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Contributed Paper

Impact of Palm Olein Addition on the Thermooxidative Degradation of Canola Oil During Frying

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ABSTRACT

The aim of this study was to evaluate the effects of palm olein (PO) addition on the thermooxidative degradation of canola oil (CO) during frying of potato pieces at $185 \pm 5^\circ\text{C}$. The blends were prepared in the volume ratios of 20:80 (PO:CO, PC1) and 40:60 (PO:CO, PC2). Refractive index, free fatty acid content, peroxide value, *p*-anisidine value, total oxidation value, viscosity, specific extinction, polymer content, polar compounds, food oil sensor value and color of the oils all increased, whereas iodine value and $C_{18,2}/C_{16,0}$ ratio decreased as frying progressed. The percentage of linoleic and linolenic acids tended to decrease, whereas the percentage of palmitic, stearic and oleic acids, increased. In DSC analysis, addition of PO to CO altered the shapes of endo- or exotherm peaks of CO and became sharp; might be due to the change in fatty acid composition. Based on the most oxidative stability criteria investigated, it could be concluded that the frying process caused the formation of comparatively lower amounts of oxidation products in the blends compared to CO, indicating a lower extent of thermooxidative degradation of the blends. However, higher amounts of free fatty acids and higher color units were both detected in the blends compared to pure CO at the end of frying trial. It appeared that proper blending of highly unsaturated CO with PO could result in oil blends which could meet nutritional needs with improved stability for domestic cooking and deep-frying.

Keywords: frying oil, fatty acids, oxidative stability, DSC

1. INTRODUCTION

Deep-fat frying is one of the oldest and most popular methods for the preparation and manufacturing of foods in the world. During deep-fat frying of food, in the presence of air, a number of chemical

reactions occur in the oil, thus leading to the decomposition of the frying oil and formation of volatile and non-volatile oxidized derivatives, and dimeric, polymeric, or cyclic substances, thereby affecting both the

oil and finished product qualities [1]. There is evidence that some products of triacylglycerol oxidation reactions, particularly those with an altered chemical nature, may pose potential hazards to human health [2]. Stability to oxidation during a prolonged exposure to high temperatures is one of the main characteristics that industrial frying oil should possess, as its physical, chemical and nutritional properties may undergo significant modifications during thermo-oxidation [3]. Therefore, use of oil that can resist oxidation as much as possible is very important. Canola is one of the most important oil seed crops in the world. Research indicates that the fatty acid composition of canola oil is especially favorable in terms of health benefits when used as part of a nutritionally balanced diet. It contains the lowest concentration of saturated fatty acids (SFA, 7 %) among the vegetable oils [4]. The lack of frying stability and poor frying performance of CO related to high levels of linoleic and linolenic acids has been documented [5]. Moreover, the relatively high cost restricts usage of CO on a major scale. Therefore, the use of more stable frying oils of comparatively low price would be desirable. Palm oil and its products mainly palm olein are available in huge amounts to a comparatively low price and used as suitable raw material and as major cooking oil for various types of dishes [6-8]. The availability of high oleic oils is limited at the moment, resulting in a higher price for the oil. Bertrand [9] stated that palm oil and its products have a similar frying performance compared to the new so-called "high-oleic" oils. PO is generally used as frying oil because it has natural antioxidants like tocopherols, β -carotene and balanced unsaturated and saturated fatty acid contents which are good for health [10]. Addition of oxidative-stable PO to canola oil might affect the thermo-oxidative stability of canola oil during frying.

To date, very few studies have been conducted on the deteriorative changes of CO blended with PO during deep fat frying [11-13]. Additionally, most of the publications deal with results obtained from frying of single CO or PO or their blends with other commercial oils [3,10,14-16]. In the present study, efforts had been made to investigate the effects of PO addition at 20 and 40% levels on the thermo-oxidative degradation of CO during frying by a combination of the most effective analytical and instrumental methods.

2. MATERIALS AND METHODS

2.1 Food Materials and Chemicals

Refined canola oil (Wintercorn Edible Products, Australia) and palm olein (Sime Darby Food and Beverages, Malaysia) were purchased from local super market. Fresh potato was from local food store. The food materials were kept in the refrigerator below 4°C for storage. Potatoes were peeled, washed with water and sliced into 6 cm × 0.5 cm × 0.3 cm sizes and then dried with a towel prior to being submerged into the oil for frying. The vegetable oil blends were formulated by blending PO with CO in the volume ratios of 20:80 (PO:CO, PC1) and 40:60 (PO:CO, PC2). The mixtures were stirred in a magnetic stirrer for 20 min for homogenization. All chemicals and solvents used were of analytical grade. *p*-Anisidine and silica gel were products of Merck (Darmstadt, Germany). Standards of fatty acid methyl esters were purchased from Supelco Chemical Co. (Bellefonte, PA, USA). All other chemicals and solvents were from J.T. Baker (Phillipsburg, USA) or RCI Labscan Ltd. (Pathumwan, Thailand) unless otherwise stated.

