Research Article

Chemical Changes in Crude Palm-Oil and Refined Palm Kernel-Oil Employed in Deep-Frying

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Abstract Crude palm oil and refined palm kernel oil samples were used in the frying of plantain and were compared to same oil samples ordinarily heated without frying, these served as control. The chemical analyses covered free fatty acid, peroxide, anisidine, iodine and saponification values. These values measure the extent of the oil degradation, i.e oxidation, hydrolysis, splitting and polymerization. From the results, there is no noticeable change between the free fatty acid values of oil samples used for frying and the oil samples used as control. The much higher values of peroxide formation in refined palm kernel oil used as control compared to crude palm oil used as control may be due to the presence of some natural antioxidants in crude palm oil used as control. It is plausible to suggest that the higher rise in the anisidine values of oil samples used as control compared to those of oil samples used for frying is due to the absorption, by the fried plantain, of parts of the products of secondary oxidation formed in the oil samples used for frying. The data obtained for the iodine value of all the oil samples fall within the acceptable range for the respective oils. The saponification value of refined palm kernel oil sample used for frying decreases while that of refined palm kernel oil used as control decreases at the first instance then increases steadily. The data collected show the suitability of these two oil samples for frying purposes and indicate that, in terms of chemical composition, refined palm kernel oil (RPKO) performs more satisfactorily as frying oil, because it has higher oxidative stability than crude palm oil (CPO).

Keywords anisidine, iodine, saponification, oxidation, hydrolysis, and polymerization.

Introduction

Fats are chemically defined as esters of long chain fatty acids with glycerol. Crude palm oil is deep orange in colour and has a characteristic odour which has been described as "sweetish" and somewhat "nutty". It is solid at ambient temperatures in a temperate climate. At tropical temperatures, it is a liquid with certain fractions held in crystalline form. Refined palm kernel oil is light yellow in colour or nearly colourless. It belongs to the group of oils classified as lauric oils. Other members of the group include coconut oil with which it is readily interchangeable. It is solid at ambient temperatures in temperate countries, but it is liquid at tropical temperatures. Fats undergo oxidation by atmospheric oxygen. The result of prolonged oxidation is deterioration accompanied by loss of appeal and acceptable flavour. Many investigators have studied the mechanism of the reactions involved in the oxidation of fats and oils while others have sought for methods of evaluating deterioration in vegetable fats and oils [1-4]. None of these methods has been able to proffer solution to these problems. During cooking or frying, palm oil is always heated in air during which hydrolysis and oxidation take place. Hydrolysis result in the formation of free fatty acids, while oxidation leads to formation of hydroperoxides, epoxides, peroxides, hydroxides and carbonyls- which subsequently may undergo fission into smaller fragments [1]. Palm oil is used repeatedly for frying. This repeated use is probably dictated by economic consideration.

During deep frying, the fat is exposed continuously or repeatedly to elevated temperatures in the presence of air and moisture. A number of chemical reactions, including oxidation and hydrolysis, occur during this time as do changes due to thermal decomposition. As these reactions proceed, the functional, sensory and nutritional qualities of the fat

change and may eventually, reach a point where it is no longer possible to prepare high quality fried products and the frying fat will be discarded. This thermal degradation should be controlled, not only for technological reasons, but also for safety and nutrition [5].

The popularity of deep-fried products is due in part to the basic structure imposed on them by the way in which they are cooked. In deep frying, the food is totally immersed in the hot fat with the fat acting as the medium of heat transfer. Cooking in this way is more efficient than the dry heat of an oven and more rapid than boiling in water since the higher temperatures possible with deep frying result in more rapid penetration of heat into the product being cooked. The result of deep frying is a food with a distinctive structure [6].

It is important to the food industry, household and food regulatory agencies to have simple and objective methods for quality evaluation of used frying oil. A significant economic advantage can be gained from the ability to determine the appropriate point at which a frying oil is no longer suitable for use. In addition such methods, on the one hand, would provide information regarding the safety and nutritional quality of their final products. On the other hand, regulatory authorities are interested in methodology to enforce proper usage of frying fats [7].

The objective of this work was to assess the chemical changes in crude palm oil and refined palm kernel oil on extended deep frying, by frying batches of plantain and monitoring the changes in certain parameters of the oils namely free fatty acids, peroxide, anisidine and saponification values.

