A study on monitoring of frying performance and oxidative stability of virgin coconut oil (VCO) during continuous/prolonged deep fat frying process using chemical and FTIR spectroscopy

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Abstract The performance or quality of the Virgin coconut oil (VCO) during continuous/prolonged deep fat frying of soaked bengal gram dhal was evaluated at $180 \pm 5^\circ\text{C}$ for 8 h with the help of physico-chemical and rheological parameters. Chemical changes indicated that the free fatty acid (FFA) content and TBA increased significantly ($p \leq 0.05$) from 0.11 to 0.98 % lauric acid and 0.06 to 0.61 malonaldehyde/kg of oil respectively. Initially, the peroxide value (PV) of VCO sample was 3.25 meqO₂/kg which increased to 9.12 meqO₂/kg after 6 h of frying but at the end of frying the value of PV was again found to decrease (8.01 meqO₂/kg). The regression coefficients (R^2) between CD₂₃₂, CT₂₇₀ and frying time were 0.964 and 0.983 respectively. The L*, a* and b* colour values measured on the CIELAB colour scale showed a decrease in L* and increase in a*, b* values after 8 h of continuous frying. The *p*-AV and total polar compounds were increased significantly ($p \leq 0.05$) from 2.41 to 17.93 and 2.77 to 8.14 % respectively. Initially, the viscosity of VCO was 49.87cp which increased to 69.87cp after 8 h of continuous frying. The FTIR spectra justify that VCO samples after 8 h of frying found to be stable and acceptable as there was no change occurred at $1,739 \text{ cm}^{-1}$ frequency which mainly corresponded to carbonylic compounds resulted from the hydroperoxide decompositions after 8 h of continuous frying.

Keywords Virgin coconut oil (VCO) · Viscosity · Peroxide value (PV) · Total polar compounds · Specific absorptivity · FTIR

Abbreviations

VCO	Virgin coconut oil
FFA	Free fatty acid
PV	Peroxide value
CD	Conjugated diene
CT	Conjugated triene
<i>p</i> -AV	<i>p</i> -anisidine
IV	Iodine value
PUFA	Polyunsaturated fatty acids
MUFA	Monounsaturated fatty acids
TPC	Total polar compounds
TBA	Thio barbituric Acid
FTIR	Fourier transform infra red spectroscopy

Introduction

Deep fat frying is one of the most common domestic practices or an intense process for inducing many of chemical reactions in the frying medium and generating a plethora of chemical compounds (Belitz et al. 2004). It is the process in which food is heated in the presence of air and fat. Therefore, the fat is exposed to the action of moisture from the food stuff, oxygen from atmosphere and high temperature at which the operation takes place (Krishnamurthy and Chang 1967). During frying, the quality of fat decrease as evidenced by a decrease in heat capacity, surface, interfacial tension while increases in specific gravity, viscosity, acid values and polymer content (Blumenthal and Stier 1991). The moisture from the foodstuffs causes hydrolytic reactions giving rise to free fatty acids, monoglycerides, diglycerides and glycerol. The atmospheric oxygen causes oxidative reactions giving rise to oxidized monomers, dimmers and polymers. With prolonged heating time the amount of polar substances rises

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steadily. Oil is considered to be thermally abused when the polar compounds reached 24 % levels; whereas the absolute upper limit is 27 % (Firestone 1993). Oils with high linolenic acid have been reported to be poor frying oils since they rapidly deteriorate when subject to frying conditions (Bracco et al. 1981).

The term VCO refers to an oil that is obtained from fresh, mature kernel of the coconut by mechanical or natural means, with or without the use of heat and without undergoing chemical refining (Villarino et al. 2007). Virgin coconut oil, now a days coined as emerging functional food oil. Term ‘virgin’ comes out from the method of extraction of oil which leads to the retention of more biologically active components. Presently public awareness has been increasing on functional food oil and it is expected that VCO will gain dramatic growth in the market. It has many health benefits such as preventing the oxidation of low density lipoprotein, increasing the anti-oxidant enzymes, helps in foot crack healing, scar removal, reducing the cholesterol and triglyceride level (Nevin and Rajamohan 2004). Among the all carrier oils, VCO has as high potential as carrier oil for aromatherapy because solubility of polar phenolic substances in non polar coconut oil is certainly improved at high temperature (Kapila et al. 2009). Chen man and Wan Hussin (1998) studied frying performance of palm olein and coconut oil by frying of potato chips at 180 °C for 5 h/day for consecutive days. Warner and Knowlton (1997) reported that refined bleached deodorized palm oil was superior to refined bleached deodorized coconut oil in frying performance. Lu and Tan (2009) studied the storage stability in virgin coconut oil and extra virgin olive oil upon thermal treatment and found that VCO was considered as good frying oil as it has relatively high oxidative stability as compare to extra virgin olive oil.