2.2 Frying Protocol

Frying test was carried out on PO and CO and the same test was performed for

their blends. Several batches of potato pieces (50 g) were fried in a 2.5 L domestic electric fryer (Philips HD-6159) at $185 \pm 5^\circ\text{C}$ at intervals of 20 min up to 6 h per day for a total of 5 days. Two and a half liters of each oil sample to be tested were used for the frying. Fryer was switched on 15 min before beginning of frying each day to heat oil up to the desired frying temperature. Fresh oil was added after collection of fried sample to make up oil to the initial level in the fryer [13]. The oil samples were collected and stored at -16°C for analyses each morning before replenishment. Initial physico-chemical analyses of the fresh samples (day 0) were also carried out.

2.3 Fatty Acid Composition

Fatty acid composition of the oils was determined as their methyl esters prepared by the PORIM [17] test method p3.4. Fatty acid methyl esters (FAME) were quantified using an auto-system XL gas chromatograph (Perkin Elmer Incorporate, Massachusetts, USA) equipped with a fused silica capillary column ($60 \text{ m} \times 0.25 \text{ mm i.d} \times 0.20 \mu\text{m}$ film thickness, Perkin Elmer, USA) and a flame ionization detector. Nitrogen was used as carrier gas with a flow rate of 20 mL/min. Initial temperature was set to 100°C , raised to 170°C at $20^\circ\text{C}/\text{min}$, then programmed to 230°C at $10^\circ\text{C}/\text{min}$, and finally heated to 250°C at $30^\circ\text{C}/\text{min}$. The detector and injector temperatures were both maintained at 250°C . Methyl esters were quantified by comparing the retention times and peak area of the unknowns with known FAME standard mixtures.

2.4 Standard Physicochemical Analyses

American Oil Chemists' Society official methods [18] were used for determining refractive index (method Cc 7-25), free fatty acid content (method Ca 5a-40), iodine value

(method Cd 1b-87) and peroxide value (method Cd 8-53). Specific extinctions (method p2.15) at 233 and 269 nm ($E_{233}^{1\%}$ and $E_{269}^{1\%}$) and *p*-Anisidine value (method p2.4) of the samples were determined by means of a Jenway 6305 Spectrophotometer (Barloworld Scientific Ltd., Staffordshire, UK) according to the PORIM [17] test methods.

2.5 Viscosity Measurement

Viscosity of the oils was measured by using a Brookfield DV-II+ viscometer (Brookfield Engineering Laboratories Inc., Middleboro, USA). One milliliter of oil was placed on the plate of the viscometer with spindle S-42; the viscosity of the sample was read in cP (centipoises) directly from the viscometer, which was maintained at 40°C .

2.6 Polymer Content

Polymer content was determined according to the method described elsewhere [19]. The oil sample was initially reacted with 1% sulfuric acid in methanol. The solution was then refluxed with a reflux condenser for about 2 h with stirring throughout. The methanolic miscella was thoroughly decanted off and the methanol-insolubles were washed with methanol. The insolubles were dissolved in 40 mL petroleum ether ($60\text{-}80^\circ\text{C}$). The solvent was then removed using a rotary evaporator and the residue was dried in an oven at a temperature of 140°C . The dried residue was finally weighed after cooling at room temperature.

2.7 Polar Compounds

The total polar compound contents were determined by the mini column method [20]. Briefly, about 1.0 g of oil was diluted in light petroleum ether/diethyl ether (90:10, v/v) and made up to 10 mL with the same solvent mixture. Five milliliters of the solution were applied to a silica gel (Merck grade 60, 70-

230 mesh) column. The nonpolar fraction was eluted with 60 mL of light petroleum ether/diethyl ether (90:10, v/v) while the polar fraction was eluted with 50 mL of diethyl ether. The solvent was removed by rotary evaporator; afterwards the flask was flushed under a stream of nitrogen for complete dryness. The completeness of fractionation was evaluated by analytical thin-layer chromatography in the elution system light petroleum ether: diethyl ether: acetic acid (70:40:1; v:v:v).

2.8 Food Oil Sensor

Food oil sensor values were measured by using the food oil sensor instrument (CapSens 5000, C-Cit Ag, Wädenswil, Switzerland).

2.9 Color Measurement

Color was determined using a Lovibond Tintometer Model E (The Tintometer Ltd., Salisbury, England) according to PORIM [17] test method (p4.1). The oil samples were placed into 1 inch cell and the color was determined at 60°C by achieving the best possible match with the standard color slides of red and yellow indices.

2.10 Thermal Analysis

Thermal properties were evaluated by differential scanning calorimetry (DSC) at different frying times (for day 0, 1, 3 and 5) on the substrate oil CO and its blends PC1 and PC2 using a Perkin- Elmer precisely diamond DSC (Perkin- Elmer Corp., Norwalk, CT, USA). Nitrogen (99.9% purity) was used as the purge gas at a rate of 20 mL/min. The melted sample (5-9 mg) was placed in a standard DSC aluminum pan and then hermetically sealed. The instrument was calibrated using indium and zinc. In order to obtain cooling profiles, the oil samples were subjected to the following temperature

program: cooled from 80 to -50°C at the rate of 5°C/min and held for 5 min at -80°C; heated from -50 to 80°C at the rate of 5°C/min and held for 5 min at -50°C. The major peak at maximum temperatures and enthalpy of melting were analyzed from thermograms using the Pyris software (version 2.04, 1997).

2.11 Statistical Analysis

All data were expressed as the mean and standard error (SE) and were subjected to one way analysis of variance (ANOVA). Mean values were compared at $P < 0.05$ significant level by Duncan's multiple range test using SPSS 11.5 software package.

