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EFFECTS OF CHEMICAL ALTERATION AND PROCESS CONDITIONS IN RECURRENTLY HEATED GROUNDNUT OIL

Selvaraj Rama Jeba and Kandasamy Karthikeyan
Department of Food Science and Nutrition, Periyar University, Salem, Tamil Nadu, India.

ABSTRACT:

Deep-heating exposes edible oils to high temperature and oxygen for long periods causing its rapid breakdown. Oxidation products present in abused frying fats and oils are the compounds most suspected of impairing the nutritional properties of the oils or involving adverse physiological effects. High temperatures and complex substrates cause the occurrence of complicated reactions and the formation of numerous products during the heating process. Not only the constituents of heating oil, such as TAGs and other minor compounds are involved in the complex reactions, but also the constituents of fried food, such as water, proteins, carbohydrates, and lipids, are involved. Thus, the study indicates that the chemical alterations by spectroscopic recognition technique, and the percentage of adulteration in groundnut oil.

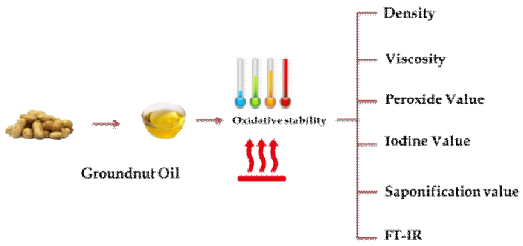
KEYWORDS: *Groundnut oil, Chemical alterations, FT-IR spectroscopic, Temperature, Oil oxidation.*

INTRODUCTION:-

Our eating routine contains an intricate blend of fats and oils comprising of various unsaturated fats which may influence human wellbeing (Trichopoulou *et al.,2014*). A joint Food and Agriculture Organization of the United Nations/World Health Organization (FAO/WHO) report from 2009 cases that there is persuading proof that supplanting dietary soaked unsaturated fats with polyunsaturated unsaturated fats (PUFA) diminishes the danger of cardiovascular infections (Houston . 2018). The report suggests supplanting SF in the eating regimen with PUFA. Practically speaking, this might be finished by supplanting sustenance, for example, high-fat dairy items and greasy meat, with nourishment, for example, a few vegetable oils (not palm oil and coconut oil), greasy fish and fish oils.

Rate of oxidation relies upon the level of unsaturation and increments with increment in the twofold obligation of unsaturated fats (Binkoski *et al.,* 2005). At the point when oxygen responds with unsaturated lipids, a wide assortment of oxidation items are delivered by lipid peroxidation (Kerr *et al.,* 2015). Lipid oxidation items have mutagenic, cancer-causing and cytotoxic properties and viewed as a hazard factor for human wellbeing (Barrera G. 2012). These metabolites cause extreme medical issues, for example, development of tumor cells through lipid peroxidation as hydroxides of unsaturated fats are cytotoxic. Oxidation of long-chain unsaturated fats causes

neuromyopathic infection both in newborn child and grown-ups (Wajner and Amaral, 2016). Oxidation in marine lipids causes loss of nutritive esteem and improvement of unsavory flavor (Hernández-López *et al.,* 2016). Lipid oxidation lessens the time span of usability of numerous intricate nourishment items and nutritive estimation of sustenance by constraining the substance of fundamental polyunsaturated unsaturated fats (Prat., 2011).