The present study is in line with the continuing efforts of researchers to provide more information and shed light on the frying performance and chemical changes occur in VCO during 6 h continuous/prolonged frying of soaked Bengal gram dhal (chick pea).

Materials and methods

Extraction of VCO

VCO can be extracted directly from the fresh coconut meat or from coconut milk. It involves two major steps: production of coconut milk and extraction of oil. Extraction of oil can be done by two ways cold and hot extraction process.

Preparation of coconut milk

The production of coconut milk involves selection of nut, dehusking, deshelling, testa removal, washing, grating and

milk extraction. Fully matured 10–11 months old coconut nuts were selected for VCO production. As an indicator of maturity of the nut, the husk will be yellowish to brown in colour and makes a sloshing sound when shaken. By a special type of tool the shell was removed and two halves kernel was scoop out by knife. The testa of coconut kernel removed by testa remover machine. The coconut kernel free from testa was fed to the mechanical grating machine (contain rotating blades). Coconut milk was extracted from the gratted coconut meat using manually operated hydraulic coconut milk press. The coconut milk obtained from the first extraction was collected separately and residue was utilized for second and third extraction. Pool the first, second and third milk extracts by stirring vigorously for few minutes.

Preparation cold extracted VCO

In cold extraction method coconut milk was allowed to stand for 20–24 h. Under favorable conditions (35–40 °C, 75 % Relative Humidity), the oil separated from the water and the protein. The air borne lactic acid bacteria, which has the capability to break the protein bonds, act on the coconut milk mixture causing the VCO separation. By proper operating conditions and sanitary precautions were strictly followed, four distinct layers could be visible in the container after settling for 20–24 h. The bottom layer was made up of gummy sediment. The next layer was the watery, fermented skim milk that is no longer fit for human consumption. The next layer was the separated oil for recovery as VCO. The top layer was floating fermented curd. The fermented curd also contained a considerable amount of trapped oil. By carefully separating the distinct layers, the oil can be separated. The separated oil contained some adhering particles of fermented curd and it need filtration. Oil was filtered through sterilized filter paper placed in big funnel.

Preparation of hot extracted VCO

Coconut milk is an emulsion of oil and water that is stabilized by protein. To recover the oil from coconut milk, the protein bond had to be broken by heat in double walled boiler known as VCO cooker under slow heating to coagulate the protein and release the oil. Separate the class A oil from the protenacious residue (kalkam) by straining the mixture through a muslin cloth. The remaining kalkam can be further slow heated to remove more oil (Class B).

Frying test design

Laboratory scale frying test was carried out initially on commercially available oils namely sunflower oil, palm oil, soybean oil. The operation cycle for the frying was optimized by the acceptance of the fried dhal at different temperature (150,

160, 170, 180, 200 °C) and time (1 min, 2 min, 3 min, 4 min, 5 min) by 25 persons. Each person was presented dhal fried in respective oil sample and was asked to grade the sample in respect of flavor, taste, aroma, texture of the dhal and surface feel of the fried item like oiliness, greasiness etc. on a 9 point, hedonic scale with 1 for highly disliked while 9 for highly liked sample.

Frying protocol

Bengal gram dhal (8 kg) was soaked in water (25 L) for 4 h. The soaked dhal was filtered through a muslin cloth and tightly squeezed to remove excess water. Soaked Bengal dhal was placed in a stainless steel wire mesh basket and fried in VCO. In order to study the frying performance of VCO, the oil sample (4 L) was heated to 180 °C $\pm$ 5 °C in a frying pan and soaked Bengal gram dhal (400 g at a time) were fried continuously for 8 h (48 frying cycles) at the rate of 2.4 kg soaked dhal per hour. The oil temperature was found to be decreased to 150 °C $\pm$ 5 °C when soaked dhal added during frying operation. The oil was not replenished with fresh oil during frying operation. After every hour of frying, oil samples (100 ml) were withdrawn into a screw cap vial for chemical (free fatty acid, peroxide value, refractive index at 40 °C, iodine value, total carbonyl, anisidine value, polar compounds) and physical parameters (CIE color value, viscosity, specific gravity).

