

Quality characteristics and oxidative stability of coconut oil during storage

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Abstract

The main objective of this study is to investigate some quality characteristics based on which we can evaluate oxidative stability of coconut oil during 12 month of storage. The progress of lipid oxidation was assessed by measuring peroxide value (PV), p-anisidine value (AV) and total oxidation value (TOTOX). The low peroxide value (0.24–0.49 meq/kg oil) signifies a high oxidative stability, while p-anisidine values were in the range 0.19-0.87. Fourier transform infrared (FTIR) spectroscopy was used to monitor the peak changes as effect of oxidation during storage. The prominent peak change observed during storage of coconut oil was at frequency 1742 cm⁻¹ which corresponded to the ester carbonyl functional group of the triglycerides resulted from the hydroperoxide decompositions. These results suggest that coconut oil during 12 month on storage keeps its good chemical properties.

Keywords: coconut oil, peroxide value, p-anisidine value, oxidative stability, FTIR spectroscopy

1. Introduction

The coconut palm is the species *Cocos nucifera*, which grows well in the humid regions a few degrees' latitude either side of the equator. Fresh coconut kernel contains: moisture (50%), oil (34%), ash (2.2%), fibre (3.0%), protein (3.5%) and carbohydrate (7.3%) [1]. Coconut oil is produced by crushing copra, the dried kernel, which contains about 60- 65% of the oil. The oil has the natural sweet taste of coconut and contains 92% of saturated fatty acids (in the form of triglycerides). Coconut oil has a long shelf life and is used in baking industries, processed foods, pharmaceuticals, cosmetics and as hair oil [2]. The oil degradation can be caused by oxidation, hydrolysis, polymerization, pyrolyses and absorption of external flavors and odors. The oxidative reactions can be influenced by several factors such as light, heat, ionization, traces of metals, and metaloprotein, oxygen reaction with unsaturated lipids, and by chemical, and enzymatic mechanisms such as

autoxidation, photo-oxidation and lipoxygenases [3]. The coconut oil is highly stable towards atmospheric oxidation [2]. Oxidative stability of oils is the resistance to oxidation during processing and storage [4]. Oxidative stability is an important parameter for the quality assessment of fats and oils. Autoxidation is affected by atmospheric oxygen and the oxidation process proceeds via free radical reactions involving unsaturated fatty acids. The primary products formed are hydroperoxides, which subsequently break down in a series of complex reactions, to yield secondary products including alcohols and carbonyl compounds. These can be oxidized further to carboxylic acids [5]. FTIR spectroscopy has been used for determination of molecular structures, identification of compounds in oil samples and investigation of complex polymer. Currently, FTIR spectroscopy has gained a special attention as a reliable technique for fat and oil analysis, due to its finger print technique [6].

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In our country the coconut is known but about coconut oil needs to be said more; the objective of this study is to analyze some characteristics and oxidative stability during storage because this parameters have a significant influence on oil quality

2. Materials and methods

Oil extraction. Oil samples were obtained from grated coconut flakes and were extracted using an automated extractor (Velp Scientifica, Italy) with petroleum ether (1:5) for 3h. In order to assess the oxidative stability, oil samples were stored in a dark bottle at room temperature (25°C) during 12 month. Classic chemical methods for determining primary and secondary oxidation products (peroxide value and p-anisidine value) were determined periodically (at 3 month). Oxidative stability by FTIR spectroscopy was made on fresh (non oxidized) oil and after one year of storage.

Determination of oil quality: The peroxide value (PV) was determined iodometrically according to standard methods for the oils analysis and the results were expressed in meq/kg oil [7].

The p-anisidine value (p-AV) is a measurement of carbonyl content in the oils or fats, and was determined by the standard method according to AOCS [7]. It is based on the reactivity of the aldehyde carbonyl bond on the p-anisidine amine group, leading to the formation of a Schiff base that absorbs at 350 nm. 2 g (w) of coconut oil samples were dissolved in 25 mL isooctane and absorbance (A1) of this fat solution was measured at 350 nm against a blank of isooctane. An aliquot (5 mL) of this solution, respectively 5 mL of isooctane (as blank) was transferred to each of two test tubes of 10 mL and 1 mL anisidine solution (0.25% g/v glacial acetic acid) was added to each. After 10 min, the absorbance (A2) was measured at 350 nm against isooctane containing p-anisidine. p-AV was calculated according to the formula (1):

$$p-AV = 25 \times \frac{1.2 \times A_2 - A_1}{w} \quad (1)$$

The total oxidation value (TOTOX) was used to estimate the oxidative deterioration of lipids. TOTOX value is defined as the sum of both values (PV and p-AV) to total oxidation and was calculated according to the formula (2) [8]:

$$TOTOX \text{ value} = 2PV + p-AV \quad (2)$$

All determinations were carried out in triplicates. All of the reagents and solvents used were of analytical reagent grade.