Graphical Schematic diagram of oxidative stability measurement

Groundnut oil is normally utilized as a conclusive flavoring, however, it is additionally utilized with cooking purposes at high temperatures (Das *et al.,* 2016). In this sense, after warm handling, changes and debasement procedures are normal in groundnut oil; the most regular changes comprise of triglyceride polymerization and hydrolysis, unsaturated fat and sterol oxidation, and Maillard responses. Oxidation can likewise change the flavor and nourishing nature of groundnut oil because of the loss of useful substances and the age of new lethal mixes including oxidized unsaturated fats, sterols or TAG polymers, which can possibly affect human wellbeing and make olive oil less worthy or unsatisfactory to shoppers(Aydenız and Yilmaz., 2016; Yorulmaz and Konuskan., 2017) . In this sense, differential examining calorimetry (DSC) is a method dependent on the estimation of the vitality changes that happen when an example is warmed, cooled, or held isothermally, just as the assurance of the temperature at which these progressions happen (Otun *et al.,* 2015). These estimations empower the portrayal of tests for a few complex occasions, for example, softening procedures or glass changes. As indicated by the official definition, additional virgin olive oil must be removed by cold and technician conditions in a sans oxygen air so as to safeguard the normally present cancer prevention agents(Schett *et al.,* 2017). In refined olive oil, cell reinforcements are corrupted because of refining procedures and high temperatures amid the olive oil generation; as a result, the enlistment time frame is shorter in lower quality olive oils and can be utilized to study and analyze the thermo-oxidative security of tests. In this sense, the oxidation of palatable oils shows the acceptance time frame, and toward the finish of the enlistment time frame, the nature of the oil all of a sudden falls apart with the goal that the enlistment period is considered as an estimation of the oil strength (Kozłowska and Gruczyńska, 2018). Another procedure that can be found in the writing is "Rancimat steadiness" which comprises of uncovering the olive oil to constrained oxidation at 100°C until its most extreme oxidation, estimating the time required for an unexpected change in conductivity from a fluid arrangement where the unstable mixes conveyed by the oil were gathered (Giacometti *et al.,* 2018; Yorulmaz and Konuskan., 2017). The length time of this period is considered as the file of protection from foulness of the fat being tested.

The point of the present examination is the quantitative investigation of the properties of groundnut the impact of temperature on the properties of oils in the wake of warming d likewise the utilization of same oil for fricasseeing three cycles to check the adjustments in oil quality. Changes in the physicochemical properties of oils are likewise broke down by FT-IR investigation to assess the level of oxidation in the wake of warming and browning.

MATERIALS AND METHODS

Chemicals

Hydrochloric acid (HCl), sodium hydroxide (NaOH), potassium hydroxide (KOH), idobromine (IBr), sodium thiosulphate ($Na_2S_2O_3$), potassium iodide (KI), and acetic acid (CH_3COOH) were of A.R Grade and purchased from Merck.

Heating materials

A domestic deep-fat fryer pan with a capacity of 3 liters was used. The oil of maximum capacity of fryer was taken and heated continuously at 180 °C for 3hrs per day and the sample was taken for analysis. The process was continued up to 3 days i.e. a total of 9 hrs of heating of oil. No new fresh oil is being added until the end of 3 hr in each day heating process. Fresh oil was added in the same pan (next day) with the previously heated oil for reuse after taking the reheated oil sample for analysis from each day.

Viscosity measurement

The trial measures were performing with Cannon-Fenske (Fisher Scientific, Pittsburgh, PA) glass capillary kinematic viscometers in a constant- temperature bath. (Kinematic viscosity = apparatus constant X efflux time). A programmable water bath (Model F25-HE, Julabo USA Inc. Allentown, PA) was used to ensure correct and stable temperature during measurements. The procedures in the ASTM D445 for viscosity determination were followed. Variations in viscosity as a function of temperature were measured.

$$V = c \times t$$

Where,
C = viscometer constant (mm^2/s^2)
T = time

$$\mu = v \times \rho$$

Where,
V = viscosity in mm^2/s^2
P = density of the oil

Density measurement

Densities of oil samples before and after heating were measured by an R.D bottle with a capacity of 10 mL.