Determination of viscosity, FTIR, specific gravity and CIE color value

Dynamic rheological studies of VCO were performed on Modular Compact Rheometer (Physica, Model MCR 100, USA). The data were recorded using US 200/32 V₂; 3021001472-33024 software (USA) using the probe CC 27. Samples were loaded in the cup of the rheometer and covered with flap. A circulatory water bath was employed to keep the temperature of measurement at 25 $\pm$ 0.1 °C using 100 s⁻¹ as shear rate.

The Specific gravity which is considered as a good index of purity of oils was analyzed by the method described Kazadi et al. (2011). The color values of the samples were recorded using a colour meter (Mini Scan XE Plus, Model 45/0-S; Hunter Associates Laboratory, Inc., Reston, VA, USA) as reflected in CIELAB (L*, a*, b*) colour space. All the measurements were referenced to the CIE (Commission Internationale de l'Éclairage) using the standard illuminant D 65 and 10° observer, and the equipment was calibrated using a white and black standard ceramic tile.

Infrared spectra were recorded in a Nicolet 5700 interfaced to a personal computer operating with Windows-based Nicolet Omnic software (version 3.1). A film of the oil sample was deposited between two disks of NaCl. The

spectra were recorded from 4,000 to 500 cm⁻¹, the number of scans being 256 at a resolution of 4 cm⁻¹.

Estimation of free fatty acid (FFA) content, peroxide value (PV), iodine value, anisidine value, polar compounds, TOTOX value, total carbonyl, antioxidant activity and polyphenol content

Polar compounds were analysed according to the AOCS (1989) method, Cd11C-93 by column chromatography. Free fatty acid (FFA) content, peroxide value (PV), iodine value of control and fried oil samples were determined as per AOCS (1989), method No. Ca 5a-40, cd 8-53 and Cd 1-25/93 respectively. Anisidine value and total carbonyl were estimated by List et al. (1974) and Henick et al. (1954) respectively. All the analyses were done in triplicates and average values were calculated. Total amount of intermediate polar compounds (peroxides and aldehydes) that result from lipid oxidation was measured as totox number (Shahidi and Wanasundara 2002). The antioxidant activity and total polyphenolic compounds were measured by a method described by Karioti and Hadjipavlou Litina (2004) and Singleton et al. (1999) respectively. TBA was measured by the method of Arya and Nirmal (1971). Refractive index was estimated by Abbes refractometer according to AOAC (1989) method.

Estimation of fatty acid composition and specific absorptivity (CD₂₃₂ and CT₂₇₀)

Fatty acid composition of oils were determined by standard AOCS (1989) methods using gas liquid chromatography (Model HR 1000, Chemito, Chennai, India) with 10 % diethylene glycol succinate (DEGS) column. Conjugated diene and conjugated triene were determined by specific absorptivity (CD₂₃₂ and CT₂₇₀) as described by Rohman et al. (2011) using UV–vis spectrophotometer (Shimadzo, UV 1601, Japan).

Statistical analysis

Data (5 replicates) were subjected to statistical analysis of variance (ANOVA) and Duncan's Multiple Range Test (DMRT) was applied to differentiate among the means of different samples at a probability of $p \leq 0.05$.

