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Storage and thermal behavior of some cooking oils consumed from the local market of Sudan

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Abstract
This work aims to assess the quality of some cooking oils consumed in Sudan. Six samples (peanut, sunflower, sunflower/peanut blends, sesame, corn and palm oils) were collected from the local markets. Some of their physicochemical properties were determined and compared to Sudanese Standard and Metrology Organization (SSMO). The effect of storage and heating on these oils was also examined. The results showed that most of these oils have acceptable properties values as compared to (SSMO), except palm oil showed higher saponification value than the maximum limit of SSMO. During storage, over 60 days, corn and palm oils exhibited the least rate of peroxidation and acid formation, whereas, the highest rate of peroxidation was recorded for the sunflower oil. The oils were heated at 165 °C for 30 minutes. The highest rate of peroxidation was observed in corn oil, whereas, palm oil showed the least rate of peroxidation.

Keywords: Cooking oils, physicochemical characterization, peroxidation, thermoxidative stability, effect of storage

Introduction

Fats and oils are valued as essential nutrients in the diet of human or animal. The main components of edible fats and oils are triglycerides. The minor components, which comprise about two percent of the composition, include mono and diglycerides, free fatty acids, phosphatides, sterols, fat-soluble vitamins, tocopherols, pigments, waxes, and fatty alcohols. The free fatty acid content of crude oil differs, widely, based on the source. Chemically, fats or oils are triesters of glycerol and fatty acids. “Oils” are usually, liquids at room temperature, while “fats” are solids. Nutritionally, they are rich sources of energy; essential fatty acids and are a transferor for the oil soluble vitamins A, D, E, and K. They also supply an essential linoleic and linolenic acid, which are accountable for growth. In addition, they improve the taste of the foods we eat, relating flavor and subsidizing to the feeling of satiety after eating. Fats and oils also play significant role in the preparation of many food products. They act as soaking agents and provide a heating medium for food preparation [1, 2].

It is generally known that fats and oils can deteriorate during storage in an oxidizing atmosphere, which is known as lipid oxidation. Lipid oxidation is, probably, the most important factors affecting the shelf life of edible oils. The oil stabilities during storage or upon heating are vital parameter for ensuring that oil appears the good performance at elevated temperature. Several methods have been used to evaluate the extent of oxidative deterioration, which are related to the measurement of the concentration of primary or secondary oxidation products. The most frequently used are peroxide value (PV), free fatty acid (FFA) and specific absorptivity in ultraviolet region at 232 and 270 nm. PV is related to the concentration of hydroperoxide, meanwhile the specific absorptivity at 232 and 270 nm measures the contents of conjugated dienes (CDs) and conjugated trienes (CTs).The oxidative deterioration of edible oils can be retarded by antioxidants, the main additives used to protect the quality of oil. Synthetic antioxidants, such as butylated hydroxyanisole (BHA) and butylated hydroxytoluene (BHT), are commonly added to oils in order to retard or prevent the oxidative changes during storage due to their effectiveness [3].

Sudan is one of the major oilseed producing countries. The major oilseeds that commercially cultivated in Sudan are, peanut, sesame and recently, sunflower. They represent an important contribution to its export trade and major cash crops in several parts of the country as well as an important food items [4].

The main objective of this study is to assess the quality of some local and imported cooking oils consumed in local markets of Sudan. The specific purposes includes:

- To determine some physicochemical properties of the oils and discuss it in the light of Sudanese standards.
- To examine the thermal behavior of the oils at elevated temperature.
- To observe the effect of time on the oxidative stability of the oils.

Materials and Methods

Six samples of cooking oils sunflower, peanut, sunflower/peanut blend (Sabah Company), corn and palm were collected from the local markets of River Nile State, Sudan. These are the common oils in the markets. Reagents like potassium hydroxide flakes, potassium iodide, hydrochloric acid, chloroform, acetic acid glacial, sodium thiosulphate, ethanol absolute anhydrous, phenolphthalein indicator and cyclohexane were analytical grade and were used as received without any further treatment.