Peroxide value (PV) Measurement

Peroxide value is a measure of peroxides contained in the oil. PV is determined by measuring iodine released from potassium iodide. A known measured weight of oil samples is dissolved in acetic acid then chloroform and saturated KI mixture is added to the sample and the amount of iodine liberated from KI by the oxidative action of peroxides present in the oil is determined by titration with standard sodium thiosulphate using the starch solution as an indicator. Titration was also performed for blanks. (AOAC, 1984)

PV (meq/kg oil) = (S-B) X W X N
Where,
B is the volume of sodium thiosulphate used for blank,
W is the weight of the sample,
S is the volume of sodium thiosulphate consumed by the sample oil and
N is the normality of standard sodium thiosulphate

Saponification value measurement

The saponification value is determined by taking 1.0 g of oil sample in a conical flask to which is added 15 mL 1 N KOH and 10 mL of distilled water and heated under a reserved condenser for 30–40 min to ensure that the sample was fully dissolved. After this sample was cooled, phenolphthalein was added and titrated with 0.5 M of HCl until a pink endpoint was reached. A blank was determined with the same time conditions.

Iodine value (IV) measurement

A known weight of the oil sample is treated with an excess of iodobromine (IBr) in glacial acetic acid. Unreacted iodobromine is countered with potassium iodide which adapts it to iodine. The iodine absorption is then determined by titration with standard sodium thiosulphate. (Singh *et al.,* 1981)

IV = (*b- v)* x N X 126:9 X 100/w X 1000

Where,

B is the quantity of sodium thiosulphate used for blank,
V is the quantity of thiosulphate for sample,
N is the normality of thiosulphate solution,
W is the weight of the oil sample and
126.9 is the molecular weight of iodine

Evaluation by FT-IR

FT-IR spectra of oil samples before and after heating were recorded with the help of a Fourier Transform Spectroscopy Model FTIR-8400S Shimadzu. It is used to study the saturation and unsaturation composition of heated and unheated oils at room temperature for monitoring the oxidation process in oils.

RESULTS AND DISCUSSION

The nature of groundnut oil was broke down by assessing physicochemical properties, for example, thickness, consistency, peroxide, iodine, and saponification esteems. Oils with lower estimations of consistency and thickness are exceedingly calculable to customers. So as to plan a progressed mechanical procedure these properties are significant parameters. The impact of temperature on these properties and the impact of warming multiple times up to their separate breaking points utilizing similar oil were additionally contemplated.

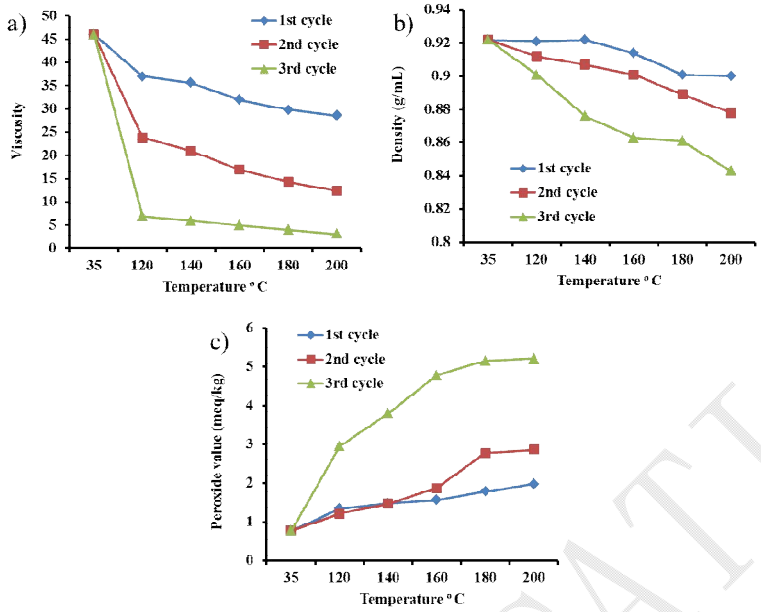


Figure 1 a) Viscosity, b) density and c) peroxide values of groundnut oils at temperature with three days cycles using the same oil.