Result and discussion

Changes in peroxide value (PV), free fatty acid content (FFA), TBA, total polar compounds (TPC), total oxidation (TOTOX value) and p-anisidine value

The results showed that initially frying leads to significant ($p \leq 0.05$) increase in peroxide value from 3.25 to 9.12 meq

Table 1 Changes in peroxide value (PV; meq O₂/kg oil), free fatty acid (FFA; % lauric acid), thiobarbituric acid (TBA; mg malonaldehyde/kg oil), polar compounds (PC; %), iodine value (IV; g I₂/100 g), anisidine value (AV), total carbonyl (TC; mg hexanal/100 g oil), totox value (TV) of VCO after 8 h of continuous frying of soaked bengal gram dhal

Frying time (h)	PV	FFA	TBA	PC	IV	AV	TC	TV
0	3.25 ^a ±0.01	0.11 ^a ±0.01	0.06 ^a ±0.001	2.77 ^a ±0.01	7.91 ^a ±0.02	2.41 ^a ±0.11	4.25 ^a ±0.01	8.91 ^a ±0.24
1	5.13 ^b ±0.02	0.19 ^b ±0.02	0.09 ^a ±0.002	2.89 ^a ±0.02	7.86 ^a ±0.11	3.67 ^b ±0.12	4.39 ^a ±0.02	13.93 ^b ±0.12
2	6.97 ^c ±0.11	0.23 ^b ±0.03	0.11 ^b ±0.001	3.11 ^b ±0.10	7.54 ^a ±0.10	5.01 ^c ±0.23	5.26 ^b ±0.04	18.95 ^c ±0.38
3	7.21 ^{cd} ±0.10	0.35 ^c ±0.01	0.15 ^b ±0.001	3.49 ^b ±0.11	7.41 ^a ±0.13	7.56 ^d ±0.14	6.87 ^c ±0.03	21.98 ^d ±0.19
4	8.12 ^{de} ±0.12	0.57 ^d ±0.02	0.21 ^c ±0.002	4.49 ^c ±0.12	7.21 ^a ±0.13	8.98 ^e ±0.21	8.25 ^d ±0.01	25.21 ^e ±0.10
5	8.24 ^{efg} ±0.13	0.74 ^e ±0.01	0.32 ^d ±0.002	5.02 ^d ±0.13	7.01 ^{ab} ±0.10	11.72 ^f ±0.13	9.12 ^e ±0.02	28.21 ^f ±0.29
6	9.12 ^f ±0.12	0.86 ^f ±0.02	0.45 ^e ±0.003	6.67 ^e ±0.14	6.90 ^b ±0.09	14.14 ^g ±0.32	10.23 ^f ±0.04	32.38 ^g ±0.41
7	8.33 ^g ±0.11	0.93 ^f ±0.03	0.54 ^f ±0.001	7.51 ^f ±0.17	6.89 ^b ±0.08	16.35 ^h ±0.24	12.56 ^g ±0.03	33.01 ^h ±0.14
8	8.01 ^g ±0.09	0.98 ^f ±0.01	0.61 ^g ±0.002	8.14 ^g ±0.07	6.72 ^b ±0.09	17.93 ⁱ ±0.25	14.65 ^h ±0.05	33.95 ^h ±0.13

Mean values with the same superscript letters within the same column do not differ significantly ($p \leq 0.05$)

O₂/kg after 6 h of frying then there was significant ($p \leq 0.05$) drop to 8.01 meq O₂/kg after 8 h because generally peroxides formed are unstable at the frying temperature and as oil deterioration continues the hydroperoxides decomposes forming carbonyl, aldehydic compounds causing the peroxide value to decrease. This is the reason why the amount of peroxides in the oil cannot be used to estimate the extent of oil deterioration (Shahidi and Wanasundara 2002).

Initially, the free fatty acid of VCO was 0.11 % lauric acid but after 8 h of continuous frying there was significant ($p \leq 0.05$) rise in FFA to 0.98 % lauric acid. The amount of FFA in fats and oils is a good indicator of the extent of its deterioration due to hydrolysis of exposed triglycerides and oxidation of fatty acid double bonds during frying process. FFA (by titration) can not differentiate between acids formed by oxidation and that by hydrolysis, the increase in FFA is a poor measure of frying fat deterioration if used alone (Abdulkarim et al. 2007). On the other hand, there was a significant ($p \leq 0.05$) increase in TBA value observed after 1 h of frying of soaked bengal gram dhal. The correlation coefficient between frying time and TBA value was high i.e. 96.9 %. The regression equation ($Y = 0.0673x + 0.0012$) revealed that

the frying time needed about 14.84 h for the formation of 1 mg malonaldehyde for 1 kg of oil when same heating condition were employed (Hassan and Abou Arab 2004).

