

Comparative Study of Stability Measurements for Two Frying Oils: Soybean Oil and Refined Palm Oil

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Abstract: The quality of soybean oil (SO) and refined palm oil (RPO), frying at 180°C for 12 h was investigated. The purpose of the study was to find out the quality deterioration of the two oils with respect to time as affected by fritters frying and to generate equations that can be used for predicting the quality parameters. The physicochemical characteristics of two oils were evaluated by taking the oil samples (100 mL) in the pan (fryer) after 1h of frying. The parameters evaluated were K233, K269, viscosity, polar compounds, fatty acids methyl ester analysis by Gas Chromatography (GC), Differential Scanning Calorimetry (DSC). There was a gradual increase in K233, K269, viscosity and polar compounds with during frying of the two samples. Linoleic acid was degraded during frying in the two oils. Viscosity correlated well ($r > 0.99$) with polar compounds and time of frying. K233 and K269 correlated well ($r > 0.99$) with during frying, polar compounds duration of frying and absorption capacity of oils in fritters.

Key words: DSC, oxidative, palm oil, polar compounds, soybean oil, specific extension and viscosity

INTRODUCTION

During frying, oils are degraded from thermal oxidation to form volatile and non-volatile decomposition products (Melton *et al.*, 1994). The chemical changes in frying oil also result in changes in the quality of fried food. The fatty acid composition of the frying oil is an important factor affecting fried food flavor and its stability; therefore, it should be low level of polyunsaturated fatty acid such as linoleic or linolenic acids and high level of oleic acid with moderate amounts of saturated fatty acid (Kiatsrichart *et al.*, 2003; Mehta and Swinbum, 2001). As a result, the quality of frying oil is important because of absorbed oil of fried products during deep frying. Soybean oil has a good nutritional profile due to high level of unsaturated fatty acid but less oxidative stability (Stenson and Min, 2000). Various method to improve oxidative stability of soybean oil has been developed and studied, for example, partial hydrogenation, fatty acid modification and blending with more saturated or monosaturated oils to reduce the amount of polyunsaturated fatty acids (Cuesta *et al.*, 1993; Hunter and Applewhite, 1991; Su and White, 2004). Partial hydrogenation decreases polyunsaturated

fatty acid but increases saturated fatty acid and trans-fatty acid to produce more stable frying oil. However, trans-fatty acid may have adverse effects on cardiac health (Ascherio *et al.*, 1994). palm oil, is considered value domestic oil in many countries of Africa and Asia. Nowadays, palm oil becomes useful for cooking because of very low cost. The advantages of the palm oil are not only economic. The high content in mono-unsaturated acids drop rates of LDL – " bad " cholesterol – all while maintaining the HDL or " good " cholesterol. It is also an excellent source vitamins A and E for Africa and Asia population (Zagre and Tarini, 2001). This work is to undertake a comparative study on the deterioration and the thermal stability of the two oils (soybean oil and refined palm oil) sold on the markets during cracklings of fritters.

MATERIALS AND METHODS

This study was led to the laboratory of engineering and biomolécule of the ENSAIA-INPL, Vandoeuvre - lès-Nancy (France) for the period of Jan. 5, 2009 to Feb. 27, 2009.

Food materials: Wheat flour, refined oils of soya and palm, and other ingredients were purchased at local market "Total of Bacongo" in the southern part of Brazzaville (Congo).

Fritter flour dough preparation: Flour dough prepared from wheat flour (900 g), distilled water (500 mL), salt (2 g), sugar (100 g), baker yeast (10 g) was mixed in a basin (5 L of volume). Flour dough is fermented, let at rest during 2 h and to be prepared at frying.

Treatment of oils: A series of tests were used to fry the spherical sections of fritters dough (thickness 4 cm). For each test, 300 g of sections of fritters dough was fried in 5000 mL oil at a temperature of 120°C; the busy oil bath of 180°C before introduction of the sections, to 120°C, to stabilize itself at this temperature. With end of 10 min of frying, the operation is stopped and the taken fritters, drained during 10 min on a grid at ambient temperature. Samples of oil for analysis were taken each morning after the oil had cooled overnight at 20°C. One sample for each oil of frying was collected at day 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12. Day 0 oil was collected after the oil conditioning before the start of the frying. All the oil samples collected were analyzed using the same procedure used for the initial oil analysis. Taking away carried out each morning, made it possible to follow the oxidative and thermal evolution for two studied oils. During frying was 1 h per day.

