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ENVIRONMENTAL INFLUENCE ON THE OXIDATIVE RANCIDITY OF TROPICAL SOYBEAN OIL IN OGUN STATE NIGERIA

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ABSTRACT

The environmental influence on the oxidative rancidity of tropical soybean oil found in local markets in Ogun state Nigeria has been investigated in aqueous, alkaline, neutral, metal and acid environments and the results shows that the peroxide values measured as $MeqO_2/Kg$ were in the range of 3.48 – 11.82 for the acid environment, 3.24 – 10.94 in alkaline environment, 3.27 – 10.22 in metal environment, 3.16 – 9.86 in aqueous environment and 2.48 – 4.46 in neutral or normal environment. The peroxide value showed significantly high values for the acid environment and closely followed by the alkaline and metal environments. The aqueous environment also showed high values as compared to the neutral or normal environment. The % FFA showed similar profiles in the range of 1.46 – 8.87 for the acid environment, 1.42 – 8.66 in alkaline environment, 1.28 – 6.48 in metal environment, 1.24 – 6.22 in aqueous environment and 1.12 – 2.48 in neutral or normal environment with the acid and alkaline environments showing high values of over 8.7. There was an observed close relationship in the acid and alkaline environments as well as metal and aqueous environments as shown in the plot. The Saponification values measured as mg(KOH)/g of oil also showed similar trend in the range of 194 – 284 for the acid environment, 192 – 285 in alkaline environment, 188 – 278 in metal environment, 186 – 273 in aqueous environment and 182 – 248 in neutral or normal environment. The effect of increasing the temperature on the peroxide value of the oil was also marked. It was shown that as the temperature increased from 30 °C to 120 °C, the peroxide value increased from 3.16 Meq/Kg to 15.22 $MeqO_2/Kg$

KEYWORDS: *environment, metal, acid and alkaline, liquids, oils*

INTRODUCTION

Fats and oils are generally grouped under lipids but whereas fats are usually solids originating from animals, oils are predominantly liquids from plants. However, both are esters of trihydric alcohol (glycerol or propan 1, 2, 3 - triol) with each molecule esterifying three molecules of fatty acid. In which ever form or source, fats and oils are unstable in the environment at room or elevated temperatures as well

as in moist and dry conditions. Lipids containing polyunsaturated fatty acids readily oxidize in the presence of oxygen, making oxidative rancidity one of the most critical factors affecting the shelf-life of foods.