Determination of physical and chemical properties

Physical and chemical properties for all oil samples were determined according to the standard procedures described for relative density [5], viscosity and refractive index [6], acid and peroxide values [7] and saponification value [8]. Each sample was analyzed in duplicate and the mean ± SD was calculated.

Storage stability

To examine the effect of storage on oils stability, the oils sample were exposed to atmospheric and light for sixty days then the acid value and peroxide value of all sample were determined at 0, 30 and 60 days.

Thermoxidative stability

Samples (25gms) of each oil were weighed into 50 ml open beaker and placed in a drying oven (Model: N4, PHILIP HARRIS, ENGLAND), previously adjusted at 165 °C for 30 min. After completion of the heating time, the oil samples were cooled to ambient temperature. Then, the acid and peroxide values of all cooled samples were determined to assess the thermal degradation of the oil.

The oxidative stability of the oils was further investigated by determining the concentrations of conjugated trienes (CTs) for fresh and heated oils using UV-Visible spectrophotometer (Model 7305, Jenway, U.K.). Oil sample (0.5gms) were weighed into 50 ml open beaker and dissolved at ambient temperature in a few milliliters of cyclohexane, then the solution was transferred to 50 ml volumetric flask and made up to the mark with the same solvent and mixed thoroughly [9]. The prepared solution was used to determine the specific absorbance at 270 nm to determine the CTs at ambient temperature.

Results and discussion

Relative density

Oils with low density are highly recommended for consumer [10]. As it can be seen from table 1 and figure 1 the palm oil showed the lowest value of density (0.8878±0.0003 g/cm^3), whereas, crude sesame oil showed the highest value (0.8964±0.0007 g/cm^3).The densities of all sample are below the maximum limits set by SSMO for oils.

Table 1: Results of relative density of six vegetable oils

Oil type	Relative density g/cm^3	SSMO,2016
Peanut oil	0.8924 ± 0.0001	0.912 – 0.920
Corn oil	0.8924 ± 0.0007	0.891 – 0.899
Sesame oil	0.8964 ± 0.0007	0.915 – 0.924
Sunflower oil	0.8957 ± 0.0018	0918 – 0.923
Palm oil	0.8878 ± 0.0003	0.917 – 0.925
Sabah oil	0.8936 ± 0.0007	-

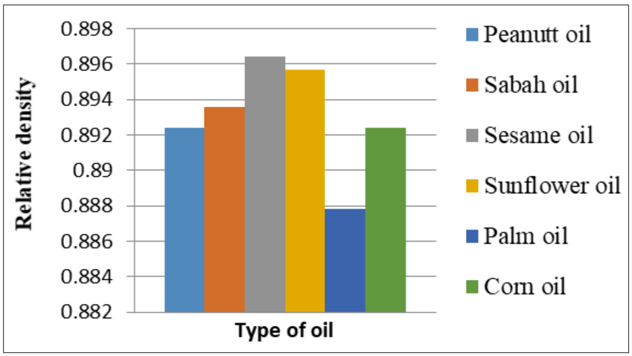

Fig 1: Relative density of vegetable oil samples

Refractive index

From table 2 the values of refractive index fall in the range of 1.4589- 1.4739. The values of all oils are in good agreement with the range of the SSMO (2016). The palm oil showed the lowest value, whereas, corn oil shows the highest value as presented in figure 2. It has been reported that refractive index is, inversely, proportional to the degree of saturation [11].

Table 2: Results of refractive index values of the six vegetable oils

Oil type	Refractive index	SSMO, 2016
Peanut oil	1.4628±0.0011	1.460 – 1.465
Corn oil	1.4739±0.0005	1.465 – 1.468
Sesame oil	1.4711±0.0011	1.465 – 1.469
Sunflower oil	1.4663±0.0025	1.461 – 1.468
Palm oil	1.4589±0.0047	1.449 – 1.455
Sabah oil	1.4633 ± 0.0021	-