Absorption Capacity of fritter oils: Absorption Capacity of fritters oils was determined by extraction at solvent (Ndjouenkeu and Ngassoum, 2002). One hundred and fifty gram of ground fritter were placed into a cellulose paper cone and extracted using light petroleum ether (bp 40-60°C) in a 5-l Soxhlet extractor for 8 h (Pena *et al.*, 1992). The oil was then recovered by evaporating of the solvent using rotary evaporator Model N-1 (Eyela, Tokyo Rikakikal Co., Ltd., Japan) and residual solvent was removed by drying in an oven at 60°C for 1 h and flushing with 99.9% nitrogen.

Determination of fatty acid composition: Total fatty acids were transmethylated according to Frega and Bocci (2001). About two drops of oil (SO and RPO) were dissolved in six drops of a solution of 2 N KOH in methanol and then 2 ml of n-hexane were added. The mixture was vigorously shaken with a vortex for 2 min, sodium sulfate was added and the mixture was shaken again. The sample (0.4 µl) was injected 10 min later into a gas chromatograph (Hewlett-Packard 5890 CG) equipped with a split-splitless injector and a flame ionization detector. A DB-225, 30 x 0.25 mm ID and 0.15 µm column (J and W Scientific, Agilent) was used. The injector and detector temperatures were set at 250°C. The oven temperature was kept at 190°C for 1 min, then programmed from 190-210°C at 4°C min⁻¹, kept at 210°C

for 5 min, then heated from 210-215°C at 3°C min⁻¹ and finally kept 18 min at the last temperature. Nitrogen was used as carrier gas at a flow rate of 1.0 mL min⁻¹. The peak identification was carried out by comparing the peak retention time with those of the standard mixture. An internal standard was used for the quantification of fatty acids. The GC response factor of each fatty acid was calculated by using the internal standard. The results were expressed as g fatty acid/100 g total fatty acids (%).

Polar compound measurements: Measurement of polar compounds (in percentage) was done with a rapid method that is, using a Testo Ebro Model type FOM 310 based on dielectric constant measurement. This instrument allows measurement from 40-210°C and there is an interpretation that corresponds to every temperature. A number of frying cycles was done until the sensitivity limit of the instrument (40% polar compounds) was reached.

Viscosity measurements: A rheometer as described by Nzikou *et al.* (2006) was used to measure the different oil viscosities. By this procedure, a concentric cylinder system is submerged in the oil and the force necessary to overcome the resistance of the viscosity to the rotation is measured. The viscosity value (mPas) is automatically calculated on the basis of the speed and the geometry of the probe. Temperature (20°C) was controlled with a water bath connected to the rheometer. The experiment was carried out by putting 3 ml of sample in a concentric cylinder system using 100 sec⁻¹ as shear rate.

Differential scanning calorimetry (DSC): Calorimetric evaluations of sample melting behavior were performed in a Perkin-Elmer (Model Pyris 1, Perkin Elmer Corp., and Norwalk CT) as described by Nzikou *et al.* (2007). All samples were tempered in the DSC cell according to the following conditions: samples were tempered at -50°C during 10 min. DSC analysis were performed from -50°C to +50°C at a scan rate of 10°C.min⁻¹. The major peak maximum temperatures and enthalpy of melting (J.g⁻¹) were analyzed from thermograms using the Pyris software (version 2.04, 1997).

Statistical analysis: Each reported value is the mean of determinations for triplicate samples. The statistical analysis of the data, correlation and regression was carried out with Microsoft Excel 8.0 software.

RESULTS AND DISCUSSION

Fatty acids composition: Table 1 shows the contents of saturated (SFA), monounsaturated (MUFA), and polyunsaturated (PUFA) fatty acids of the oils used for the frying experiments. RPO had the highest SFA (45.38%) and MUFA (43%) contents, mainly represented by palmitic (39.65%) oleic (42.81%) and linoleic (11.04%) acids; SO was very rich in PUFA (53.88%) by

Table 1: Fatty and composition (%) of the unused frying oils

Oil samples	SFA	MUFA	PUFA
SO	11.08±0.02	35.04±0.01	53.88±0.18
RPO	45.38±0.28	43.00±0.12	11.61±0.53

Abbreviations: SFA, saturated fatty acids; MUFA, monounsaturated fatty acids; PUFA, polyunsaturated fatty acids.(mean values ± standard deviations); SO: soybean oil, RPO: refined palm oil

comparison RPO (11.61%), mainly as linoleic acid, which makes it particularly sensitive to oxidation, while the SO and RPO blend abounded in MUFA that are more stable toward oxidation reactions (Fatemi and Hammond, 1980). The most abundant PUFA, linoleic acid, was degraded during frying in the two oils because of lipid oxidation (Fig. 1). By comparison of the slope values shown in the Fig. 1, the highest degradation rate was found for SO, probably due to its lower content of natural antioxidants in comparison to RPO and also probably to the lack of tocotrienols in SO, which are instead present in RPO and act as more effective antioxidant compounds (Rossi *et al.*, 2007).