Data in Table 1 showed significant ($p \leq 0.05$) increase from 2.77 % to 8.14 % after 8 h of continuous frying in total polar compounds. The total polar compounds give information of the total amount of newly formed compounds having higher polarity than that of triacylglycerols (Fritsch 1981). The recommended acceptable value for polar compounds was 27 % for any oil (Lee 2009). There was significant ($p \leq 0.05$) correlation between FFA and total polar compounds (TPC). The correlation coefficient between frying time and polar compounds were high (95.5 %) which showed that polar compounds estimation was one of the satisfactory methods for evaluating the quality of oils.

Determination of *p*-anisidine (*p*-AV) indicates amount of aldehyde (principally 2-alkenals and 2, 4-alkadienals) in oils. Generally, *p*-AV is used in combination with peroxide value to assess the extent of oxidative rancidity. There was significant ($p \leq 0.05$) increase in the *p*-AV with frying time from 2.41 to 17.93. This may be due to the decomposition of less stable primary oxidative products (hydroperoxides) to aldehydic compounds. After 8 h of continuous frying the TOTOX value

Table 2 Changes in refractive index (RI), specific gravity, anti-oxidant activity (AA) (%) and total polyphenol (mg/kg) of VCO after 8 h of continuous frying of soaked bengal gram dhal

Frying time (h)	RI	Specific gravity	AA	Total polyphenol
0	1.4550 ^a ±0.0001	0.909 ^a ±0.001	75.11 ^a ±0.9	550.54 ^a ±1.23
1	1.4550 ^a ±0.0001	0.910 ^a ±0.001	71.24 ^b ±0.2	511.21 ^b ±1.45
2	1.4552 ^a ±0.0001	0.912 ^a ±0.001	68.36 ^c ±0.3	496.36 ^c ±2.98
3	1.4555 ^a ±0.0001	0.913 ^a ±0.001	65.98 ^d ±0.8	485.01 ^d ±4.76
4	1.4554 ^a ±0.0001	0.913 ^a ±0.001	61.02 ^e ±0.7	481.69 ^{de} ±3.88
5	1.4556 ^a ±0.0001	0.912 ^a ±0.001	59.74 ^{ef} ±0.9	479.25 ^e ±5.74
6	1.4557 ^a ±0.0001	0.914 ^a ±0.001	57.33 ^{fg} ±0.6	465.22 ^f ±6.91
7	1.4558 ^a ±0.0001	0.916 ^a ±0.001	55.67 ^{gh} ±0.8	452.97 ^g ±7.23
8	1.4559 ^a ±0.0001	0.908 ^a ±0.001	54.16 ^h ±0.9	436.75 ^h ±6.86

Mean values with the same superscript letters within the same column do not differ significantly ($p \leq 0.05$)

Table 3 Changes in fatty acid profile (%) of VCO during 8 h continuous frying of soaked bengal gram dhal

Fatty acid	0 h	2 h	4 h	6 h	8 h
Caproic(C _{6:0})	0.50 ^a ±0.01	0.48 ^a ±0.12	0.47 ^a ±0.11	0.45 ^a ±0.11	0.46 ^a ±0.01
Caprylic(C _{8:0})	7.10 ^a ±0.10	7.11 ^a ±0.09	7.08 ^a ±0.10	7.09 ^a ±0.11	7.07 ^a ±0.10
Capric(C _{10:0})	6.00 ^a ±0.10	6.13 ^a ±0.10	6.27 ^a ±0.11	6.26 ^a ±0.10	6.27 ^a ±0.11
Lauric (C _{12:0})	50.02 ^a ±0.10	49.93 ^a ±0.19	49.91 ^a ±0.12	49.98 ^a ±0.18	49.95 ^a ±0.11
Myristic(C _{14:0})	16.50 ^a ±0.16	16.77 ^a ±0.20	16.87 ^a ±0.18	16.93 ^a ±0.14	17.05 ^c ±0.16
Palmitic(C _{16:0})	8.10 ^a ±0.11	8.21 ^a ±0.10	8.31 ^a ±0.11	8.68 ^a ±0.12	8.82 ^a ±0.09
Stearic(C _{18:0})	2.82 ^a ±0.10	2.89 ^a ±0.09	2.95 ^a ±0.08	3.01 ^a ±0.10	3.11 ^a ±0.11
Oleic(C _{18:1})	6.82 ^a ±0.13	6.55 ^a ±0.11	6.59 ^a ±0.10	5.92 ^c ±0.11	5.88 ^c ±0.12
Linoleic(C _{18:2})	1.85 ^a ±0.10	1.72 ^b ±0.11	1.55 ^c ±0.11	1.45 ^d ±0.10	1.40 ^d ±0.12
Linolenic(C _{18:3})	0.10 ^a ±0.01	0.09 ^a ±0.001	0.05 ^a ±0.001	0.02 ^a ±0.11	0.01 ^c ±0.001
SFA	91.23 ^a ±1.21	91.52 ^a ±1.21	91.86 ^a ±1.41	92.40 ^b ±1.11	91.93 ^b ±1.11
MUFA	6.82 ^a ±0.13	6.55 ^a ±0.11	6.59 ^a ±0.10	5.92 ^b ±0.11	5.88 ^b ±0.12
PUFA	1.95 ^a ±0.10	1.81 ^a ±0.01	1.60 ^b ±0.01	1.47 ^d ±0.03	1.41 ^d ±0.01