Viscosity and density

Oils are blends of triglycerides (TGs) and their thickness relies upon the idea of the TGs present in the oil. The consistency changed because of the diverse course of action of the unsaturated fats on the glycerol spine of the triglyceride particle. In this way, consistency is identified with the substance properties of the oils, for example, chain length and immersion/unsaturation. It clarifies that the thickness and thickness diminish with an expansion in unsaturation and increments with high saturation and polymerization. Thickness likewise relies upon sheer pressure and temperature. Sheer pressure does not have much impact on the capacity of oils which are utilized for consumable purposes yet the temperature affects it. Results organized in Figure 1a uncovered that an expansion in viscosities was watched for the third-day cycle while a reduction was watched for the first-day cycle at the diverse temperature. At the point when the temperature builds the motor vitality additionally expands which upgraded the development of the particles and decreases the intermolecular powers. The layers of the fluid effectively ignore each other and along these lines add to the decrease of thickness. This wonder is likewise checked by different specialists since oil consistency relies upon the sub-atomic structure and diminishes with the unsaturation of unsaturated fats (Kim *et al.,* 2010).

The densities of the two oils were diminished with the ascent in temperature just as when utilizing a similar oil for warming with individual temperature. The densities of oils (Figure 1b) were identified with the first-day cycle scope of 0.90 g/mL, and second, third-day cycle and the estimations of the densities are 0.87 g/mL and 0.84 g/mL at 200°C for separately. Regularly, browning oils experience broad debasement and complex compound changes when warmed. The nearness of air and water quickened the crumbling of searing oil and brought about an expansion in the number of polar atoms as affirmed by the width of oils.

Peroxide value (PV)

Peroxide esteem (PV) is utilized as a proportion of the degree to which rancidity responses have happened amid capacity it could be utilized as a sign of the quality and dependability of fats and oils (Romero et al., 2003). The peroxide esteem was additionally found to increment with the capacity time,

temperature and contact with a demeanor of the oil tests. The PV esteems (Figure 1c) demonstrate that the peroxide esteems for third-day cycle expanded from 0.76 (35°C) to 0.50 meq/kg (breaking point 200°C) and 1.98 meq/kg (first-day cycle) and after that, it diminished at second and third-day cycle. There is a progressive abatement in PV when a similar oil was utilized for warming with an alternate cycle. The peroxide esteem decides the degree to which the oil has experienced rancidit (Xiuzhu *et al.,* 2007).

Saponification value

Saponification value (SV) is a list of the normal atomic mass of unsaturated fat in the oil test. The SV esteem acquired for the oil tests in Figure 2a demonstrated 185.38 mg KOH/g first cycle and 125.6 mg KOH/g for the second cycle. 198.09 mg KOH/g for the third cycle. The lower estimation of saponification esteems recommends that the mean sub-atomic load of unsaturated fats is lower or that the quantity of ester securities is less. This may infer that the fat particles did not associate with one another (Denniston *et al.,* 2004).

Iodine value

Iodine value (IV) measures the level of unsaturation in fat or vegetable oil. It decides the steadiness of oils to oxidation and permits the general unsaturation of the fat to be resolved subjectively. It was watched (Figure 2b) that estimated iodine esteems for the first cycle and the third cycle are 94.00 g and 68.79 g separately. This low iodine esteems may have added to its more noteworthy oxidative capacity soundness. The oxidative and compound changes in oils amid capacity are described by an expansion in free unsaturated fat substance and a reduction in the complete unsaturation of oils (Perkin, 1992).

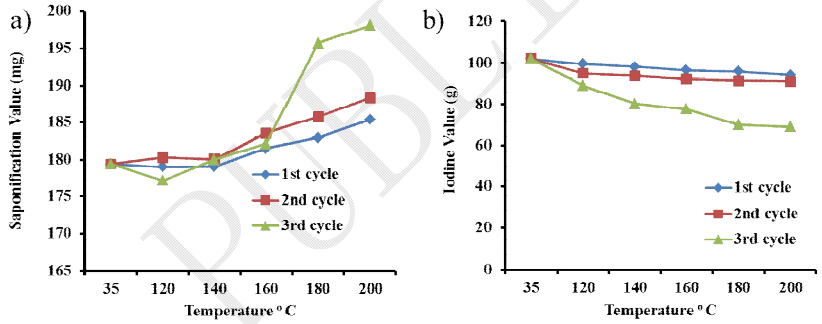


Figure 2 a) Saponification, b) Iodine value of groundnut oils at temperature with three days cycles using the same oil.