FTIR spectroscopy. Absorption spectra of oil samples were measured on a Fourier Transform Infrared Spectrophotometer - FTIR-8400S by Shimadzu (Japan) using a high sensitivity pyroelectric detector DLATGS (L-alanine-doped deuterated triglycerine sulphate) element. The detector relies upon the temperature-dependent pyroelectric effect created on the crystal surface by spontaneous ferroelectric polarization. All FTIR spectra were recorded in the wavenumber range from 4000-600 cm⁻¹. BKG scan a samples were sequentially measured at 4 cm⁻¹ resolution, and 2.8 mm/s mirror speed with 45 accumulations (1 minute scan). Background measurements were made against air. The spectrometer was connected to a computer using Windows XP Professional software to manipulate the spectra.

3. Results and Discussion

The peroxide index is the most common parameter used to characterize oils and fats [9], a product with peroxide value between 1 and 5 meq/kg is classified at low oxidation state; that between 5 and 10 meq/kg at moderate oxidation and above 10 meq/kg is classified at high oxidation state. However, Codex gives a peroxide value limit of 15 meq/kg for virgin oils in general [10]. The number of peroxides present in vegetable oils reflects its oxidative level and thus its tendency to become rancid. Theoretically, coconut oil should exhibit a low rate of oxidation due to its low content of unsaturated fatty acids. Unsaturated fatty acids easily react with oxygen to form peroxides. Oils with high peroxide values are unstable and easily become rancid [11]. The peroxide values obtained were relatively low, indicating that the samples were highly stable against oxidation.

The PV obtained in the present study showed that 0.24–0.49 meq/kg which was far below the maximum limits. PV increases from month to month but after 9 month the values decreased from 0.49 by 0.44 meq/kg (Figure 1) when the secondary oxidation products appear.

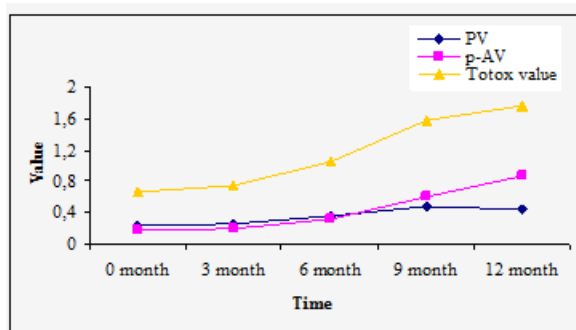


Figure 1. The PV, p-AV, TOTOX value of coconut oil samples

In the second phase of oxidation, the primary product of oxidation, peroxides decompose and develop substances such as aldehydes, which are responsible for the rancid smell and taste. Theoretically, virgin coconut oil should exhibit a low rate of oxidation due to its low content of unsaturated fatty acids. Unsaturated fatty acids easily react with oxygen to form peroxides. Oils with high peroxide values are unstable and easily become rancid [11].

Anisidine value test measures this secondary oxidation. The anisidine value measures high-molecular weight saturated and unsaturated carbonyl compounds in triacylglycerols [12]. The anisidine value for coconut oil samples ranged from 0.19 to 0.87. There were significant differences in the anisidine value among the coconut oil samples.

The lower the TOTOX value, the better the quality of oil. According to Rossell [13, 14], oils with an anisidine value below 10 were considered as good quality, while Subramaniam et al. [13, 15] considered good quality oils as having an anisidine value of less than two. Since coconut oil samples obtained in this study has anisidine values of less than 1, it indicated that the quality of the oils was good.