3. RESULTS AND DISCUSSION

3.1 Changes in Fatty Acids Composition

Fatty acids composition of the samples is presented in Table 1. Oleic acid was predominant in PO (45.20%) followed by palmitic (38.44%) and linoleic (11.59%) acids. CO was characterized by a high content of oleic acid (62.99%) followed by linoleic acid (20.12%), linolenic acid (8.99%) and palmitic acid at lesser concentration (4.68%). In the present work, frying oils containing PO had more saturated acid and less linoleic or linolenic acids than pure CO or its blends. It has been shown that heating of oil causes a fast decrease in more unsaturated fatty acid (USFA) than less unsaturated or saturated fatty acids [5]. In this study, the percentage of linoleic and linolenic acids tended to decrease, whereas the percentage of palmitic, stearic and oleic acids, increased, probably due to PUFA degradation. A similar trend was found by Sebedio *et al.* [21] in soybean oil during frying frozen potatoes. Before frying, CO and its blends contained *trans* C_{18:2} (0.18 to 0.49%), whilst no trace of *trans* fatty acid was detected in the fresh PO. *Trans* isomers in the fresh oils are supposed to be produced in the

deodorization process of crude oils [22]. *Trans* C_{18:1} was found after 1st day of frying. It is worth mentioning that the amount of *trans* C_{18:2} during the corresponding frying times, was greater than that of *trans* C_{18:1}. A high content of polyunsaturated fatty acid (PUFA) detected in the CO makes it more susceptible to the oxidative deterioration. As can be seen in Table 1, the blending of the CO with the PO led to decreases in its ratio of C_{18:2}/C_{16:0}. The starting value of the C_{18:2}/C_{16:0} ratio was high in the blends than in PO due to addition of highly unsaturated CO. The ratio C_{18:2}/C_{16:0} has been suggested as a valid indicator of the level of PUFA deterioration [23]. Our results

in the present study indicate that this ratio decreased in all oil samples during the frying process. The highest decreased amount from the initial was observed for the CO (1.11 unit) followed by PC1 (0.460 unit) and PC2 (0.225 unit) with the least in PO (0.042 unit). Present results revealed adding PO to CO slowed down the rate of oxidative degradation of CO. Onal and Ergin [24] reported a decrease in the ratio from 4.04 to 3.49 (0.55 units) for CO at the end of frying time. Alireza *et al.* [16] revealed CO had the least stability due to a high level of USFAs; conversely, CO/PO blend (1:1, w/w) had the best stability due to the smallest reduction of the C_{18:2}/C_{16:0} ratio.

Table 1. Fatty acids composition (%) of palm olein, canola oil, and their blends during frying.

Sample	Day	C _{12:0}	C _{14:0}	C _{16:0}	C _{16:1}	C _{18:0}	C _{18:1}	<i>Trans</i> C _{18:1}	C _{18:2}	<i>Trans</i> C _{18:2}	C _{18:3}	C _{20:0}	C _{20:1}	C _{22:0}	SFA	MUFA	PUFA	C18:2/ C16:0
PO	0	0.22	0.96	38.44	0.13	3.13	45.20	ND	11.59	ND	0.25	0.08	ND	ND	42.83	45.33	11.84	0.301
	1	0.24	1.06	38.81	0.13	3.34	44.81	ND	11.14	0.05	ND	0.17	0.26	ND	43.62	45.20	11.19	0.288
	3	0.26	1.09	38.75	0.13	3.46	44.73	0.13	10.67	0.36	0.23	0.18	ND	ND	43.74	44.99	11.26	0.284
	5	0.25	1.08	39.28	0.13	3.46	45.03	0.07	10.06	0.14	0.03	0.20	0.27	ND	44.27	45.50	10.23	0.259
CO	0	ND	0.05	4.68	0.16	1.68	62.99	ND	20.12	0.25	8.99	0.21	0.81	0.05	6.67	63.96	29.36	4.35
	1	0.03	0.06	5.04	0.17	1.79	63.94	ND	19.23	0.21	8.19	0.50	0.77	0.08	7.50	64.88	27.63	3.86
	3	0.03	0.07	5.23	0.17	1.80	65.90	0.17	18.20	0.67	6.86	0.19	0.66	0.06	7.38	66.9	25.73	3.61
	5	0.03	0.06	5.45	0.18	2.00	67.20	ND	17.38	0.27	6.47	0.23	0.67	0.06	7.83	68.05	24.12	3.24
PO:CO (20:80, PC1)	0	0.07	0.26	11.44	0.18	2.05	59.22	ND	18.34	0.49	7.10	0.17	0.61	0.06	14.05	60.01	25.93	1.64
	1	0.07	0.26	11.86	0.18	2.09	59.51	0.07	17.82	0.64	6.36	0.46	0.61	0.06	14.8	60.37	24.82	1.55
	3	0.08	0.28	12.28	0.18	2.26	60.93	0.19	16.35	0.71	5.54	0.53	0.59	0.08	15.51	61.89	22.6	1.39
	5	0.08	0.29	13.17	0.18	2.27	62.47	0.22	15.38	0.24	4.92	0.21	0.50	0.06	16.08	63.37	20.54	1.18
PO:CO (40:60, PC2)	0	0.12	0.48	19.05	0.14	2.32	55.35	ND	16.50	0.18	5.25	0.15	0.44	ND	22.12	55.93	21.93	0.875
	1	0.12	0.48	18.68	0.16	2.55	55.73	ND	15.68	0.85	4.74	0.50	0.46	0.05	22.38	56.35	21.27	0.884
	3	0.13	0.51	19.93	0.18	2.61	57.34	0.18	14.15	0.57	3.82	0.19	0.36	0.05	23.42	58.06	18.54	0.738
	5	0.13	0.52	20.89	0.16	2.60	57.76	0.22	13.39	0.20	3.52	0.21	0.35	0.05	24.4	58.49	17.11	0.650

ND-not detected.

