International Journal of Science and Research (IJSR)
ISSN (Online): 2319-7064
Index Copernicus Value (2015): 78.96 | Impact Factor (2015): 6.391

Re-Cycling of Cooking Oils and the Effect on the Quality and Stability

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Abstract: ***The quality and stability of industrially processed Palm (Korie & Safi) and Sunflower (Sundrop) oils as affected by repeated heating and cooling processes (re-cycling) were investigated. The oils were subjected to different cycles of heating and cooling and the variation in the stability and quality was determined after different numbers of cycles. The samples were analyzed for physicochemical properties in terms of acid value (AVs), free fatty acids (FFAs) and peroxide value (PVs) by titration method. Repeated heating and cooling showed pronounced increased values in peroxide values while the Acid value (AV) and Free Fatty Acids (FFAs) increased slightly. Relatively, higher range of PVs variations were detected in Safi oil that in which the highest levels went above the acceptable limit of 10meq/kg as set by the Tanzania Bureau of Standards (TBS). Among the three brands of oil tested, Sundrop stood to be the most stable after several cycles of heating and cooling processes, thus recommended for food frying over the other two oils. This study recommends more precautions in food frying processes to avoid the health effects due to formed auto oxidative compounds.***

Keywords: Acid value, free fatty acids, peroxide value, *Sundrop*, *Korie* , *Safi*, and oil stability

1. Introduction

The physicochemical changes taking place at the high temperature in the frying process and the compounds formed in deteriorated frying oil have been extensively studied showing that deep frying tends to increase the foaming, colour, viscosity, density, amount of polymeric and polar compounds and free fatty acid content of frying oil (Andrikopoulos *et al.* 2002). The oil absorbed in foods tends to accumulate on the surface of fried food during frying eventually moves into the interior of foods during cooling (Moreira *et al* 1997). Frying time, food surface area, moisture content of food, types of breading or battering materials, and frying oil influence the amount of absorbed oil to foods (Moreira *et al*, 1997 and Choe *et al*, 1993). Intermittent frying with a lower turnover rate and higher temperature accelerates the oxidation and polymerization of oil during deep-fat frying (Choe & Min, 2007). The hydrolysis, oxidation and polymerization of oil are the common chemical reactions in frying oil which produce volatile and nonvolatile compounds. Most of volatile compounds evaporate in the atmosphere with steam and the remaining non volatile compounds in oil undergo further chemical reactions or are absorbed in fried foods. Non-volatile compounds affect flavor stability and quality and texture of fried foods during storage. Deep-fat frying decreases the unsaturated fatty acids of oil and increases foaming, color, viscosity, density, specific heat, and contents of free fatty acids, polar materials, and polymeric compounds. Oils with high degree of unsaturation are highly susceptible to auto oxidation giving rise to oxidative rancidity due to peroxide formation (Kaleem *et al*, 2015). Different oils are known to support growth of fungi and bacteria especially when it contains moisture. Under unfavourable conditions lipolytic enzymes of oils are active and produce free fatty acids (FFAs) of less than 2% (Adams & Moss, 1999). Different micro organisms survive in oils producing heat resistant spores that enable them to survive in anaerobic conditions. These microbes are responsible for a number of problems associated with consumption of rancid oil like cancer due to formation aflatoxins, food poisoning, bacteremia and endocarditis (Okechalu, *et al*, 2011). The free fatty acids (FFA) released during the rancidity process can smell unpleasant and allow free radical to form in the human diet, harming body cells and increase the risk of generating diseases such as cancer, diabetes, alzheimer's diseases and atherosclerosis, and thickening of artery walls due to build up of fatty materials (Okechalu, *et al*, 2011). Acid value is also explained as a measure of the extent to which glycerides in the cooking oil are decomposed by lipase enzyme (hydrolytic rancidity) or by the action of heat or light which is accompanied by the formation of free fatty acid (Pearson, *et al,* 1981). Studies show that different foods fried under the similar conditions result to different values of AV, PV and FFAs in the oil (Diop *et al*, 2014).

In most parts of the world especially for the young generations eating of deep fried foods is very common basically due to enhanced palatability of the foods. Many studies have been reported on the effect of heat on the oil used in frying the foods including the changes that may be contributed by the fried foods. The aim of the current study was to determine the value of indicators of rancidity; acid value, free fatty acids and peroxide value for oils subjected to repeated heating cooling cycles and hence evaluate the effect on the oils alone.