Materials and Methods

The crude palm oil and the refined palm kernel oil used for this work were purchased from Okitipupa oil palm industry, Okitipupa and Igele market in Ondo town respectively. Both oils were analysed for their initial free fatty acid (FFA), peroxide, anisidine, iodine and saponification values.

Aluminium pots were used for the frying. Ripe plantains used were bought from Igele market, and their initial moisture content taken before frying. Frying was carried out at 150 for 35 minutes in two pots, one containing the crude palm oil and the other containing the refined palm kernel oil of equal volume (2 L). The same oils were put into two separate pots, of equal size with the first set of pots, and heated ordinarily without frying, under the same conditions to serve as control.

After frying or heating for 35 minutes at 150 °C, the oil sample was taken and allowed to cool to room temperature, before analysis. In this study, the manner in which the samples were taken and the time elapsing before analysis was the same for all samples.

Analytical grade reagents were collected from the Chemistry Laboratory, Adeyemi College of Education, Ondo and duly purified before use. The A.O.A.C standard methods [8] were used to determine all the parameters in triplicates.
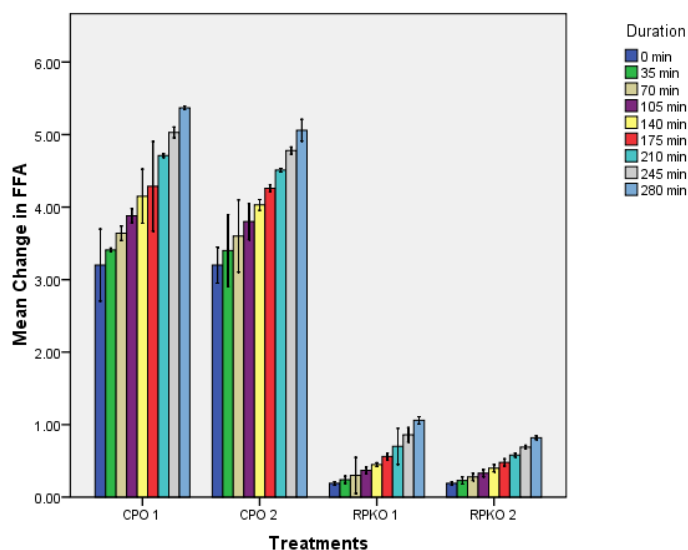
Results and Discussion

Figure 1: Mean Change in FFA.

Where: CPO 1 represents crude palm oil sample used for frying; CPO 2 represents crude palm oil sample used as control; RPKO1 represents refined palm kernel oil sample used for frying; RPKO 2 represents refined palm kernel oil sample used as control.

Moisture content
The average moisture content of the plantains used was found to be 79.09 %.

Free fatty acids
This measures the amount of free fatty acid present in the fat and is therefore a measure of the degree of hydrolysis of triglycerides.

As can be seen in Fig. 1, there is a negligible increase in free fatty acid values of all the oil samples analyzed.

Deterioration of a fat leads to the liberation of free fatty acids (FFA) from triglycerides. The amount of free fatty acid (FFA) in a fat or oil is indicative of its level of spoilage. When oil sample is heated, there may be an increase in free fatty acids depending upon the temperature. Okiy and Oke [1] studied the chemical changes in palm oil at the early stages of heating and found that there was no change in free fatty acids of palm oil heated at $150^{O}C$. These results are similar to those of Egan et al [9] who reported that FFA/acid value is a measure of the extent to which the glycerides in the oil have been decomposed by lipase or other action and that decomposition is accelerated by heat and light. The results of FFA determination in Figure 1 is in agreement with those of Ekpa and Ekpe [10] who reported that oil samples exposed to normal room conditions (room temperature, $28^{O}C$) were observed to have higher FFA values than the corresponding unexposed samples.

From the results, there is no noticeable change between the free fatty acid values of oil samples used for frying and the oil samples used as control.