Mean values with the same superscript letters within the same row do not differ significantly ($p \leq 0.05$)

of VCO samples was significantly ($p \leq 0.05$) increased. This was may be due to presence of polyunsaturated fatty acids (PUFA) and monounsaturated fatty acids (MUFA) (Table 1).

On the other hand there was significant ($p \leq 0.05$) decrease in polyphenol content observed in VCO sample after 8 h of continuous frying. Generally, the higher the frying temperature and time leads to the more polyphenols oxidation. Furthermore, a saturated lipid matrix and the existence of water in the lipid matrix can accelerate polyphenol oxidation which leads to decrease in antioxidant activity (Table 2).

The fatty acid composition of various VCO is listed in Table 3. The prominent fatty acid of VCO is lauric acid (50.21 %) and myristic acid (16.50 %). Based on fatty acid composition the amount of saturated fatty acids (SFA), monounsaturated fatty acids (MUFA) and polyunsaturated fatty acids (PUFA) have been calculated and results showed that

PUFA was much more affected as compare to MUFA and SFA during frying operations (Table 3).

The multiple regression equations were established to evaluate the changes in different quality parameters. Table 4 presents the most important mathematical models which express the relationship between all independent and dependent variables. The multiple regression equation 1 shows the relationship between CT (independent variable) and dependant variables (CD, viscosity, FFA, TBA, PC, AV, TC and Time).

Change in specific absorptivity (CD₂₃₂ and CT₂₇₀), iodine value (IV), specific gravity and FTIR spectra of VCO samples

The process of formation of peroxides is concurrent with conjugation of double bonds in PUFA which can be measured using the specific absorptivity of conjugated dienes

Table 4 The best mathematical model employed for accurate evaluation of different parameters of VCO after 8 h of continuous frying of soaked bengal gram dhal

SN.	Best mathematical models	R ²	SE
1	CT=0.7764-0.1204CD-0.0186Vis+0.0117FFA-0.6145TBA+0.1183PC+0.0128AV-0.0284 TC+0.1191Time	0.999	0.0355
2	CD=6.4481-8.3047CT-0.1546Vis+0.0972FFA-5.1029TBA+0.9822PC+0.1065AV-0.2358TC+0.9892Time	0.998	0.0894
3	Vis=41.6881-53.6927CT-6.4653CD+0.6288FFA-32.9922TBA+6.3501PC+0.6882AV-1.5249TC+6.3957Time	0.998	4.9921
4	PV=7.7458+3.3494CT+11.5032CD-5.9267FFA+0.4615TBA+0.3834PC-0.4402AV-0.9619TC+1.8959Time	0.999	0.6177
5	FFA=1.3069+0.5651CT+1.9409CD-0.1687PV+0.0778TBA+0.0647PC-0.0743AV-0.1623TC+0.3198Time	0.997	0.1135
6	TBA=0.0265-0.0607PV-0.2953FFA+0.0717PC-0.0065AV-0.0810TC-0.0039AA+0.0013Poly+0.2151Time	0.998	0.0689
7	PC=123.9580-70.9736CT-58.3077CD-24.6280FFA+2.0103AV-0.4587TC-2.6333AA+0.1437Poly+3.2965Time	0.998	0.6912
8	AV=17.5957+7.6086CT+26.1311CD-2.2716PV-13.4632FFA+1.0483TBA+0.8709PC-2.1852TC+4.3068Time	0.997	1.8720
9	TC=0.3274-0.7498PV-3.6438FFA-12.3401TBA+0.8848PC-0.0800AV-0.0492AA+0.0612Poly+2.6540Time	0.999	1.2119
10	AA=224.4778+149.2920CD-38.0274FFA+288.6301TBA-14.3962PC-4.0715AV+5.9730TC-0.2537Poly-25.3880Time	0.998	2.445
11	Poly=313.908-325.474CT+28.184 L*-34.510a*+8.675b*+15.316PV+241.242FFA+104.643TBA-12.278PC	0.998	11.1183
12	Time=-18.5476+15.5033CT-5.7085CD+0.3392Vis+0.0668 L*-1.6151PC+0.2510TC-0.0717AA+0.0170Poly	0.994	0.9129