3.2 Changes in Standard Physicochemical Parameters

Refractive index (RI) values of frying oils were increased insignificantly ($P < 0.05$) as the number of fryings performed by the oils increased (Table 2). A similar trend was followed by Leyla *et al.* [25] who heated hazelnut, olive, grape seed and sunflower oils at frying temperature for 5 days. The lowest

amount of increment (0.0010 unit from initial) was found in PO and the increment in CO and its blends almost similar (0.0018 to 0.0021 unit from initial). However, adding PO to CO did not change significantly the RI value of CO. The accumulation of free fatty acid (FFA) contents of all frying oils were significantly increased ($P < 0.05$) with increasing frying time (Table 2). At the end of frying, the amount

of FFA was found to be higher in PO (0.77%) or oil blends PC1 (0.68%) and PC2 (0.70%) as compared to CO (0.61%). The higher level of FFA contents in PO was confirmed by other authors [26]. Enríquez-Fernández *et al.* [13] reported the higher FFA contents in PO compared to those of a blend PO/CO (1:1, w/w) at the end of frying period. However, in this study, addition of PO to CO increased FFA level of CO and the highest FFA figure

found in PO at the end of frying was still far below the accepted limit of 2% [27]. Using FFA content as an indicator of frying oil degradation and of fried food quality is still controversial. In practice, FFA levels may not affect frying performance or have significant adverse effects on health or sensory evaluation [26]. Till now, FFA is still being used widely because of very simple titration method for its estimation.

Table 2. Refractive index, free fatty acid, peroxide value, *p*-anisidine value and TOTOX value of palm olein, canola oil, and their blends during frying.