2. Materials and Methods

2.1 Oil Samples

Two brands (SAFI and KORIE) of industrially processed and refined palm oil (*Elaeis guineensis*) and one brand (SUNDROP) of sunflower (*Helianthus annuus*) oils were purchased from the local market at Kariakoo, Dar es Salaam. The samples were transported to the Dar es Salaam Institute of Technology (DIT) Chemistry laboratory for analysis. Analytical grade reagents were used. All glassware were cleaned with liquid soap, rinsed with distilled water and then dried before use.

2.2 Experimental Set up

Three groups of samples were collected from the three brands of oil that is *Safi, Korie* and *Sundrop*. Group A contained samples of fresh oil collected from the bulk samples before heating, group B samples collected and analyzed after one heating to boiling for ten minutes then cooled, group C contained samples of oils taken after two cycles of heating to boiling and held for ten minutes then cooled. Group D contained samples taken after prolonged boiling for about 20minutes and then cooled. The duration of the experiment took seven days and managed to collect 21 samples. In each case 50ml samples were collected for analysis. Samples were drawn once from each container for four consecutive experimental days at the specific time of the day. In each case the samples were analyzed for Acid Value (AV), Free Fatty Acids (FFA) and Peroxide Value (PV).

2.3 Sample Analyses

Determination of acid value (AV) and Free Fatty Acids (FFA) were determined by titration as follows: A 5g of the vegetable oil sample was neutralized with 100ml of ethanol and then boiled for about five minutes. This was followed by addition of phenolphthalein indicator and the solution titrated while hot against standard aqueous sodium hydroxide to neutral point (faint pink). The Acid Value (AV) was calculated as

$$AV = 56.1VM/m$$

Where: V = volume in ml of standard sodium hydroxide solution used; M= molarity of standard sodium hydroxide (NaOH) solution; *m* = mass in g of vegetable oil sample. The free fatty acid (FFA) is equivalent to half of the Acid Value. 4g of the oil sample *was* weighed into dry 250ml stopper conical flask, A 10 ml of chloroform was added and the sample *was* dissolved by swirling. 15ml of acetic acid was added and 1ml of fresh saturated aqueous potassium iodide solution was added, swirled for one minute and placed the flask in the dark place for 5 minutes. This was followed by 75 ml of distilled water and 1% of starch indicator. The mixture was titrated with 0.1M sodium thiosulphate solution with constant and vigorous shaking until the yellow colour almost disappeared.

Calculation of peroxide value (PV) = $1000VM/m$
Where;
V = volume in ml of sodium thiosulphate solution used, M= morality of sodium thiosulphate solution, m = mass in g of vegetable oil sample.

2.4 Data Analysis

The mean values of acid value (AV), free fatty acid (FFA) and peroxide value (PV) were calculated and compared by bar charts. The magnitude of oil deterioration was considered to be indicated by the amount of AV, FFA and PV values. The maximum values were also compared to the acceptable values of the tested physical parameters as given by the Tanzania Bureau of Standard (TBS), World Health Organization (WHO) and Food and Agricultural Organization (FAO).

3. Results and Discussion

3.1. Acid value (AVs)

The acid value (AVs) of the oils increased with the number of heating-cooling cycles (Figure 1). *Sundrop* oil showed a slight increase in acid value compared to other oils ranging from 0.45-0.52(r=0.07). On the other hand AVs in *Safi* and *Korie* oils were in the range of 0.1-0.45(r=0.35) and 0.56 - 1.6(r=1.04), respectively. This indicates that *Sundrop* oil is more stable to re-heating cycles than other oils and hence can be preferred over the others.