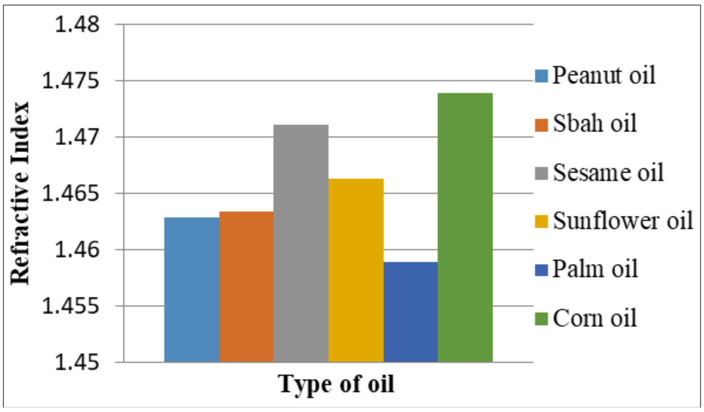

Fig 2: Refractive index of the vegetable oil samples

Viscosity

The results from table 3 show great variation in the values of viscosities for all sample. This variation could be attributed to the fact that viscosity depends on the fatty acid composition of the oils. It decreases with the increase of unsaturation of fatty acids and increases, substantially, with saturation [12]. As presented in figure 3, the lowest value of viscosities (0.02880 ±1.66971 Pa.s) was observed for the corn oil, which is known with high degree of unsaturation. The high saturated palm oil, showed the highest viscosity (0.05350 ±2.4042 Pa.s) among the all samples. The relatively high viscosities of crude peanut (0.03655 ± 0. 919200) and sesame (0.03440 ± 0.8485) indicate the impurity of these oils.

Table 3: Results of viscosity value of six vegetable oils

Oil type	Viscosity Pa.s
Peanut oil	0.03655 ± 0. 919200.
Sabah oil	0.03185 ± 1.3435
Sesame oil	0.03440 ± 0.8485
Sunflower oil	0.00300 ± 0.3536
Palm oil	0.05350 ±2.4042
Corn oil	0.02880 ±1.66971

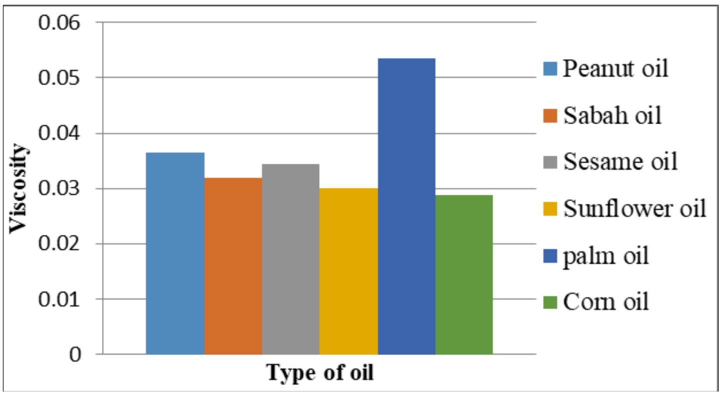

Fig 3: Viscosity of the vegetable oil samples

Acid values and free fatty acid contents

Acid value of oils indicates the amount of the free fatty acid present in the oil. It determines the purity of oils. Higher values indicates that triglycerides of oil are convert into fatty acids and glycerol which cause rancidity of the oil [10]. The variation of acid values and free fatty acid contents in vegetable oils, usually, is attributed to inadequate refining, de colorization and presence of soaps from the reaction of free fatty acid with metal salts present in the edible oils [11].

Oils examined in this study, varied in their free fatty acid content and acid values (table 4, figure 4a and figure 4b), possibly because of variation in moisture contents, refining and deodorization processes used. The free fatty acid content for refined oils (sunflower, corn, palm and blend of peanut/ sunflower oils) ranged from 0.113 ± 0.000 to 0.197 ± 0.020 mg KOH/g; in a good agreement with the limits of SSMO (≥0.2%). Higher values 0.986 ± 0.020 and 0.620 ± 0.000 were observed for peanut and sesame oils respectively.

