidation kinetics of oil samples.

			R ²	T (k)	Rate constant, K (mol/l s)
Zero order					
	Sesamum indicum oil	Control	0.9802	302	5.98415E-08
		Pepper.ex	0.9602	302	4.81881E-08
		TBHQ	0.9573	302	4.52053E-08
	Arachis Hypogea oil	Control	0.9835	302	3.81243E-08
		Pepper.ex	0.9638	302	2.93264E-08
		TBHQ	0.9571	302	2.62646E-08
First order					
	Sesamum indicum oil	Control	0.7294	302	3.06713E-07
		Pepper.ex	0.7079	302	2.83565E-07
		TBHQ	0.7048	302	2.77778E-07
	Arachis Hypogea oil	Control	0.7198	302	3.26389E-07
		Pepper.ex	0.6996	302	3.00926E-07
		TBHQ	0.6992	302	2.91667E-07
Second order					
	Sesamum indicum oil	Control	0.4062	302	-0.000796651
		Pepper.ex	0.4085	302	-0.000796651
		TBHQ	0.4104	302	-0.000796651
	Arachis Hypogea oil	Control	0.385	302	-0.001586205

	Pepper.ex	0.3937	302	-0.001586205
	TBHQ	0.401	302	-0.001586205

The results of zero – order kinetic model are summarize in table 3. The rate of oxidative deterioration of the oils at room temperature (sesamum indicum oil and arachis hypogea oil) increase with increase in temperature. The zero-order model could fit the data means that the deterioration of the oils which was measured by the increase in Acid values with increasing storage duration is independent of concentration of FFAs in the reactants (oils) (Goksunger, 2011; javidipour et al, 2017). This means that moment oils are extracted, they begin to spoil irrespective of stabilization or antioxidants or storage temperatures involved. Efforts applied can only retard the rate of oxidation. In spite of the higher content of Unsaturated Fatty Acids (UFAs) in Sesame oil, R^2 values were higher in groundnut for the same kind of anti-oxidant used respectively. This means the sesame oil was more resistant to oxidative deterioration which is corroborated by previous works (Manley et al, 1974; Kikugawa et al, 1983). This remarkable stability as shown by the slow progress in the regression equation (R^2) is due to the presence of endogenous anti-oxidants sesamol and sessaminol together with tocopherols (Yoshida, 1994). Values obtained for the rate of deterioration (mol/l s) were higher in sesamum indicum oil samples than in arachis hypogea because of the initial high FFAs content. Unbound fatty acids are more prone to oxidation compared with fatty acids bound to the glycerol molecules. This is reason for the higher K values in sesamum indicum. The results of first order kinetic model for hexanal formation as shown in table 3 means that the rate of formation of FFAs is directly proportional to the concentration of fatty acids in the oils. This also means that the rate depends on only one reactant and is proportional to the amount of the reactant. Again it is also stated as the reaction rate depending solely on first power of single reactant concentration (Javidipour et al, 2017). Lower reaction rate observed for samples with antioxidants means a retarding influence occasioned by the release of hydrogen by the antioxidants to quench and scavenge free radicals generated. The rate of oxidative deterioration was explained by the second order model as shown in Table 3. Using this model means that the rate of formation of FFAs or deterioration of the oils is proportional to the square of the concentration of the fatty acids in the oils. It could also mean that the rate of formation of FFAs is proportional to the product of the concentration of two reactants.

IV. CONCLUSION

The results show that TBHQ and capsicum extract showed good antioxidants activities. Though sesamum indicum is more unsaturated than arachis hypogea oil, its inherent content of more antioxidants such as sesamin, sesaminol and lignans made it more resistant to oxidation at prolong storage duration and ambient conditions. Acid values of the oils increased with increase in storage duration. Control (samples without antioxidants) showed highest storage stability. Storage stability was in the order TBHQ >Capsicum > Control showing that the antioxidants were effective in retarding the rate of oxidation with TBHQ offering better stability.

Declaration of interest

The authors have approved after reading the manuscript and have declared no conflict of interest.

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Ejikeme.P.C.N, et. al. "Effect of storage duration on the acid value stability of sesamum indicum and arachis hypogaea raw oils reinforced with TBHQ and capsicum annuum extracts." *American Journal of Engineering Research (AJER)*, vol. 10(6), 2021, pp. 212-221.