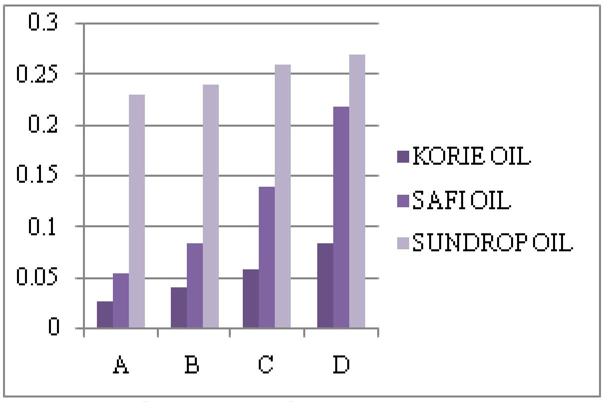

Figure 1: Variation of acid values in *Korie*, *Safi* and *Sundrop* oils (in *mg/(KOH)g)*

The changes in physical appearance of the oil included the increased viscosity and darkening in color indicating auto oxidation process (Diop, et al, 2014, Kaleem et al, 2015). Acid values indicate the extent to which glycerides in the cooking oil are decomposed by lipase enzyme (hydrolytic rancidity) or by the action of heat or light which is accompanied by the formation of free fatty acid (Pearson, et al, 1981). The amount of FFAs in the oil is proportional to that of AVs.

3.2 Free Fatty Acids (FFAs)

Free Fatty Acids were determined as the percentage of oleic acid for *Sundrop* oil and as palmitic oil for *Korie* and *Safi* oils. The general trend showed increased FFAs with the number of heating and cooling cycles of the oils. *Sundrop* oil showed relatively high levels of FFAs even before heating that upon heating demonstrated a slight increase in the FFAs from 0.23 to 0.27 (r=0.004). (Figure 2). In all cases the trend was Sundrop>Safi>Korie but the magnitude of variation due to heating cycles were *Korie>Safi> Sundrop*. Presence of high FFA levels in *Sundrop oils* is a typical characteristic of unsaturated oils but the slight increase upon heating showed that despite the unsaturation still *Sundrop* oil is more stable than the rest.

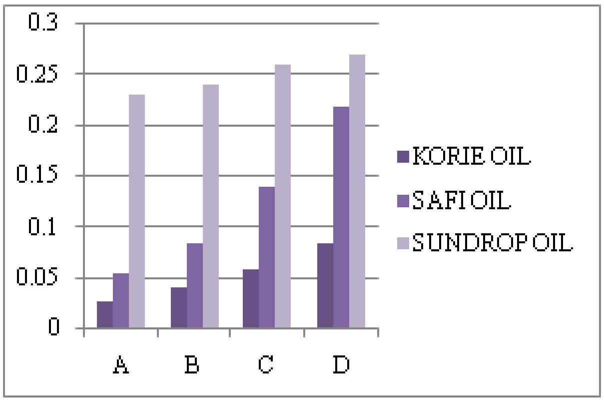

Figure 2: Variation of free fatty acid of *Korie*, *Safi* and *Sundrop* oil (in % Palmitic/Oleic acid)

Safi and *Korie* oils are from palm oil (saturated oils), the two demonstrated a quite different behavior in the FFA contents. Whereas *Korie* changed from 0.028 to 0.084 (r=0.06), *Safi* changed from 0.056 to 0.220(r=0.16). This variation suggests variation of degree of unsaturation in the refining processes. Common reactions of the Fatty acids include auto-oxidation where oxidation occurs with unsaturated fats by a free radical mediated process. These chemical processes can generate highly reactive molecules in rancid food and oils which are responsible for producing unpleasant odours and flavours, also destroy nutrient in food, under same condition, rancidity and the destruction of vitamins occur very quickly(Othman & Ngassapa, 2001)

3.3 Peroxide values (PVs)

The general trend showed increasing of peroxide values with the number of heating and cooling. *Safi* oil ranked with higher values of Peroxides that increased sharply with the number of heating (Figure 3). Peroxide Value (PV) indicates the initial rancidity of oil due to formation of intermediate products while the deterioration of the quality is indicated by both the PV and FFA values of the oil (Frank *et al*, 2011). Peroxide values in Sundrop varied slightly from 3.2 to 16.5 (r=13.3). Peroxide values in *Safi* and *Korie* were in the range of 10-36 (r=26) and 8-26 (r=18), respectively. The stability of peroxide in oils is affected by repeated heating that results to a series of chemical reaction like oxidation, hydrolysis and polymerization and it is during this process many oxidative product such as hydroperoxide and aldehydes are produced which may destroy nutrient and vitamins in food (Othman &Ngassapa , 2001).