R² regression coefficient, SE Standard Error, CD Conjugated Diene, CT Conjugated Triene, Vis Viscosity, AA Antioxidant activity, Poly Polyphenol content

Fig. 1 The relationship between the specific absorptivity values of conjugated diene (CD) and conjugated triene (CT) during 8 h of continuous frying of soaked bengal gram dhal

and trienes at 232 and 270 nm in the UV spectrum (Rohman et al. 2011). In the present investigation initially specific absorptivity CD_{232} and CT_{270} of VCO sample was 0.04 and 0.03 which was increased up to 0.79 and 0.31 respectively after 8 h of continuous frying (Fig. 1). The low level of both conjugated dienes and trienes is due to the low PUFA (1.95) and MUFA (6.82) content in VCO. Generally, PUFA is more prone to oxidation than MUFA and SFA. Higher the percentage of PUFA (linoleic and linolenic) in oil leads to the higher the levels of conjugated dienes and trienes formed during frying (Abdulkarim et al. 2007). It was found from the present investigation that the levels of conjugated dienes are higher than trienes, this is indicated by the higher values specific absorptivity at 232 nm. This may be due to the richness in natural polyphenols content in VCO which can inhibit the peroxide formation (Marina et al. 2009).

The early increase in absorption showed formation of conjugated dienes at the early stages of oxidation (Farmer and Sutton 2002). There was no significant ($p \leq 0.05$) change observed in the specific gravity of VCO samples after 8 h of continuous frying (Table 2). This may be due to the generation of dipoles in heated oil samples which may interact with each other and increase the specific gravity of oils (Shazia et al. 2012).

In the same context a decrease in iodine value (IV) can be attributed to the destruction of double bonds by oxidation and polymerization. Changes in IV of the oils during 8 h of frying were listed in Table 1. The data reveals that there was significant ($p \leq 0.05$) decrease in iodine value of fried oil sample after 8 h of frying. Similar, trend of IV has been reported in palm oil, soybean oil, moringa oil and canola oil after 5 days of frying (Abdulkarim et al. 2007).

Fig. 2 FTIR spectra of VCO and fried VCO samples (1) after 2 h of frying (2) after 4 h of frying (3) after 8 h of frying of soaked bengal gram dhal

Fig. 3 Changes in viscosity (cp) with frying time of VCO after 8 h of continuous frying of soaked bengal gram dhal