Parameter	Day	Palm olein (PO)	Canola oil (CO)	Palm olein : Canola oil	
				20:80 (PC1)	40:60 (PC2)
Refractive index (25°C)	0	1.4652 ± 0.0003 ^{aA}	1.4710 ± 0.0002 ^{cA}	1.4707 ± 0.0003 ^{cA}	1.4689 ± 0.0001 ^{bA}
	1	1.4652 ± 0.0003 ^{aA}	1.4716 ± 0.0002 ^{cAB}	1.4711 ± 0.0002 ^{cAB}	1.4692 ± 0.0001 ^{bA}
	2	1.4655 ± 0.0002 ^{aAB}	1.4718 ± 0.0003 ^{cABC}	1.4714 ± 0.0002 ^{cAB}	1.4702 ± 0.0001 ^{bB}
	3	1.4657 ± 0.0002 ^{aAB}	1.4722 ± 0.0002 ^{cBC}	1.4716 ± 0.0002 ^{cBC}	1.4705 ± 0.0001 ^{bBC}
	4	1.4661 ± 0.0001 ^{aB}	1.4724 ± 0.0002 ^{cBC}	1.4723 ± 0.0001 ^{cCD}	1.4708 ± 0.0002 ^{bCD}
	5	1.4662 ± 0.0001 ^{aB}	1.4728 ± 0.0002 ^{cC}	1.4726 ± 0.0002 ^{cD}	1.4710 ± 0.0001 ^{bD}
Free fatty acid (%)	0	0.12 ± 0.00 ^{aA}	0.10 ± 0.00 ^{aA}	0.11 ± 0.00 ^{aA}	0.11 ± 0.01 ^{aA}
	1	0.26 ± 0.01 ^{bB}	0.18 ± 0.00 ^{aB}	0.20 ± 0.01 ^{aB}	0.20 ± 0.02 ^{aB}
	2	0.42 ± 0.01 ^{cC}	0.24 ± 0.02 ^{cC}	0.29 ± 0.01 ^{bC}	0.30 ± 0.01 ^{bC}
	3	0.47 ± 0.02 ^{bD}	0.32 ± 0.01 ^{aD}	0.39 ± 0.02 ^{abD}	0.44 ± 0.02 ^{bD}
	4	0.68 ± 0.00 ^{cE}	0.50 ± 0.02 ^{cE}	0.56 ± 0.02 ^{abE}	0.60 ± 0.02 ^{bE}
	5	0.77 ± 0.01 ^{cF}	0.61 ± 0.00 ^{aF}	0.68 ± 0.00 ^{bF}	0.70 ± 0.01 ^{bF}
Peroxide value (meq/kg of oil)	0	1.16 ± 0.03 ^{aA}	1.24 ± 0.03 ^{aA}	1.22 ± 0.01 ^{aA}	1.20 ± 0.02 ^{aA}
	1	2.05 ± 0.02 ^{aB}	3.23 ± 0.03 ^{dB}	3.08 ± 0.03 ^{bB}	2.67 ± 0.01 ^{bB}
	2	3.17 ± 0.10 ^{aC}	6.90 ± 0.04 ^{bC}	4.09 ± 0.03 ^{aC}	3.90 ± 0.08 ^{aC}
	3	5.02 ± 0.07 ^{aD}	10.89 ± 0.10 ^{dE}	6.88 ± 0.02 ^{cD}	6.10 ± 0.04 ^{bD}
	4	7.29 ± 0.07 ^{aE}	10.59 ± 0.12 ^{cE}	8.76 ± 0.02 ^{bE}	8.72 ± 0.07 ^{bE}
	5	6.61 ± 0.03 ^{aE}	9.95 ± 0.12 ^{cD}	8.12 ± 0.10 ^{bE}	7.96 ± 0.07 ^{aE}
<i>p</i> -Anisidine Value (unit)	0	2.38 ± 0.02 ^{aA}	4.32 ± 0.09 ^{cA}	3.40 ± 0.02 ^{bA}	3.17 ± 0.07 ^{bA}
	1	17.23 ± 0.21 ^{aB}	60.13 ± 0.40 ^{dB}	45.75 ± 0.24 ^{cB}	41.35 ± 0.34 ^{bB}
	2	37.10 ± 0.13 ^{aC}	85.14 ± 0.44 ^{dC}	66.00 ± 0.37 ^{cC}	57.56 ± 0.13 ^{bC}
	3	48.09 ± 0.41 ^{aD}	100.20 ± 0.25 ^{dD}	77.88 ± 0.35 ^{cD}	68.89 ± 0.30 ^{bD}
	4	53.55 ± 0.49 ^{aE}	109.00 ± 0.42 ^{dE}	85.44 ± 0.18 ^{cE}	75.12 ± 0.46 ^{bE}
	5	55.11 ± 0.46 ^{aF}	116.12 ± 0.39 ^{dF}	90.32 ± 0.31 ^{cF}	78.37 ± 0.70 ^{bF}
TOTOX value (2PV + <i>p</i> -AV)	0	4.70 ± 0.06 ^{aA}	6.80 ± 0.13 ^{cA}	5.84 ± 0.03 ^{bA}	5.57 ± 0.05 ^{bA}
	1	21.33 ± 0.25 ^{aB}	66.59 ± 0.35 ^{dB}	51.91 ± 0.20 ^{cB}	46.69 ± 0.33 ^{bB}
	2	44.84 ± 0.20 ^{aC}	98.94 ± 0.49 ^{dC}	74.18 ± 0.43 ^{cC}	65.36 ± 0.11 ^{bC}
	3	58.13 ± 0.55 ^{aD}	121.98 ± 0.14 ^{dD}	91.64 ± 0.37 ^{cD}	81.09 ± 0.35 ^{bD}
	4	68.13 ± 0.57 ^{aE}	130.18 ± 0.19 ^{dE}	102.96 ± 0.21 ^{cE}	92.56 ± 0.41 ^{bE}
	5	68.33 ± 0.39 ^{aE}	136.02 ± 0.16 ^{dF}	106.56 ± 0.10 ^{cF}	94.29 ± 0.69 ^{bF}

Each value in the table represents the mean of three replicates ± SE.

Values within a row with the same lowercase letters are not significantly different at $P < 0.05$.

Values within a column with the same uppercase letters are not significantly different at $P < 0.05$.

Table 2 shows the peroxide value (PV) of the COs as affected by the PO over 5 days frying at 185°C. There was an initial sharp increase in the PV for CO from day 0 to day 3 after which the rate slowed down, while PO and CO blends showed a slower rate of increment; this might be attributed the high amounts of linoleic acids present in the former than the latter ones. Peak values were attained as follows: PO (7.29), CO (10.89), PC1 (8.76) and PC2 (8.72). The PV decreased in all oils after the peak was reached. The PV peak for the CO was reached after day 2 as compared to day 3 in cases of all other oils. For peroxides, the data confirmed the results showed in early studies [14], with an increase in the peroxides until a maximum was reached, followed by a decrease of those compounds due to their reactions and degradations to other compounds. Addition of PO to CO significantly decreased ($P < 0.05$) the increment of peroxide value of CO, might be attributed to decreasing amount of linoleic acids present in the blended oils. Based on the PV, the order of stability of pure oils and blends was as follow: PO > PC2 > PC1 > CO indicating that both blends were able to retard oxidative and also hydrolytic reactions. However, during the frying operation, only CO exceeded the acceptable level of 10 mequiv O₂ kg⁻¹ given by the Guidelines of the German Food Codex as the limit for edible fats and oils [28] after 2nd day of frying. Compared to PV, the *p*-anisidine value (*p*-AV) is a more reliable and meaningful test, because it measures the secondary oxidation products, which are more stable during the heating process [29]. The *p*-AV in all the oils increased significantly ($P < 0.05$) with frying time during the course of frying (Table 2) and similar trend for some vegetable oils was followed by other researchers [14]. The change in *p*-AV of PO was found to be significantly lower ($P < 0.05$) followed by PC2 and PC1, with the highest

value obtained in CO. This confirms the results of the PV that showed the CO to be more susceptible to oxidation at high temperature than PO or blends. The COs containing the 20 and 40% of the PO underwent the *p*-AV increases (86.92 and 75.20 units respectively, from the initial); being lower than that of the CO (111.80 units). So, *p*-AV values increased in the order: CO > PC1 > PC2 > PO. *p*-AV is often used in the industry in conjunction with PV to calculate the so-called total oxidation or TOTOX value given as: TOTOX = 2PV + *p*-AV [30]. During frying TOTOX values increased significantly ($P < 0.05$) with frying days and after the end of frying operation, the TOTOX values were found to be 68.33, 136.02, 106.56 and 94.29 for PO, CO, PC1 and PC2, respectively (Table 2). The lower TOTOX value of the blends indicated more stable to oxidative rancidity than CO.