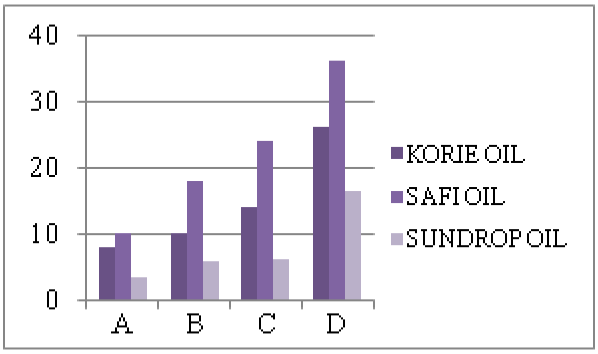

Figure 3: Variation of peroxide value (PV) of *Korie*, *Safi* and *Sundrop* oil (in meq/kg)

3.4 Variation of Acid value, Free Fatty Acid and Peroxide values in the three oils.

The comparison of the three oils in terms of AVs, FFAs and PVs was performed was in the trend of PVs > AVs > FFAs. The levels of Peroxides were very high in all the oils with the highest values in *Safi* oils followed by *Korie* oils. Repeated heating of peroxides results to production of hydroperoxide and aldehydes which are responsible for oil rancidity as well as affecting the nutritional value of the foods fried in the oils (Othman & Ngassapa, 2001). The Acid Values and FFAs were detected in relatively small amounts in the oils increasing slightly with the number of repeated heating of the oils.

3.5 The Quality of the Oils and the Health Implication

The variation of AVs, FFAs and PVs was compared that of the acceptable limits from TBS, WHO and FAO (Table 1). The acid values after several heating and cooling cycles were recorded above the acceptable limits for *Korie* oil (up to 1.6 mg KOH/g) against 0.6 mg KOH/g and 0.5 mg KOH/g recommended by WHO/FAO and TBS, respectively.

Table 1: Recommended Characteristics of Edible Oils as Given by FAO/WHO and TBS.

Oil Brand	FFA[1]	AV[1]	PV[1]	FFA[2]	AV[2]	PV[2]	FFA[3]	AV[3]	PV[3]
	%Oleic acid	Mg KOH/g	Meq/kg	%Oleic	Mg KOH/g	Meq/kg	%Oleic	Mg KOH/g	Meq/kg
Sundrop	**0.085**	**0.6**	**10**	**0.085**	**0.5**	**-**	**0.270**	**0.52**	**16.5**
Korie	**1.376**	**0.6**	**10**	**1.376**	**0.5**	**3**	**0.084**	**1.60**	**26.0**
Safi	**0.225**	**0.6**	**10**	**0.225**	**0.3**	**-**	**0.220**	**0.45**	**36.0**

1=WHO/FAO standard, 2=TBS standard and 3= Values observed in the current study

The three brands of oil depicted high levels of PVs in the order of *Safi (36meq/kg) > Korie (26meq/kg) > Sunflower (16.5meq/kg)* oils against that of **≤ 3 and ≤ 10** *meq/kg* as recommended by TBS and WHO/FAO, respectively. The AVs and PVs indicate the degree of the oil rancidity, thus indicating that sunflower oil is more stable compared to other oils.

4. Conclusion

The variations in the AVs, PVs and FFAs were determined before heating and after several cycles of heating and cooling. In all cases *Sundrop* exhibited the slightest variation in AVs, PVs and FFAs over the four heating cooling cycles. The levels AVs and PVs in the oils were higher in *Korie* and *Safi* oils where as the *Sundrop* demonstrated relatively higher FFA values before heating explaining the presence of more unsaturated fats in *Sundrop* compared to the other oils.

However, changes during heating were very minimal in *Sundrop* demonstrating its higher stability over the rest. This concludes that although *Sundrop* is more unsaturated having higher values of the FFAs before heating still demonstrated the highest stability to frying process. *Korie* was found to be the most unstable oil and hence going to rancidity faster than *Safi* oil. Since both *Safi* and *Korie* are from Palm oil (saturated fats) it may suggest that refining of oils enhance their stability on heating and hence reduced rancidity process.

5. Recommendations

Among the three brands of oil tested, *Sundrop* stood to be the most stable after several cycles of heating and cooling processes**.** It is therefore recommended to use *Sundrop* oils in frying foods rather than the other two brands. It is recommended that frying foods in Korie oil to be avoided due to high levels of AVs that may destroy the nutritional values of the fried foods.

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