Peroxide Value
This represents a quality assessment measuring the extent of primary oxidative deterioration in fats and oils.
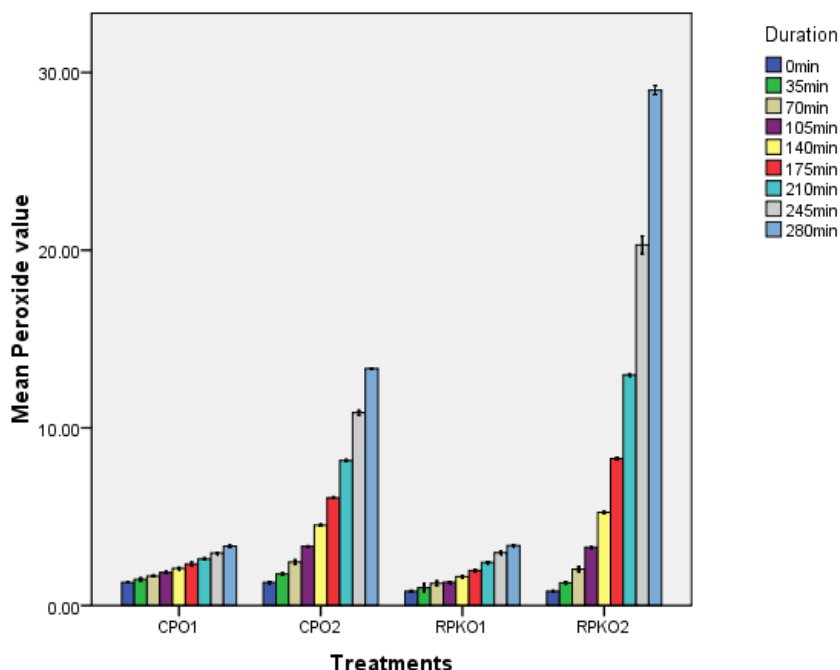

Figure 2: Changes in Peroxide value

Where: CPO 1 represents crude palm oil sample used for frying; CPO 2 represents crude palm oil sample used as control; RPKO1 represents refined palm kernel oil sample used for frying; RPKO 2 represents refined palm kernel oil sample used as control.

Figure 2 shows changes in peroxide value of oil samples analyzed. The peroxide value increases steadily in oil samples used as control, while in oil samples used for frying, it increases slightly as shown in Table 2.

Experimental findings reported by Holman [2] have shown that there is increase in peroxide formation when palm oil sample is heated, but that the rate of formation depends on the temperature. At low temperatures, more peroxides are formed than at high temperatures because high temperatures promote rapid breakdown of peroxides. The spoilage of fats and oils during storage is called rancidity and is associated with the production of foul odours [11].

The result recorded for the PV of oil samples is similar to those of Egan et al [9] who reported fresh oils usually have low peroxide values. A rancid taste often begins to be noticeable when the peroxide value is low.

Metallic impurities particularly iron and copper, are pro-oxidants and are undesirable.

They accelerate the rate of peroxide formation in the oil [12], while the presence of natural antioxidants for example tocopherols, or synthetic anti-oxidants inhibit the formation of peroxides [9].

Peroxide value determines the degree of oxidation of the oil. The peroxide value alone is unreliable because it cannot measure products of secondary oxidation. Anisidine value and carbonyl value are commonly in use [12]. By itself, however peroxide is not very useful as a guide because it is readily destroyed by heat. Peroxide must be measured in conjunction with *p*-anisidine value, the latter increases when peroxides decompose [13].

The higher rise in the peroxide formation of oil samples used as control compared to the peroxide formation of oil samples used for frying may be attributed to the absorption of part of the peroxide formed, by the fried plantain. The much higher values of peroxide formation in RPKO 2 vs CPO 2 may be due to the presence of some natural antioxidants in CPO 2.

Anisidine value

This is a quality assessment measuring the extent of secondary oxidative deterioration of the oils. Baldheads, particularly α, β-unsaturated baldheads are estimated by spectrophotometer measurement at 350nm after reaction with *p*-anisidine.
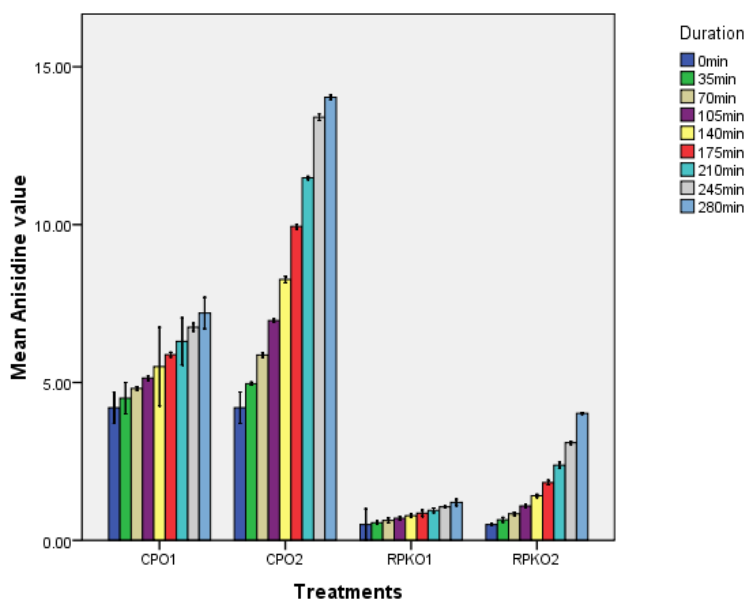