Table 4: Results of acid value (AV) mg KOH/g and free fatty (FFA) acid% as oleic acid of six vegetable oils

Oil type	AV *	SSMO, 2016	FFA %	SSMO, 2016
Peanut oil	1.234 ± 0.000	Crude 4.0, Refine 0.6	0.620 ± 0.000	Crude 2.0, Refine 0.3
Sabah oil	0.393 ± 0.079	Crude 4.0, Refine 0.6	0.197 ± 0.020	Crude 2.0, Refine 0.3
Sesame oil	1.963 ± 0.079	Crude 4.0, Refine 0.6	0.986 ± 0.020	Crude 2.0, Refine 0.3
Sunflower oil	0.224 ± 0.000	Crude 4.0, Refine 0.6	0.113 ± 0.000	Crude 2.0, Refine 0.3
Palm oil	0.393 ± 0.079	≤ 4.0	0.197 ± 0.020	≤ 2.0
Corn oil	0.224 ± 0.000	Crude 4.0, Refine 0.6	0.113 ± 0.000	Crude 2.0, Refine 0.3

*Acid value = 1.99 × FFAs% [7]

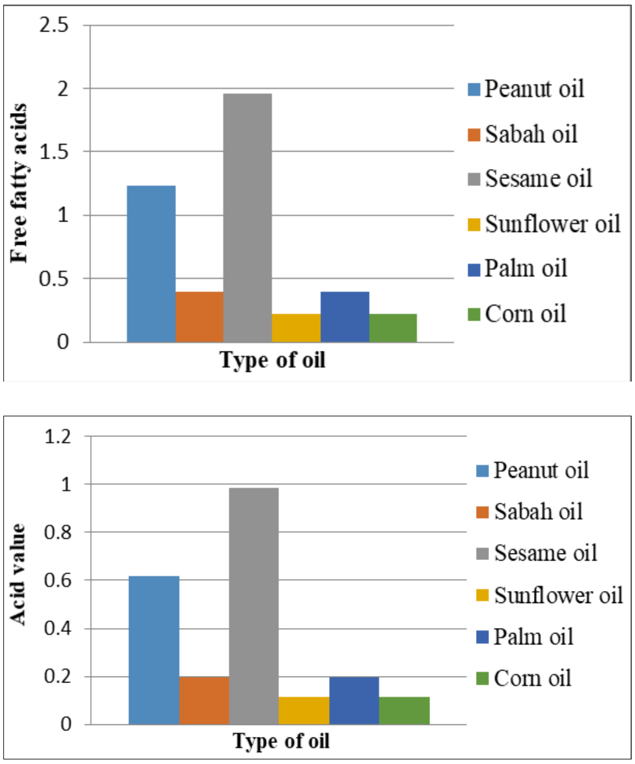

Fig 4: a) Free fatty acids and **b)** Acid values of vegetable oil samples

Peroxide value

Peroxide value is used as a measure of the extent to which rancidity have occurred during storage due to the oxidation reaction when the oils exposed to light and heat [10]. The quality and stability of fats and oils can be assessed based on the peroxide value. According to SSMO, rancidity is not noticeable if the peroxide value does not exceed the limit of 10 meq O_2/Kg. From table 5 peroxide values for the different types of the vegetable oils ranged between 2.5 – 8.4 meq O_2/Kg. These low values of peroxide value indicates the suitability of these oil for human consumption. As depicted in figure 6; the maximum value of the peroxide value was observed for sunflower oil, whereas, palm oil exhibited the lowest value. It is reported that the oils with high degree of unsaturation is more prone to oxidation [12].

Table 5: Results of peroxide value in meqO_2/kg of six vegetable oil

Oil type	Peroxide value	SSMO, 2016
Peanut oil	5.10 ± 0.14	Crude 15, Refine 10
Corn oil	4.60 ± 0.00	Crude 15, Refine 10
Sesame oil	4.20 ± 0.00	Crude 15, Refine 10
Sunflower oil	8.40 ± 0.57	Crude 15, Refine 10
Palm oil	2.50 ± 0.14	≤ 10
Sabah oil	4.90 ± 0.14	-