in the ultraviolet absorption K at 233 and 269 nm are associated with the changes in the conjugated dienes and trienes that are produced due to the oxidation of polyunsaturated fatty acids (Abdulkarim *et al.*, 2007). The resulting conjugated dienes exhibit an absorption at 233 nm; similarly the conjugated trienes absorb at 269 nm. The changes in K at 233 and 269 nm during frying for SO, RPO, are shown in Fig. 2 and 3. The K at 233 and 269 nm for the two samples increased with frying time throughout the frying days. The levels of conjugated dienes throughout the frying period are lowest in the two samples. The levels of conjugated trienes are also lowest in the two samples. The low levels of both conjugated dienes and trienes of both samples are indications of good oxidative stability of the oil, and it is because of the high percentage of monounsaturated/oleic acid it contains (35% SO and 43% RPO). The higher the percentage of polyunsaturated acids in the oil, the higher the levels of conjugated dienes and trienes formed during frying. This was the reason why SO and RPO, that contained high percentages of polyunsaturated acids (linoleic and linolenic), have accumulated more conjugated dienes and trienes. In contrast, K_{233} and K_{269} , another oxidation index, related to conjugated diene and triene formation, was higher and increased more rapidly in SO, this is in relationship with the higher degradation rate of linoleic acid observed in SO.

Changes in the ultraviolet spectrum have been used as a relative measure of oxidation. Farmer and Sutton (2002) indicated that the absorption increase due to the formation of conjugated dienes and trienes is proportional to the uptake of oxygen and formation of peroxides during the early stages of oxidation. Correlation coefficients (R^2) between K at 233 nm and frying during the initial stage of oxidation were found to be positive and very high; at 0.987 and 0.985 respectively for RPO and SO. Specific extinction is thus a very sensitive means of measuring

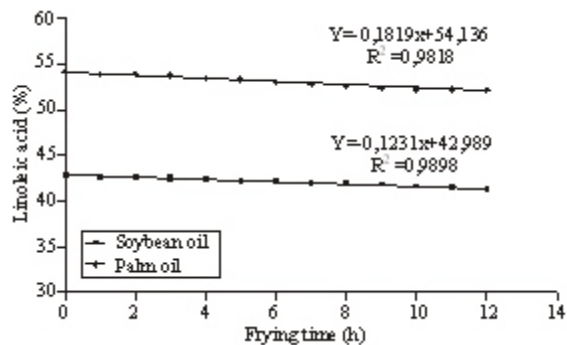


Fig. 1: Relationship between Linoleic acid degradation and the frying during for SO and RPO. Data points represent mean values, Standard deviations ranged between 0% and 0.38%.

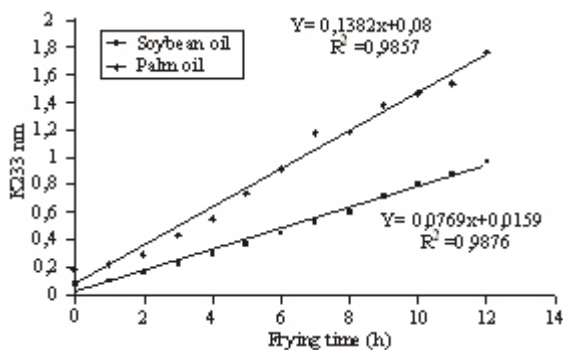


Fig. 2: Relationship between specific extinction K_{233} and the frying during for SO and RPO. Data points represent mean values, Standard deviations ranged between 0.005 and 0.450.

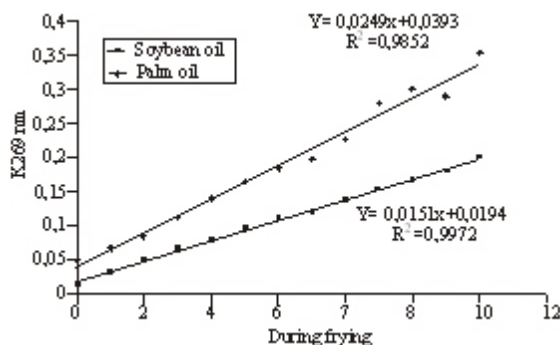


Fig. 3: Relationship between specific extinction K_{269} and the frying during for SO and RPO. Data points represent mean values, Standard deviations ranged between 0.005 and 0.400.

differences of lipid oxidation. It was found that in the two samples, the levels of conjugated dienes are higher than trienes, this is indicated by the higher values of K at 233 nm.