Figure 3: Changes in Anisidine value

Where: CPO 1 represents crude palm oil sample used for frying

CPO 2 represents crude palm oil sample used as control

RPKO1 represents refined palm kernel oil sample used for frying.

RPKO 2 represents refined palm kernel oil sample used as control.

Figure 3 shows a steady increase in the anisidine values of the oil samples analyzed. From the results it is shown that the rise in the anisidine values of the oil samples used as control is more than those of oil samples used for frying.

The steady increase in the anisidine values of the oil samples corroborates the work of Okiy and Oke [1]. It further confirms that the higher the peroxide value the lower the anisidine value and vice versa.

It is plausible to suggest that the higher rise in the anisidine values of oil sample used as control compared to those of oil samples used for frying is due to the absorption, by the fried plantain, of parts of the products of secondary oxidation formed in the oil samples used for frying.

Iodine Value

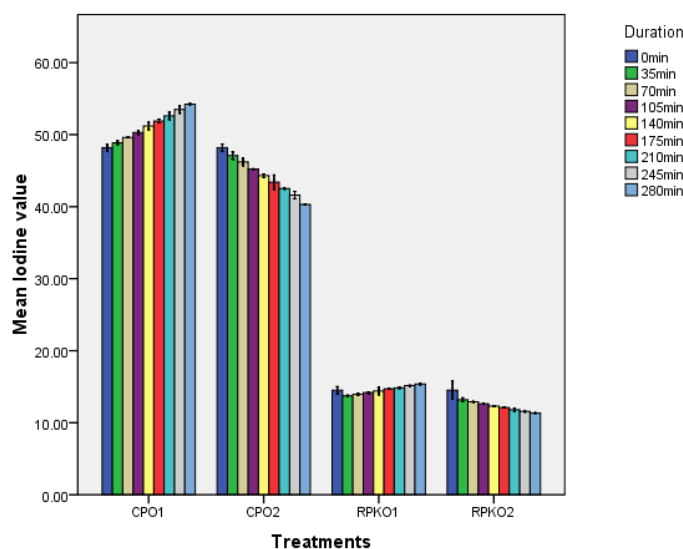This is a measure of degree of unsaturation in fats and oils.

Figure 4: Changes in Iodine value

Where: CPO 1 represents crude palm oil sample used for frying; CPO 2 represents crude palm oil sample used as control; RPKO1 represents refined palm kernel oil sample used for frying; RPKO 2 represents refined palm kernel oil sample used as control.

Oil samples were observed to solidify at room temperature. This is in accordance with Egan *et al* [9] who reported that for natural oils and fats the less unsaturated fats with low iodine values are solid at room temperature or conversely, oils that are more highly unsaturated are liquids (showing there is a relationship between melting points and iodine values (IV)). In general, the greater the degree of unsaturation (high IV), the more readily the oil or fat becomes rancid.

Most vegetable oils are predominantly unsaturated and have high iodine value whereas animal fats tend to be predominantly saturated and show low iodine values [9].

The data obtained for the iodine value of all the oil samples fall within the acceptable range for the respective oils. Therefore there is no significant change in the iodine value of the oil samples during the frying period.
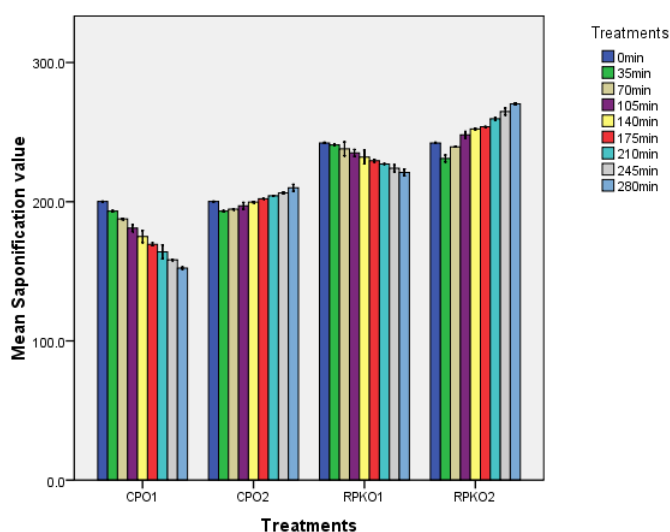
Saponification value