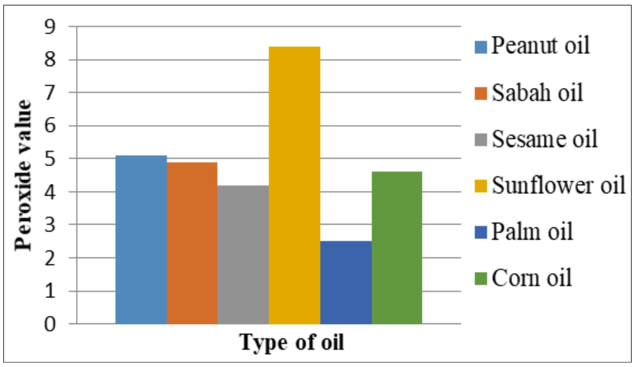

Fig 5: Peroxide value of vegetable oil samples

Saponification value

Saponification value is, inversely, proportional to the length of carbon chains of the fatty acids present in the triglycerides. Hence, saponification value gives preliminary information of molecular weight of the vegetable oil. High saponification values indicate low molecular weights and hence low volatility and high calorific values [12].

As it can be seen from table 6 and figure 7 the highest and lowest value of saponification value is 234.70 ± 0.45 and 178.44 ± 0.52 mg KOH/g for palm oil and corn oil, respectively. The saponification value of palm oil is higher than the maximum value (210) of SSMO (2016), whereas, the value exhibited by the corn oil is lower from the minimum value (187mgKOH/g) of SSMO (2016). The value obtained for the sunflower oils was in a good agreement with the standard of SSMO (2016). Peanut and sesame oils showed, slightly, higher saponification values than the maximum value specified by SSMO (2016).

Table 6: Results of Saponification value in mg KOH/g of six vegetable oil

Oil type	SV	SSMO, 2016
Peanut oil	202.64 ± 11.11	187-196
Sesame oil	198.65 ± 11.55	186-195
Sunflower oil	188.50 ± 15.11	188-194
Palm oil	234.70 ± 0.45	195-210
Corn oil	178.44 ± 0.52	187-195
Sabah oil	190.10 ± 11.96	-

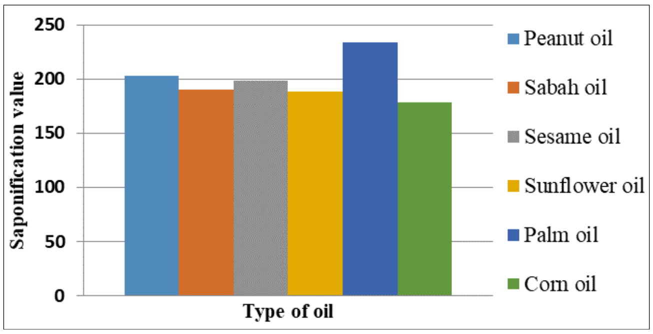

Fig 6: Saponification values of vegetable oil samples

Storage stability

All the samples were stored at the ambient temperature (25 °C) on the shelf exposing to the day light and atmospheric oxygen for two months. The change of oxidative stability was followed by determination of both acid value and peroxide values at 0, 30 and 60 days. The results showed a gradual increase in acid values for the all oils samples during the time of storage. As it can be seen from table 7 and figure 8 the highest increase in the acid value from the initial time to final time storage period, is exhibited by sesame and pure peanut oils followed by the pure sunflower oil and the blend of sunflower / peanut (Sabah) oil. Least increment in acid value was observed for palm and corn oil. Peroxide value increased for all oil samples during the sixty days of storage with different rates (Table 8). The variation in the rate of degradation may be due to the different antioxidant contents and fatty acid composition of these oils [13]. Table 8 and figure 9 show that Sunflower oil has highest rate of peroxidation followed by Sesame oil and peanut oils. The lowest rate of peroxidation was observed in palm and corn oils. The rate of peroxidation of sunflower/peanut blend (0.12) is, significantly lower compared to pure sunflower (0.54) or pure peanut oils (0.19).