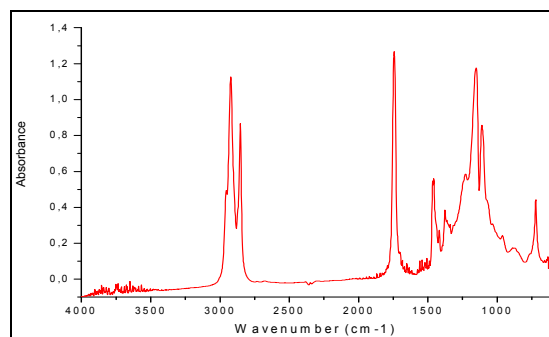


Figure 2. FTIR spectra of non oxidized (fresh) coconut oil

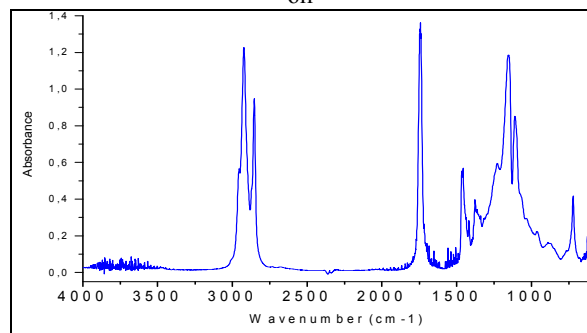


Figure 3. FTIR spectra of coconut oil during storage

Figures 2 and 3 show FTIR spectra of non oxidized coconut oil and at the end of storage time. The functional groups responsible for infrared absorption at each frequency in virgin coconut oil spectrum are as reported by Rohman et al. [6]. The FTIR spectra of vegetable oils present a series of bands with different intensities and forms. Some regions of the spectra present a very good signal/noise ratio, which corresponds to various types of vibration characteristic to different types of atoms [16]. The results obtained by measuring the intensity of FTIR absorption at different frequency for the analyzed coconut oils are presented in Table 1.

Table 1. FTIR absorption for non oxidized coconut oil and during storage

Oil sample	Frequency (cm-1)										
	2922	2953	2852	1742	1450	1417	1377	1151	1111	962	721
Non oxidized oil	1.12	0.49	0.86	1.26	0.39	0.27	0.38	1.17	0.85	0.24	0.44
During storage	1.22	0.56	0.55	1.36	0.38	0.27	0.39	1.18	0.85	0.22	0.41

The vegetable oils do not have infrared absorption to interval $4000\text{-}3100\text{ cm}^{-1}$ because corresponding by O-H functional group (polymeric and water impurities) [16].

The spectrum showed that the band of C-H stretching with wavenumber of $3000\text{-}2800\text{ cm}^{-1}$ indicates the presence of alkanes groups in the oil [17]. The asymmetrical or symmetrical stretching vibration of methylene band was observed at 2922 cm^{-1} and 2852 cm^{-1} [4,6]. The asymmetrical stretching vibration of methyl ($-\text{CH}_3$) causes a shoulder at wavenumber of 2953 cm^{-1} , where as the symmetrical vibration of methyl band is not observed.

The absorption of carbonyl (C=O) functional group from ester linkage of triacylglycerol of coconut oil can be seen at frequency 1742 cm^{-1} with strong intensity due to the great difference of electronegativity between carbon and hydrogen atoms [17]. The spectral differences were observed between non oxidant coconut oil (1.26) and during storage oil (1.36), where oil presented high absorbance.

The intensity from interval $1600\text{-}1400\text{ cm}^{-1}$ has a linear variation and therefore can be used for identifying the storage oxidation. The C=C stretching vibrations from FTIR spectrum indicate presence of aromatics compounds. This band can be used to determine the total unsaturation [16]. An absorption band at 1417 cm^{-1} is attributed from rocking vibrations of CH bonds of alkenes with *cis*-disubstituted

The symmetric bending vibration of CH_3 group can be seen at wavenumber 1377 cm^{-1} .

The bands 1151 and 1111 cm^{-1} are attributed from the vibrations of stretching mode from the C-O group in esters [17]. An absorption band at 1111 cm^{-1} is attributed from $-\text{CH}$ bending and $-\text{CH}$ deformation vibration of fatty acids; has the same value (0.85) for non oxidized coconut oil and during storage. An absorption band at frequency of 962 cm^{-1} is related to bending vibration of *cis* disubstituted olefinic groups.

Finally, absorption peak at frequency 721 cm^{-1} is resulted from the rocking vibrations of methylene group which overlaps with bending vibration on out of plane mode of alkenes with *cis*-disubstituted [4, 6].

The storage conditions have not change the peak intensities of coconut oil at studied frequencies that prove the high stability of this oil during investigated time.

4. Conclusion

Accordingly, based on our results we can say that PV of coconut oil samples significantly increased during 12 months of storage. The physico-chemical oxidation of this oil kepted at room temperature was negligible. No significant differences between the oxidative parameters recorded for non oxidized coconut oil samples and those registered at the end of storage were obtained, which means that coconut oil is stable for a long time. It was concluded that coconut oil quality is not affect during 12 months of storage. FTIR spectroscopy may be able to substitute classic chemical methods being a valuable tool to assess the oxidative stability of vegetable oil.

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