During frying, a progressive decrease in unsaturation was observed in all oils by the determination of iodine value (IV) (Table 3). CO had the highest initial IV (109) due to its higher PUFA content. The decrease amounts in the IV from the initial over the five days of frying were 3.50, 11.40, 8.54 and 8.01 units for the frying media PO, CO, PC1 and PC2 respectively. The highest significant ($P < 0.05$) change in the IV was shown by the frying medium CO, thus indicating that the highest decrease in double bonds occurred due to oxidative rancidity in that frying media. The present results revealed adding PO to CO led to the reduction in the decreasing rate of the IV of CO. The decreased amounts in IV values of the blends at the end of frying were lower than that of pure CO. Alireza *et al.* [16] reported that the blend PO/CO (1:1, w/w) was the stable frying medium while CO proved to be most unstable due to the lowest and highest reduction of the IV in PO/CO and CO respectively during frying. The E^{1%} at

233 and 269 nm for all the samples increased significantly ($P < 0.05$) throughout the frying periods (Table 3). The levels of conjugated dienes and trienes at the end of frying were however lowest in PO followed by PC2 and PC1, with highest level found in CO. The lower levels of both conjugated dienes and trienes in the blends are indications of good

oxidative stability compared to CO, and it is because of the lower percentage of PUFAs content. It was found that in all the samples, the levels of conjugated dienes were higher than trienes; this is indicated by the higher values of $E^{1\%}$ at 233 nm. However, PO addition to the CO decelerated conjugated dienes and trienes formation in CO.

Table 3. Iodine value, specific extinction, viscosity and polymer content of palm olein, canola oil, and their blends during frying.