Table 7: Acid values (mgKOH/g) for oils exposed to both atmospheric and light during storage time

Oil type	Storage time in days			Rate mgKOH/g day
	0	30	60	
Peanut oil	1.2342 ± 0.000	1.6926 ± 0.14	2.5326 ± 0.00	0.021
Sabah oil	0.3366 ± 0.079	0.4578 ± 0.00	0.7002 ± 0.12	0.006
Sesame oil	1.9074 ± 0.079	2.5506 ± 0.04	3.8370 ± 0.14	0.021
Sunflower oil	0.2244 ± 0.000	0.3366 ± 0.11	0.5610 ± 0.00	0.006
Palm oil	0.3927 ± 0.079	0.4551± 1.20	0.5175 ± 1.41	0.002
Corn oil	0.2244± 0.000	0.2805 ± 0.00	0.3366 ± 0.00	0.002

Table 8: Peroxide values (meq O_2/Kg) for oils exposed to both atmospheric oxygen and light during storage time

Oil type	Storage time in days			Rate (meq O_2/Kg day)
	0	30	60	
Peanut oil	5.10 ± 0.14	10.70 ± 1.47	16.70 ± 0.07	0.19
Sabah oil	4.90 ± 0.14	9.40 ± 0.00	12.10 ± 0.07	0.12
Sesame oil	4.20± 0.14	13.00 ± 0.00	20.00 ± 0.00	0.26
Sunflower oil	8.40 ± 0.14	22.70 ± 0.14	40.25 ± 0.04	0.54
Palm oil	2.50± 0.14	4.40 ± 1.41	6.70 ± 0.07	0.07
Corn oil	4.60 ± 0.14	7.70± 0.14	9.10 ± 0.07	0.08

Thermo oxidative stability

Temperature is one of the main factors that affects, negatively, the quality of frying oils. It has been reported that at high temperature vegetable oils exhibit changes in color, low smoke point, low iodine value, high polar material content, high acid value, and high peroxides. Peroxide value is considered as an indicator for the formation of primary oxidative products i.e. peroxides [14]. Kaleem *et al.* [15] examined the thermal stability of 20 vegetable oils at 130 C and 170 C. Their study revealed that the high unsaturated oils exhibited considerable change in peroxide value than the saturated oils.

In current study, the oil samples had been exposed to successive heat at 165 C for 30 minutes in order to investigate their thermal stability. Table 9 shows the effect of heating on peroxide value for the vegetable oils under investigation. As it can be observed, sunflower oil and corn oil showed the highest rate of thermal degradation. It has been reported that sunflower oil and corn oil have high linoleic acid content. The high rate of degradation of corn oil, by the effect of heat, compared to its degradation during storage may be attributed to the thermal decomposition of its antioxidants [16]. The remaining oils showed, relatively comparable rate of thermal peroxidation

Hydro peroxides, which are formed in the early stages of the oxidation products, are unstable. They are, rapidly, converted to secondary oxidation products especially unsaturated ketones and diketones that absorb light at of 270 nm. Therefore, specific absorption at 270 nm (K270) is considered as indicator for the formation of secondary oxidation product [17]. Referring to table 9 all the oil samples showed significant increase in K270 during heating. The order of the examined oils, based on the percentage increment in K270 is as follow:

Corn oil> sesame oil l>palm oil l>Sabah oil ≈sunflower oil≈ peanut oil

Corn oil showed the highest rate of formation for both primary and secondary oxidative products. Sunflower oil, although it showed high rate of secondary oxidative products formation, it exhibited low rate of secondary oxidative products formation.

Table 9: The effect of heating on peroxide value and CTs of oils

Oils type	Peroxide value		Rate of peroxidation (meq O_2/Kg day)	CTs (K270)		The increment of K 270 %
	25 °C	165 °C		25 °C	165 °C	
Peanut oil	5.10	9.50	0.22	1.29	1.73	34
Sabah oil	4.90	7.20	0.12	1.8	2.74	52
Sesame oil	4.20	8.90	0.24	0.55	2.84	416
Sunflower oil	8.40	17.10	0.44	3.11	4.26	37
Palm oil	2.50	4.60	0.11	0.57	2.48	335
Corn oil	4.60	12.40	0.39	0.32	2.36	637

Conclusions

Based on the results of the present study the following conclusions may be drawn:

- The physicochemical properties of all oil samples were fall in the range as stipulated in SSMO with few exceptions regarding saponification value of palm oil which was observed, relatively, high compared to the maximum limit of SSMO.
- Sunflower oil exhibited very low oxidative stability during both storage and heating.
- Corn oil has high oxidative stability during storage and very low resistance to peroxidation during heat

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