Soybean, commonly misspelled "soya bean" *glycine max* is a specie of legume, native to East Asia. It is classed as an oil seed rather than a pulse. The thermally stable oil is used in a wide range of industrial food processing all over the world (Smith and Circle, 1972). Though soybean oil has relative stability over a range of temperature, such is not true with environments like aqueous, metallic, acid or alkaline. During autoxidation, a number of polar compounds may be produced from the initially formed hydroperoxides, Ranny (1978), Sipoa and Ackman (1978). The content of these polar materials can be determined by thin layer chromatography with a flame-ionization detector (TLC-FID).This is a major problem in the use of fats and oil both for industrial and domestic purposes**.** This major drawback in the use of vegetable oils and fats from animals for industrial activities is the fact that they lack sufficient oxidative stability in their natural forms and therefore posse storage difficulties. The deterioration of fats and oils in the presence of atmospheric oxygen is termed "oxidative rancidity". By definition, the oxidative rancidity of oil is a measure of the length of time taken for oxidative deterioration to commence, (Emmanuel and Mudiakeoghene, 2008**).** On a general level, "the rates of reactions in auto-oxidation schemes are dependent on the hydrocarbon structure, heteroatom concentration, heteroatom speciation, oxygen concentration, and temperature (Ferrari, Oliveira and Scabio, 2004). When left untreated or poorly preserved, oils from vegetable origin oxidize during use as a result of interaction with atmospheric oxygen and polymerize to a plastic like consistency (Honary, 2004). Even when they are not subjected to the intense conditions of industrial applications, fats and oils are liable to oxidative rancidity (Eastman Chemical Company, 2001; Morteza-Semnani, Saeedi and Shahani, 2006). This applies predominantly to fats containing unsaturated fatty acid radicals. Indeed the ability of fats and oil to oxidize is dependent on the level of unsaturation of their olefinic compounds present in them. It has been observed that oxidative rancidity in oils seem to be aggravated by heat, metals or other agents that have the ability to cause unsaturated oil molecules to convert to free radicals. These free radicals can easily undergo oxidation to yield hydroperoxides and organic compounds as bye products, such as aldehydes, ketones, or acids which produce the undesirable odors and flavors observed in rancid fats (Eastman Chemical Company, 2001). It is the presence of the formed peroxides that is exploited in monitoring oxidative deterioration by determining the peroxide values (POV) (Mochida and Nakamura, 2006). The oxidation of fats and oil however occur by the self-induced oxidation or by the catalysis of the enzyme lipoxygenase. Lipoxygenases are metal proteins with the central metal ion as Fe^{2+} forming the active center. These proteins affect the catalysis of oxidation reaction of unsaturated fatty acids to form hydroperoxides. Enzyme activation usually occurs in the presence of hydroperoxides, even though enzyme catalyzed oxidation can occur even in the absence of hydroperoxides (Fennema, 1985). Self-induced or auto oxidation refers to a complex set of reactions resulting in the incorporation of oxygen in the structure of the lipids. Self-induced oxidation reactions have been observed and are found to progress more rapidly in oils that contain predominantly unsaturated fat molecules; other factors that may enhance the deterioration process may include the presence of light, transition metal ions, oxygen pressure, the presence or absence of antioxidants and pro oxidants, temperature and moisture content.

Many analytical procedures exist for measuring oxidative deterioration in fats and oils obtained from food and biological materials. These methods are directly related to the parameter(s) sought in the analysis and they include the determination of oxygen absorbed by oil or fat sample, the loo of initial substrate, the formation of hydroperoxides as the primary oxidation products as well as the formation of secondary oxidation products from the decomposition of the hydroperoxides, Labuza and Dugan, (1971); Pryor and Castle, (1984); Huang, Frankel and German, (1994); Dobarganes and Velasco, (2002); Some of these methods however only determine the total amount of hydroperoxides formed and are chemically, methods which are based on redox reactions while others are based on enzymatic reactions as well as the measurement of some physical properties such as infrared and ultra violet spectroscopy for the detection of functional groups and conjugate dienes, Huang et al; (1994).

Several methods have been advocated for the determination of oxidative rancidity in vegetable oils. A method utilizing thin-layer chromatography with a flame ionization detector (TLC-FID) was developed for assessing the stability of breeder's oil seed samples based on the formation of polar compounds. A method has been devised for the quantitative determination of malonaldehyde in oxidized fish oils by means of the 2-thiobarbituric acid reagent in alcoholic solution, de Koning and Silk, (1963). TBA numbers and peroxide values have been determined at intervals during hydroperoxidation of pilchard oil. The curves follow the same general pattern but the numerical relationship between them depends upon the temperature of oxidation. In alcoholic solution, the reaction between

thiobarbituric acid (TBA) and malonaldehyde is carried out in the dark, because sunlight causes a decrease in optical density of the TBA-malonaldehyde complex at 532 mμ with the appearance of a second maximum at 452 mμ.