Parameter	Day	Palm olein (PO)	Canola oil (CO)	Palm olein : Canola oil	
				20:80 (PC1)	40:60 (PC2)
Iodine value	0	57.32 ± 0.55 ^{aC}	109.00 ± 0.41 ^{dE}	98.52 ± 0.43 ^{cC}	93.01 ± 0.36 ^{bE}
	1	57.98 ± 0.41 ^{aC}	107.00 ± 0.37 ^{dD}	95.46 ± 0.24 ^{bB}	92.46 ± 0.24 ^{bE}
	2	55.89 ± 0.38 ^{aB}	105.45 ± 0.28 ^{dC}	94.33 ± 0.25 ^{cB}	90.11 ± 0.17 ^{bD}
	3	54.56 ± 0.16 ^{aAB}	103.23 ± 0.55 ^{dB}	91.34 ± 0.58 ^{cA}	87.23 ± 0.29 ^{bC}
	4	54.01 ± 0.26 ^{aA}	98.45 ± 0.55 ^{dA}	90.44 ± 0.43 ^{cA}	86.77 ± 0.22 ^{bB}
	5	53.82 ± 0.26 ^{aA}	97.60 ± 0.14 ^{dA}	89.98 ± 0.33 ^{cA}	85.00 ± 0.16 ^{bA}
$E^{1\%}_{1cm}$ at 233 nm	0	0.95 ± 0.006 ^{aA}	1.43 ± 0.02 ^{dA}	1.33 ± 0.03 ^{cA}	1.22 ± 0.02 ^{bA}
	1	1.14 ± 0.05 ^{aB}	2.78 ± 0.06 ^{dB}	2.50 ± 0.05 ^{cB}	1.92 ± 0.02 ^{bB}
	2	3.53 ± 0.10 ^{aC}	4.23 ± 0.02 ^{bC}	4.00 ± 0.09 ^{bC}	3.95 ± 0.07 ^{bC}
	3	4.80 ± 0.03 ^{aD}	8.56 ± 0.09 ^{cD}	7.10 ± 0.03 ^{bD}	6.95 ± 0.03 ^{bD}
	4	5.98 ± 0.05 ^{aE}	10.02 ± 0.05 ^{dE}	9.09 ± 0.09 ^{cE}	8.00 ± 0.12 ^{bE}
	5	6.27 ± 0.06 ^{aF}	12.04 ± 0.15 ^{dF}	10.03 ± 0.12 ^{cF}	8.90 ± 0.05 ^{bF}
$E^{1\%}_{1cm}$ at 269 nm	0	0.45 ± 0.01 ^{aA}	0.76 ± 0.05 ^{cA}	0.65 ± 0.01 ^{bcA}	0.57 ± 0.03 ^{abA}
	1	0.77 ± 0.05 ^{aB}	1.52 ± 0.03 ^{cB}	1.28 ± 0.04 ^{bB}	1.20 ± 0.02 ^{bB}
	2	1.04 ± 0.01 ^{aC}	1.61 ± 0.05 ^{bB}	1.56 ± 0.02 ^{bC}	1.51 ± 0.03 ^{bC}
	3	1.53 ± 0.03 ^{aD}	2.33 ± 0.06 ^{dC}	2.05 ± 0.03 ^{cD}	1.85 ± 0.03 ^{bD}
	4	1.60 ± 0.03 ^{aE}	2.88 ± 0.006 ^{dD}	2.33 ± 0.03 ^{cE}	2.05 ± 0.02 ^{bE}
	5	1.67 ± 0.07 ^{aE}	3.29 ± 0.14 ^{dE}	2.69 ± 0.04 ^{cF}	2.35 ± 0.04 ^{bF}
Viscosity (cP)	0	33.45 ± 0.02 ^{dA}	29.70 ± 0.09 ^{aA}	30.35 ± 0.02 ^{bA}	31.35 ± 0.07 ^{cA}
	1	34.55 ± 0.02 ^{aB}	35.10 ± 0.05 ^{bB}	35.90 ± 0.05 ^{dB}	35.55 ± 0.11 ^{cB}
	2	36.20 ± 0.05 ^{aC}	42.30 ± 0.14 ^{cC}	40.85 ± 0.02 ^{bC}	40.70 ± 0.05 ^{bC}
	3	36.55 ± 0.07 ^{aD}	45.65 ± 0.22 ^{cD}	43.95 ± 0.02 ^{bD}	43.83 ± 0.30 ^{bD}
	4	37.80 ± 0.05 ^{aE}	50.50 ± 0.14 ^{dE}	47.13 ± 0.07 ^{cE}	46.30 ± 0.17 ^{bE}
	5	38.70 ± 0.05 ^{aF}	59.35 ± 0.07 ^{dF}	52.37 ± 0.05 ^{cF}	51.70 ± 0.05 ^{bF}
Polymer content (%)	0	0.55 ± 0.03 ^{aA}	0.58 ± 0.06 ^{aA}	0.58 ± 0.02 ^{aA}	0.56 ± 0.05 ^{aA}
	1	0.74 ± 0.05 ^{aB}	0.83 ± 0.02 ^{aB}	0.75 ± 0.02 ^{aA}	0.75 ± 0.02 ^{aA}
	2	0.85 ± 0.02 ^{aB}	1.76 ± 0.07 ^{cC}	1.52 ± 0.05 ^{bcB}	1.36 ± 0.09 ^{bB}
	3	1.22 ± 0.02 ^{aC}	2.44 ± 0.05 ^{cD}	2.22 ± 0.07 ^{bC}	2.09 ± 0.05 ^{bC}
	4	1.69 ± 0.04 ^{aD}	2.97 ± 0.07 ^{cE}	2.80 ± 0.07 ^{bcD}	2.62 ± 0.11 ^{bD}
	5	2.10 ± 0.05 ^{aE}	3.87 ± 0.07 ^{cF}	3.55 ± 0.13 ^{cE}	3.10 ± 0.08 ^{bE}

Each value in the table represents the mean of three replicates ± SE.

Values within a row with the same lowercase letters are not significantly different at $P < 0.05$.

Values within a column with the same uppercase letters are not significantly different at $P < 0.05$.

3.3 Changes in Viscosity and Polymer Content

The viscosity of frying oils increased significantly ($P < 0.05$) with frying days (Table 3). CO had lower initial viscosity as compared with PO or its blends. In our study, viscosity increased from initial values of 33.45, 29.70, 30.35 and 31.35 to 38.70, 59.35, 52.37 and 51.70 cP for the PO, CO, PC1 and PC2 frying media, respectively. The viscosity of CO at day 1 was lower than PC1 and PC2; afterwards the rate of viscosity for CO dramatically increased. These results clearly indicated the higher deteriorative effect of oxidation and polymerization of CO compared to PO or blends. As can be seen from Table 3, polymer content (PC) increased significantly ($P < 0.05$) with different rates over the five days of the frying. The increase amounts in PC from the initial through the frying operation were 1.55, 3.29, 2.97 and 2.54 units for the frying media PO, CO, PC1 and PC2 respectively. The present results revealed frying media PO showed the lowest PC while CO accumulated polymer as highest compared to the blends. Addition of PO to CO slowed down the rate of polymerization in CO.

3.4 Changes in Total Polar Compound and Food Oil Sensor Value

The amount of total polar compound (TPC) in all the oil samples increased with the time and the rates of increments were significantly different ($P < 0.05$) from each other (Table 4). After 5 days of frying, the final TPC levels were: 16.78 % in PO, 33.53 % in CO, 31.10 % in PC1 and 29.72 % in PC2. However, the total polar contents in CO at 4th day of frying exceeded the limit 27 % for used frying fats based on the German standard [31]. These results indicated that CO could be used for frying of potato pieces up to day 3 while PC1 and PC2 could be up to

day 4 under the frying conditions depicted in the methodology. The formation of polar compounds during repeated frying operations has been reported to increase with oil unsaturation [32]. Hence, the faster increase in TPC levels observed for the sample CO could be attributed to its higher degree of unsaturation. If the maximal content for TPC in frying oil is accepted as 27%, the TPC-based stability ranking of these oils would be: PO > PC2 > PC1 > CO. Addition of PO to the pure CO resulted in a marked decline in TPC value of CO, thus showing enhancement of the oxidative state of this substrate oil. Despite the similar levels of food oil sensor (FOS) values in the fresh oils, the FOS values increased significantly ($P < 0.05$) with different rates over the five days of frying (Table 4). As the number of polar molecules increases, the FOS value of the oil increases. After 5 days of frying, the final FOS levels were: 2.85 units in PO, 5.80 units in CO, 5.15 units in PC1 and 4.83 units in PC2. In this case, the highest TPC content and FOS values were both detected in CO and the lowest one in PO. Addition of PO caused the lower enhancement of the FOS values at the end of the frying.