Polar compounds: The polar compounds are a product of the oxidation and they are determined by a

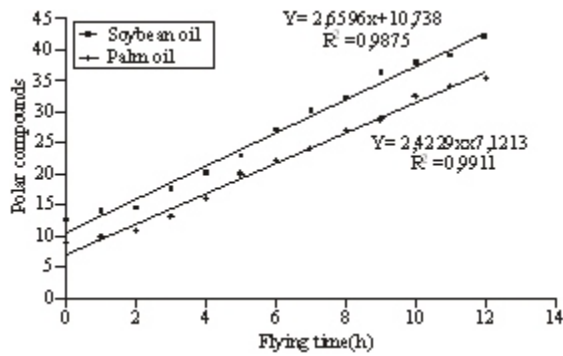


Fig. 4: Relationship between Polar compounds and the frying during for SO and RPO. Data points represent mean values, Standard deviations ranged between 0% and 0.35%.

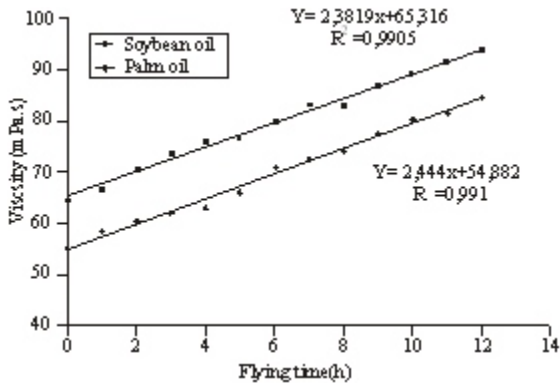


Fig. 5: Relationship between viscosity (measured at 20 °C) and the frying during for SO and RPO. Data points represent mean values, Standard deviations ranged between 0 and 0.7 mPa.s.

rapid method (Testo) in order to follow the life of the frying oil. Recently a good correlation of this method with the official one (by silica column chromatography) was established (Dobarganes, 2007).

Fig 4 shows the polar compounds content, depending on the frying number. In both oils there is a lineal behaviour with a very good correlation, although the degradation of the two oils occurs sooner, as expected, because of the fatty acid composition. The maximal sensitivity of the instrument was reached after the 12th frying process. Moreover, the limit established by the French legislation for heated fats is 25% of polar compounds (Sanchez-Gimeno *et al.*, 2008).

Changes viscosity: The viscosity of all the oils increased with frying days (Fig. 5). Increase in viscosity was caused due to the formation of high molecular weight polymers. The more viscous the frying oil, the higher the degree of deterioration. The changes in viscosity in the two oil samples had a positive and high correlation with changes in percent polar compounds during the frying period, with correlation coefficient, of 0.985 and 0.978 for

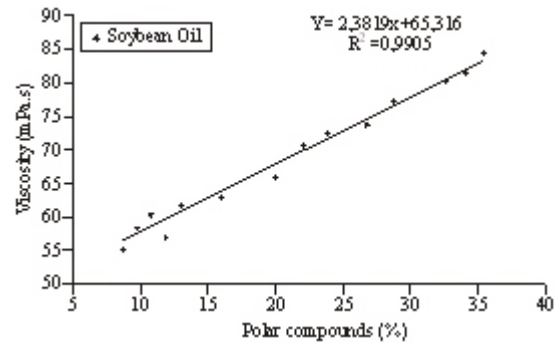


Fig. 6: Relationship between viscosity (measured at 20°C) and the Polar compounds for SO.

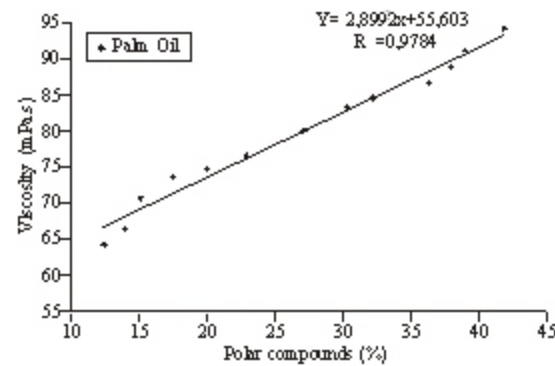


Fig. 7: Relationship between viscosity (measured at 20°C) and the Polar compounds for RPO.