MATERIALS AND METHODS

The parameters studied in this work were % free fatty acid, saponification value and peroxide value. About 5.0 Kg of soybean was cleaned, peeled and locally processed to recover the oil. The oil was then dried to a constant weight in the oven. Filtration using a fine filter cloth was carried out to remove impurities. A sample from the recovered oil was taken and in situ values of the % free fatty acid, saponification value and peroxide value were determined before the oil was divided into 5 and placed into different beakers. The acid environment was prepared by placing 0.50 ml of 1.0 M HCl in a beaker and transferring 50.0ml of the filtered oil sample into it. Basic environment was also prepared by placing 0.50 ml of 1.0 M NaOH in a beaker and transferring 50 ml of the filtered oil into the beaker. Aqueous environment was prepared by replacing the volume of acid or alkaline with water whereas the metal environment was prepared by placing 0.5 g of iron fillings in a beaker containing 50 ml of the dry oil. The neutral environment served as the control. The 5 beakers are allowed to stand on a shelf under atmospheric conditions and samples were drawn from each beaker after every day and the % free fatty acid, saponification value and peroxide value determined for 45 days on 5 day intervals. The peroxide values at varying temperatures were also determined

RESULTS

The environmental influence on the oxidative rancidity of tropical soybean oil found in local markets in Ogun state Nigeria has been investigated in aqueous, alkaline, neutral, metal and acid environments for 45 days and the results are as shown.

Environment	Day 5	Day 10	Day 15	Day 20	Day 25	Day 30	Day 35	Day 40	Day 45
Aqueous	3.16	3.48	3.86	4.57	5.84	6.86	7.54	8.62	9.86
Alkaline	3.24	4.65	5.56	6.42	7.64	8.46	9.24	10.22	10.94
Neutral	2.48	2.64	2.86	3.24	3.47	3.69	3.86	4.28	4.46
Metal	3.27	4.38	5.26	6.12	7.25	7.96	8.46	9.88	10.22
Acid	3.48	4.88	5.64	6.55	7.84	8.69	9.58	10.48	11.82

Table 1: Peroxide Values of the soybean oil sample over ten days in different environments

Environment	Day 5	Day10	Day 15	Day 20	Day 25	Day 30	Day 35	Day 40	Day 45
Aqueous	1.24	1.68	2.24	2.86	3.64	4.28	4.86	5.34	6.22
Alkaline	1.42	1.74	2.68	3.86	4.68	5.84	6.48	7.64	8.66
Neutral	1.12	1.36	1.48	1.57	1.68	1.85	1.98	2.24	2.48
Metal	1.28	1.74	2.44	2.98	3.76	4.42	4.98	5.46	6.48
Acid	1.46	1.88	2.86	3.98	4.87	5.98	6.68	7.84	8.87

Table 2: % Free Fatty Acid Values of the soybean oil sample over ten days in different environments

Environment	Day 5	Day 10	Day 15	Day 20	Day 25	Day 30	Day 35	Day 40	Day 45
Aqueous	186	191	198	208	219	232	247	254	273
Alkaline	192	199	208	219	231	243	257	273	285
Neutral	182	185	190	196	204	215	227	236	248
Metal	188	194	202	213	227	242	258	269	278
Acid	194	201	208	216	225	234	245	259	284

Table 3: Saponification Values of the soybean oil sample over ten days in different environments

Peroxide Value ($MeqO_2/Kg$)

Temp.	30°C	40°C	50°C	60°C	70°C	80°C	90°C	100°C	110°C	120°C
Per. Val.	3.16	3.45	4.26	4.65	5.64	6.86	7.36	8.13	9.65	15.22

Table 4: Peroxide Values of the soybean oil sample monitored at different temperature ranges