Figure 5: Changes in Saponification value

Where: CPO 1 represents crude palm oil sample used for frying; CPO 2 represents crude palm oil sample used as control; RPKO1 represents refined palm kernel oil sample used for frying; RPKO 2 represents refined palm kernel oil sample used as control.

The saponification value of an oil or fat denotes the weight of potassium hydroxide, expressed in milligramme, required to saponify one gramme of the oil or fat.

Figure 5 shows that the saponification value of crude palm oil sample used for frying decreases and falls out of range, while the saponification value of crude palm oil sample used as control decreases at the first instance then increases steadily.

The saponification value of refined palm kernel oil sample used for frying decreases while that of refined palm kernel oil used as control decreases at the first instance then increases steadily.

Since hydrolysis depletes esters, this accounts for why there is a decrease in the saponification value of oil samples used for frying.

Total oxidation value

Since neither determination of peroxide value nor anisidine value can independently adequately describe the state of oxidative deterioration of an oil, their combined effect is assessed by calculating the total oxidation value. The total oxidation value is calculated from the expression below:

TOTOX = twice peroxide value + anisidine value [14].

Figure 6 shows that the oxidation value for oil samples used as control is higher than those of oil samples used for frying. It is also shown in the table that the oxidation value of CPO 1 is higher than the oxidation value of RPKO 1.
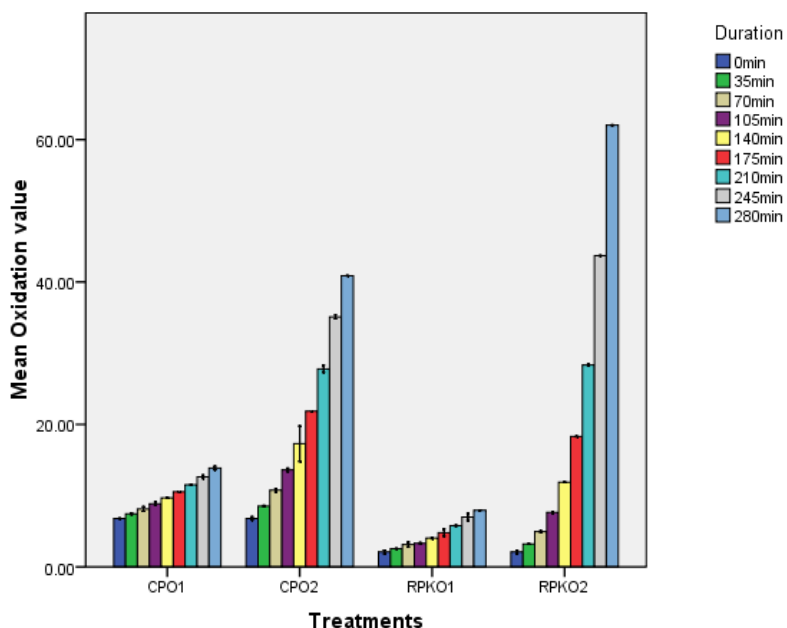

Figure 6: Total Oxidation value.

Where: CPO 1 represents crude palm oil sample used for frying; CPO 2 represents crude palm oil sample used as control; RPKO1 represents refined palm kernel oil sample used for frying; RPKO 2 represents refined palm kernel oil sample used as control.

The reverse trend is observed for oil samples used as control. This implies that in terms of oxidative stability, refined palm kernel oil is more preferable for frying than crude palm oil.

Conclusion

The primary and secondary oxidations lead to the formation of peroxides and carbonyl compounds respectively. The formation of these products of secondary oxidation is temperature dependent. Peroxide values alone are generally not used to measure frying oil deterioration.

In this study, the data collected show the suitability of these two oil samples for frying purposes and indicate that, in terms of chemical composition, refined palm kernel oil performs more satisfactorily as frying oil, because it has higher oxidative stability than crude palm oil.

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