SO and RPO, respectively (Fig. 6, 7). Colour and viscosity are the most common physical parameters used to evaluate the extent of frying oil deterioration in commercial and household frying. They are the most obvious changes that can be observed even for the non-expert. The degradation of oils during frying affects both viscosity and the composition of polar compounds. For the two samples of oil, a linear equation at summer found. Furthermore, the relationship is very similar for SO and RPO, although for the different percentage of polar compounds, and therefore the different degree of oil degradation, the viscosity is slightly lower for SO than for RPO. As both types of oils behave similarly, this shows that the viscosity seems to be more affected by thermodegradation and therefore by the percentage of polar compounds formed through oxidation and thermal and hydrolytic reactions than by the composition of the fatty acids and in particular the degree of unsaturation.

Absorption Capacity: The use of two oils for fritters frying of wheat flour seems to indicate a relatively better absorption of RPO (Fig. 8). It would be however hazardous to show a differential absorption from oils by fritter without a preliminary study from the kinetics of absorption. As a whole, the value of absorption of RPO is higher than that of SO.

Table 2: Thermal parameters of frying oils obtained by differential scanning calorimetry. Experimental conditions: temperature programm set at -50°C for 10 min, rising to +50°C at rate of 10°C min⁻¹.

	Oils samples			
	SO		RPO	
	SO ^a	SO ^b	RPO ^a	RPO ^b
Peak 1 [°C]	-22.54	-23.72	+0.99	+2.69
H _f [J.g ⁻¹]	+8.40	+9.78	+0.20	+0.93
Peak 2 [°C]	-5.97	+2.89	-	-
H _f [J.g ⁻¹]	+1.09	-1.06	-	-

SO^a, soybean oil unused; SO^b, soybean oil used after 1 h of frying; RPO^a, refined palm oil unused; RPO^b, refined palm oil used after 1 h of frying.

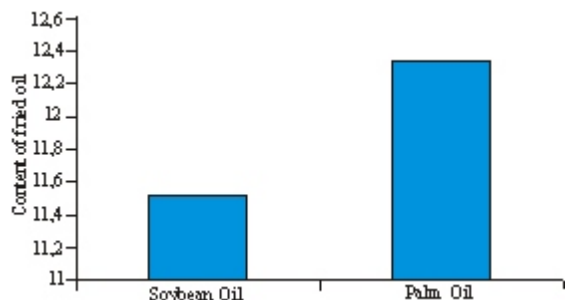


Fig 8: Relationship between content of fried oil and the oil samples (SO and MO).

Thermal profiles of oils: The DSC determines these physical properties. Results obtained from the heating with the DSC (Table 2) showed that there is two major peaks at -22.54°C (H_f = +8.40 J.g⁻¹) (SO^a) and -23.72°C (H_f = +9.78 J.g⁻¹) (SO^b) and two small peaks at -5.97°C (H_f = +1.09 J.g⁻¹) (SO^a) and +2.89°C (H_f = -1.06 J.g⁻¹) (SO^b) for both oil samples SO^a and SO^b. The two major peaks represented the melting temperature of unstable crystals of the low melting TAG that pre-maturely melted. The more stable low melting unsaturated TAG crystals melted at a higher temperature shown as peaks at -5.97°C (SO^a) and +2.89°C (SO^b). The two major peaks at -22.54°C (SO^a) and -23.72°C (SO^b) was due to PUFA presence, while the two small peaks at -5.97°C (SO^a) and +2.89°C (SO^b) was correlated to MUFA. The thermal behaviour of this oil was not significantly affected by frying. The Table 2 has only one major melting point at +0.99°C (H_f = +0.20 J.g⁻¹) (RPO^a) and +2.69°C (H_f = +0.93 J.g⁻¹) (RPO^b). Those peaks suggest the presence of mixed triglycerides groups with different melting points (Table 2).

CONCLUSION

The percentage of polar compounds, conventionally used to measure frying oil degradation, were related to viscosity for the two frying oils purchased at local market "Total of Bacongo" in the southern part of Brazzaville (Congo). Gas chromatography (CPG), specific extinction K₂₃₃ and K₂₆₉ and viscosity could be used to characterize the thermal degradation of frying oils. This study demonstrates soybean oil and refined palm oil was able to

reduce the oxidative and Thermal stability of oil during frying at 180°C since the parameters values physicochemical of soybean oil are more higher than that of palm oil during frying.

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