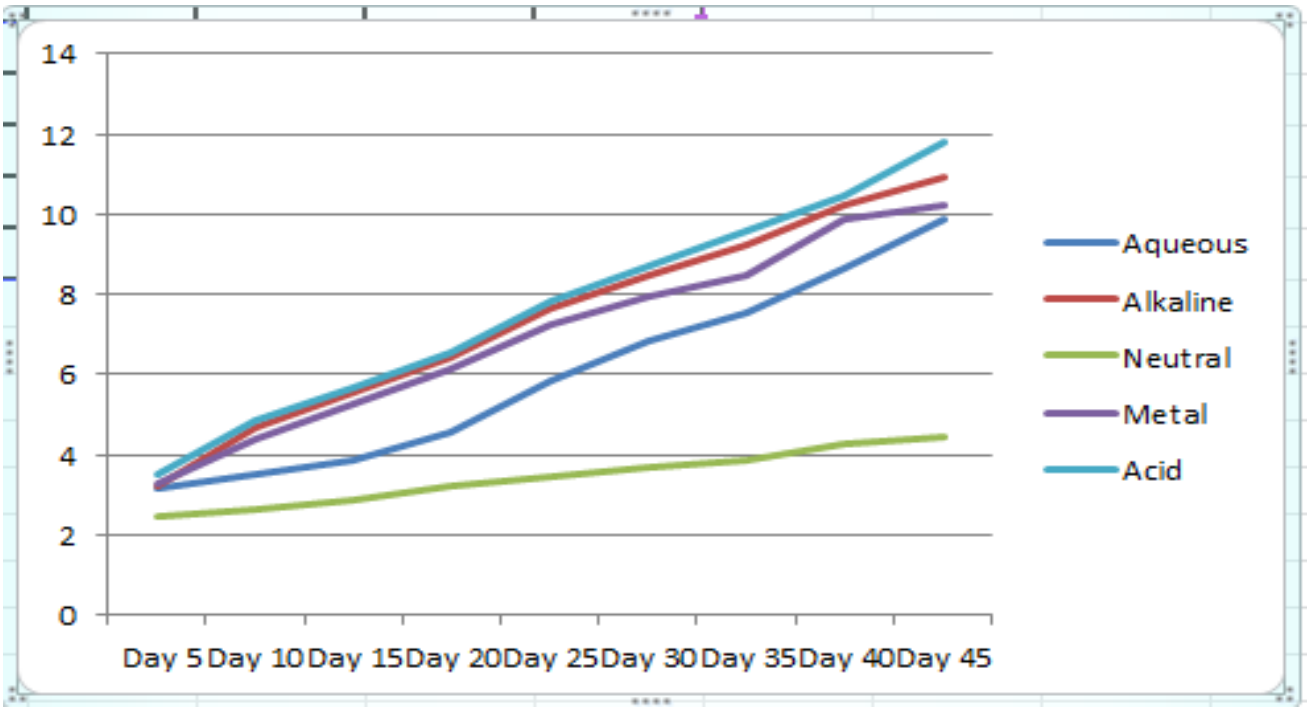

Figure 1: Plot of the Peroxide Value of the soybean oil sample over ten days in different environments