these physicochemical parameters, for example, thickness, thickness, peroxide esteem, iodine esteem, and saponification esteems are subjective properties of oils and don't demonstrate the situation of the twofold securities or the measure of olefinic carbon yet rather it gives a general status of unsaturation of the oils so it is beyond the realm of imagination to expect to bring up the situation of twofold bond(s) which are progressively defenseless to oxidation.

SPECTRAL ANALYSIS

FT-IR spectroscopy is a magnificent device for investigation as the powers of the groups in the range are relative to focus. Mid-IR spectra have been utilized to portray eatable oils and fats since they contrast in the force and the accurate recurrence at which the maximum absorbance or transmittance of the band shows up, as indicated by the nature and creation of the example.

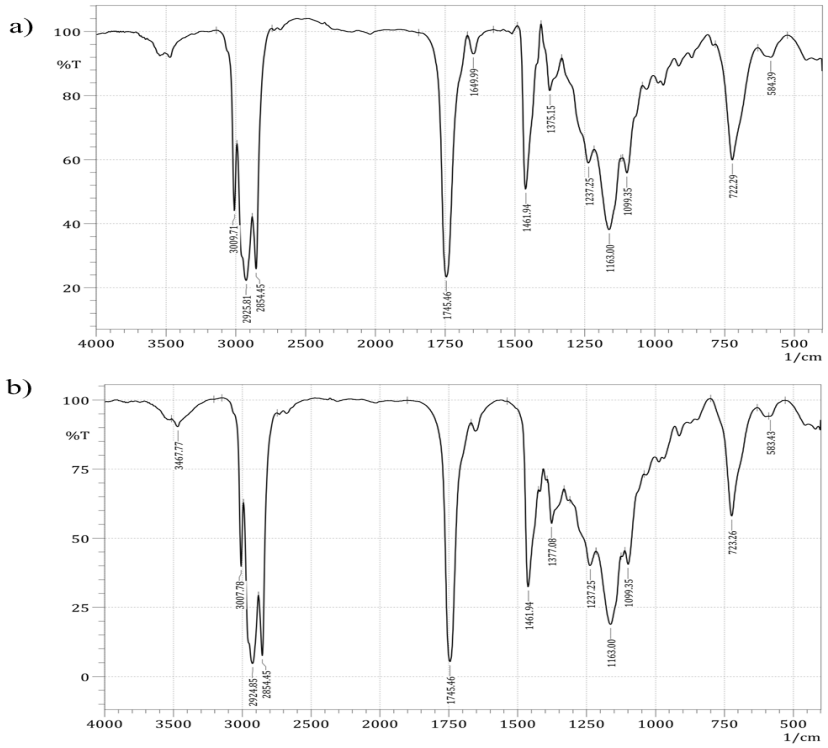


Figure 1 a) First-day cycle, b) Third-day cycle of groundnut oils of FT- IR spectrum at temperature with three days cycles using the same oil.