The FTIR spectroscopy was used to follow the course of oxidation during frying process. Figure 2 show FTIR spectra of control and fried VCO samples (after 2, 4, 8 h of frying). Visual examination of the spectra revealed that there were no appreciable differences between their spectral features. The spectra had absorption bands at wave number $2,954\text{ cm}^{-1}$ [stretching $\text{C-H}(\text{CH}_3)$], $2,921\text{ cm}^{-1}$ [asymmetric stretching $\text{C-H}(\text{CH}_2)$], $2,852\text{ cm}^{-1}$ [symmetric stretching $\text{C-H}(\text{CH}_2)$], $1,742\text{ cm}^{-1}$ [stretching C=O], $1,465\text{ cm}^{-1}$ [Bending $\text{C-H}(\text{CH}_2)$], $1,417\text{ cm}^{-1}$ [Bending C-H], $1,377\text{ cm}^{-1}$ [symmetrical bending $\text{C-H}(\text{CH}_3)$], $1,227.7\text{ cm}^{-1}$ [stretching C-O], $1,151.7\text{ cm}^{-1}$ [stretching C-O], $1,109\text{ cm}^{-1}$ [stretching C-O], 962 cm^{-1} [trans olefin bending], 888.7 cm^{-1} [bending CH_2], 721 cm^{-1} [bending $\text{-(CH}_2)_n\text{-}$]. FTIR spectra of fried oil samples did not reveal any peak around $3,300\text{ cm}^{-1}$ indicating no hydroperoxide or free fatty acids (which are normally formed during thermal oxidation). Smith et al. (2005) has reported that hydroperoxide on decomposition formed carbonyl compounds (secondary oxidation products) which results in higher intensities at $1,739\text{ cm}^{-1}$. In the present study VCO samples did not show

any effect on intensities at frequency $1,739\text{ cm}^{-1}$, $2,852\text{ cm}^{-1}$, $1,742\text{ cm}^{-1}$, 962 cm^{-1} . This can be justified by the minor change in CD and CT in fried oil samples. From the present study FTIR cannot provide sufficient quantitative data to show oxidative stability of VCO. Earlier similar observations were reported by Lu and Tan (2009) in heated VCO samples and thus, further chemical analyses have been carried out to check the thermal stability of VCO.

Changes in viscosity

The viscosity of VCO increased from 50.87cp to 91.05cp after 8 h of frying (Fig. 3). This increase in viscosity may be due to the cross linking of the carbon in the fatty acid molecules causing carbon to form cyclic compounds, dimmers, trimers, epoxides and polymers with higher molecular weight (Shyu et al. 1998). The more viscous the frying oil, the higher the degree of deterioration. The degradation of oils during frying affects both viscosity and the composition of polar compounds. A linear regression equation ($y=5.426x+48.93$) obtained between viscosity and frying time with regression coefficient of 0.984.

Change in colour value

The changes in CIE color values (L^* , a^* and b^* value) of fried VCO samples after 8 h of frying is shown in Fig. 4. Color is the visual indication for the deterioration of fried oil samples caused by oxidation. The L^* value showed decreasing trend during frying conditions. This decrease was the result of chemical reactions in frying oil i.e. hydrolysis, oxidation, polymerization and other chemical reactions (Kusucharid et al. 2009). The regression coefficient for L^* , a^* and b^* value with frying time were 0.974, 0.984 and 0.916 respectively. The rate of darkening of oil during frying was directly proportional to the frying time (Che man and Wan hussin 1998). The value of a^* and b^* of

Fig. 4 Color deterioration in terms of L^* , a^* and b^* value of VCO after 8 h of continuous frying of soaked bengal gram dhal

VCO samples upto 8 h of continuous frying were found to increase (Fig. 4). This may be due to the increase in accumulation of non-volatile decomposed compounds such as oxidized triacylglycerols and FFA. In addition to this the darkening of oils was partly due to the absorption of color from the fried food. Similar, trend in color values were reported in frying of Palm oil during vacuum and atmospheric conditions (Pambou et al. 2010). The regression equation for L^* , a^* and b^* value was $y = -0.408x + 5.470$, $y = 0.856x - 1.43$, $y = 0.591x - 0.568$ to predict the changes in color values with frying time.

Conclusions

The results of the present study showed that VCO was stable and acceptable after 8 h of soaked Bengal gram dhal (chick pea) frying. The stability of VCO was indicated by peroxide value, FFA, TBA, TC and anisidine value. The L^* value decreased with repeated frying of the oil, which contradicted the increase in a^* and b^* value. Viscosity of VCO was strongly affected by its degradation products, increasing as a result of formation of dimmers, trimers, polymers, epoxides, alcohols and hydrocarbons, all of which contribute to increase in viscosity. Increment in frying temperature and time leads to polyphenol oxidation and decrease in antioxidant activity. This can be concluded from the present study that VCO can become a good frying medium for commercial world.

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