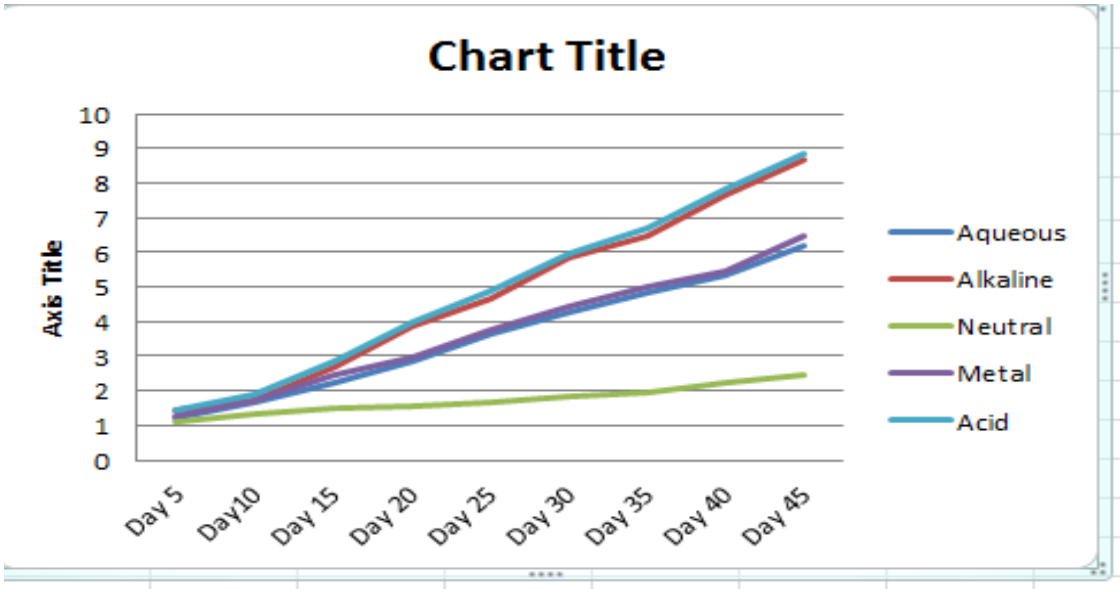

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Figure 2: Plot of the % FFA of the soybean oil sample over ten days in different environments

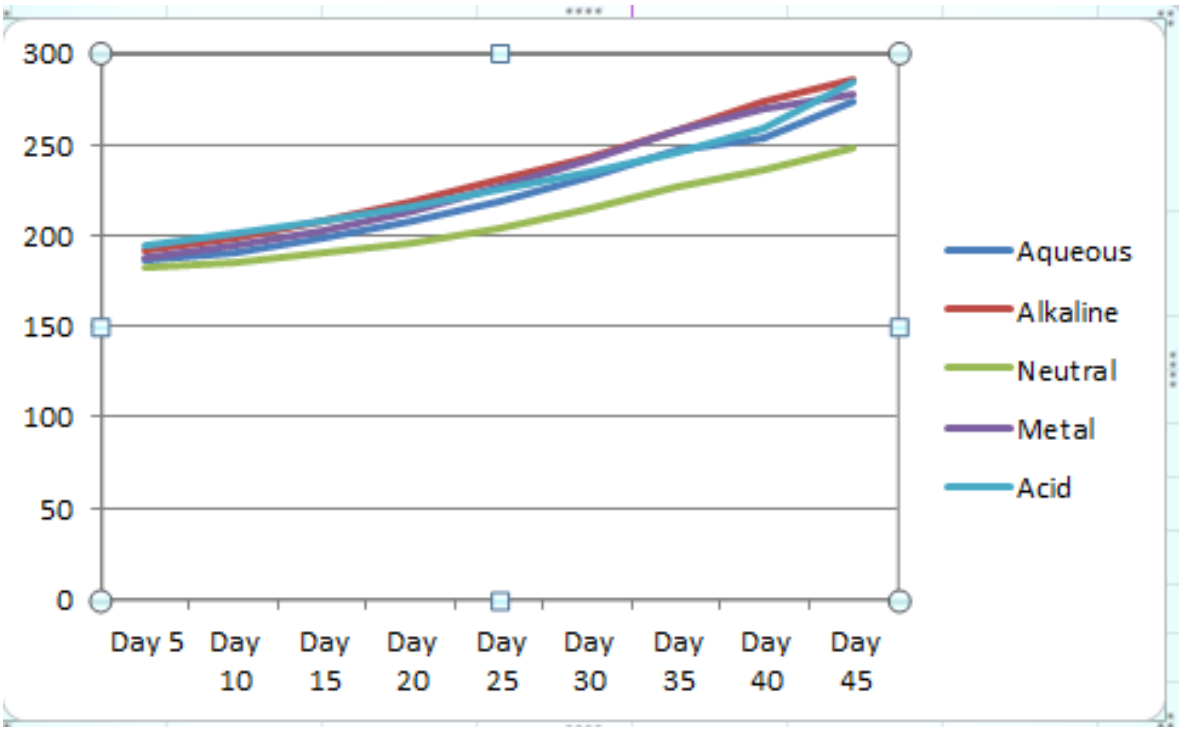

Figure 3: Plot of the Saponification Values of the soybean oil sample over ten days in different environments