FT-IR spectra of the first-day cycle and third-day cycle demonstrated that there exists a prominent contrast in the band at room temperature, at breaking point and between a similar oil utilized for warming. The oil structure influences the precise places of the band and yields a move when the extent of unsaturated fats changed. At room temperature Figure. 3a and 3b the band around 3467 cm^{-1} doled out to OAH extending vibration of hydroperoxide, 3009.71–3007.78 cm^{-1} as CAH extending vibration of the cis-twofold bond ,CAH and 2924.85–2924.81 cm^{-1} indicates CAH deviated and symmetric extending vibrations of the aliphatic CH_2. At various temperatures and amid warming multi-day cycles, the rate transmittance of practically every one of the pinnacles expanded showing a decline in absorbance which might be because of the hydrolysis of oil amid singing and the arrangement of free unsaturated fats and mono and diglycerides. These mixes collected in the browning oil with rehashed use as the hydroperoxides likewise decline which might be because of decay of hydroperoxides and auxiliary oxidation inception. At 35^{o}C Figure. 3(a) and 3(b) and at the breaking point of the First-day cycle and third-day cycle, the area of the twofold bond extending appeared 1745.46 cm^{-1} speaks to C,O ester carbonyl of triglycerides and at 1649.99 cm^{-1} demonstrates C,C extending vibration of the cis olefins as appeared in Figs. 3(a) and 3(b) separately. This perception demonstrates that there is the nearness of a soaked aldehyde practical gathering or other optional oxidation items which makes an absorbance cover with the extending vibrations at 1745 cm^{-1} of the ester carbonyl useful gathering of the triglycerides. Similar examples were seen at the breaking point. As the ghastly locales experience a few changes amid oxidation forms at the room temperature and at various temperatures oils demonstrated a few areas of different disfigurements and twisting at 1461cm^{-1} of ACAH bowing vibrations of the CH_2 and CH_3 aliphatic gatherings and at 1375.15–1377.08 cm^{-1} of ACAH bowing vibrations (Guillen and Cabo, 2000).

The real tops in these spectra that emerge from the extending vibration of CAO at 1163.0–1237.25 cm^{-1} and at 722.29, 723.26 cm^{-1} speak to (ACH_2), ACH,CHA covering of the CH_2 shaking and the out of plane vibration of cis-di substituted olefins. Every one of these adjustments in the otherworldly areas demonstrated a few changes amid the oxidation procedure. The recurrence of the 3007.0 cm^{-1} bands relies upon the oil structure as oil with a high extent of linoleic or linoleic acyl gatherings show higher recurrence information at this band than oils with a high extent of oleic acyl gathering. The band at 2854.25 cm^{-1} and the shoulder at 2925 cm^{-1} increment their force yet the band lessens its absorbance and expands percent transmittance.

The assessed consequences of First day cycle and uncover third day cycle that at the level of unsaturation is low and there are trans hydroperoxide types of esters present with essential oxidized items and as the example is treated at higher temperatures up to their separate breaking points when boiling with a bit of potato the lessening in %T demonstrates an expansion in the absorbance of peroxides. Optional oxidation starts the development of auxiliary oxidation items and free unsaturated fats were additionally present. Along these lines, each kind of oil test including crisp oil at room temperature and utilized oils (at various temperatures) demonstrated fundamentally the same as FT-IR spectra. Anyway, the statures of some particular groups were observable demonstrating the distinction in nature of the two diverse oil tests utilized in this present examination.

4. CONCLUSION

Profound heating and the utilization of the same oil for browning commonly is a general practice for the most part in business and here and there in residential cooking forms. This training creates lipid peroxidation items that might be hurtful to human wellbeing. The greater part of these mixes are non-unstable, so they stay in the heating medium and influence its physical properties at raised temperatures within the sight of air and dampness causing the oxidative debasement of their amino acids and the halfway transformation of these lipids to unpredictable chain-scission items, nonvolatile oxidized subsidiaries and dimeric, polymeric or cyclic substances promoting the arrangement of poisonous and additionally cancer-causing mixes.

The consequences of this specific examination recommended that continued/repeated heating of oil bit by bit decreased the wellbeing defensive impacts. As in groundnut oil at the breaking point, there is an extra crest at 3467.77 cm^{-1} which displays that the optional oxidized item has been framed. The estimation of physicochemical properties by FT-IR spectroscopy gives the advantage of quick examination as well as maintains a strategic distance from the concealed transfer costs just as threats related to reagents utilized in the conventional concoction technique. The present research might be sent in numerous perspectives not exclusively to upgrade the nature of oil yet additionally give open mindfulness not to open eatable oils to high temperatures for extensive stretches ordinarily.

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Selvaraj Rama Jeba
Department of Food Science and Nutrition, Periyar University, Salem, Tamil Nadu, India.