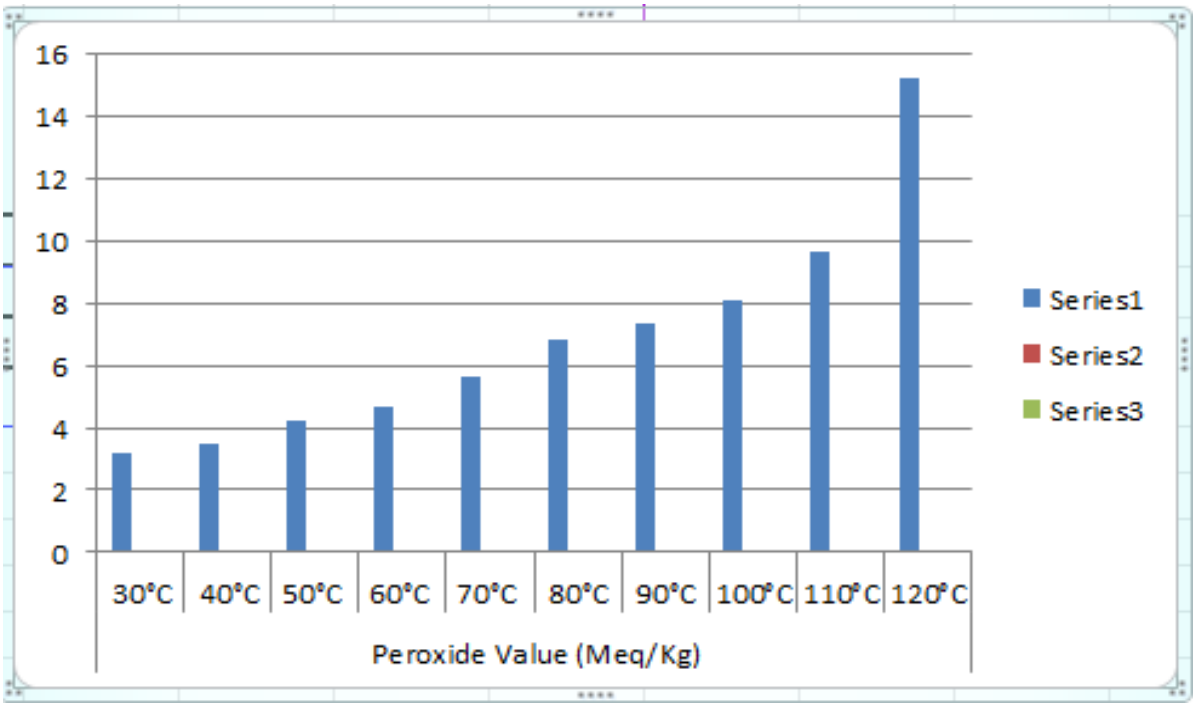

Figure 4. A histogram showing the effect of increasing temperature on the peroxide value of crude soybean oil.

DISCUSSION

The values of the peroxide values, % free fatty acids and saponification values of the plotted against the respective environments over the period of study and the following charts were obtained. The peroxide value showed significantly high values for the acid environment and closely followed by the alkaline and metal environments as in Fig. 1. The aqueous environment also showed high values as compared to the neutral or normal environment. The % FFA showed similar profiles with the acid and alkaline environments showing high values of over 8.6 as in Fig: 2. Metal and aqueous environments showed between 6.22 to 6.48 as compared to the neutral environment. However the saponification value showed a slow increase according to the same rate. There was an observed close relationship in the acid and alkaline environments and metal and aqueous environments as shown in the plot. The Saponification values also showed similar trend as shown in Fig. 3 with the acid environment highest and the neutral environment lowest. Fig. 4 showed the effect of increasing the temperature on the peroxide value of the oil. It was shown that as the temperature increased from 30 °C to 120 °C, the peroxide value increased from 3.16 Meq/Kg to 15.22 Meq/Kg. These values all show that the environments monitored can induce oxidation reaction the can accelerate the rancidity of soya bean oil and so can serve as a guide for its preservation.

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