3.5 Changes in Color Value

The color units of all the oils increased significantly ($P < 0.05$) with frying days (Table 4). In the present study, the PO showed the highest initial yellow (19.60) and red (2.67) color units; while the CO showed the least initial magnitude of the yellow (10.30) and red (0.83) color units. Since oil color can be resulted from more than one chemical process, the use of oil color to monitor quality is not valid when evaluating a wide range of frying operations [33]. Adding PO to CO resulted in the unexpected higher color units in the blends as compared to pure CO at the end of the frying process which could not be

explained easily by the marked differences in FA composition between PO and CO. Higher initial values of PO could contribute to darkness of CO during frying. Che Man *et al.* [34] reported that blending of soybean oil with PO increased the red and yellow units of soybean oil. Gary *et al.* [33] reported that

cottonseed oil and soybean salad oil formed the lowest amounts of color though these oils were clearly less stable to heating than the partially hydrogenated oils. Hence, more rapid development in color of PO or blends over CO might not be valid indicator for their stability.

Table 4. Total polar compound, FOS value and color of palm olein, canola oil, and their blends during frying.

Parameter	Day	Palm olein (PO)	Canola oil (CO)	Palm olein : Canola oil	
				20:80 (PC1)	40:60 (PC2)
Total polar compound (%)	0	6.32 ± 0.11 ^{bA}	4.71 ± 0.23 ^{aA}	4.90 ± 0.04 ^{aA}	5.12 ± 0.06 ^{aA}
	1	8.10 ± 0.15 ^{aB}	12.33 ± 0.18 ^{dB}	11.06 ± 0.15 ^{cB}	10.14 ± 0.25 ^{bB}
	2	10.81 ± 0.40 ^{aC}	20.14 ± 0.15 ^{dC}	18.28 ± 0.59 ^{cC}	16.00 ± 0.40 ^{bC}
	3	12.99 ± 0.48 ^{aD}	26.80 ± 0.30 ^{eD}	24.05 ± 0.23 ^{bD}	23.92 ± 0.36 ^{bD}
	4	14.78 ± 0.37 ^{aE}	29.48 ± 0.24 ^{dE}	26.98 ± 0.63 ^{cE}	24.86 ± 0.22 ^{bE}
	5	16.78 ± 0.42 ^{aF}	33.53 ± 0.41 ^{eF}	31.10 ± 0.27 ^{bF}	29.72 ± 0.48 ^{bF}
FOS value	0	0.95 ± 0.02 ^{aA}	1.10 ± 0.05 ^{aA}	0.99 ± 0.006 ^{aA}	0.98 ± 0.05 ^{aA}
	1	1.20 ± 0.05 ^{aA}	2.10 ± 0.05 ^{bB}	2.10 ± 0.05 ^{bB}	2.05 ± 0.02 ^{bB}
	2	1.65 ± 0.02 ^{aB}	3.50 ± 0.09 ^{bC}	3.30 ± 0.05 ^{bC}	3.25 ± 0.07 ^{bC}
	3	2.15 ± 0.07 ^{aC}	4.67 ± 0.10 ^{cD}	4.15 ± 0.07 ^{bD}	4.10 ± 0.05 ^{bD}
	4	2.50 ± 0.09 ^{aD}	5.05 ± 0.02 ^{bCE}	4.85 ± 0.02 ^{bCD}	4.75 ± 0.07 ^{bE}
	5	2.85 ± 0.07 ^{aE}	5.80 ± 0.12 ^{dF}	5.15 ± 0.05 ^{cE}	4.83 ± 0.03 ^{bE}
Red color (Lovibond)	0	2.67 ± 0.05 ^{aA}	0.83 ± 0.02 ^{aA}	1.53 ± 0.02 ^{bA}	1.57 ± 0.01 ^{bA}
	1	4.83 ± 0.02 ^{bB}	1.60 ± 0.05 ^{aB}	2.77 ± 0.072 ^{bB}	3.27 ± 0.12 ^{cB}
	2	7.47 ± 0.05 ^{dC}	3.40 ± 0.17 ^{aC}	4.80 ± 0.09 ^{bC}	5.67 ± 0.11 ^{cC}
	3	9.63 ± 0.02 ^{dD}	6.07 ± 0.05 ^{dD}	6.80 ± 0.13 ^{bD}	8.87 ± 0.11 ^{dD}
	4	15.13 ± 0.07 ^{dE}	7.63 ± 0.10 ^{aE}	9.77 ± 0.09 ^{bE}	11.90 ± 0.08 ^{cE}
	5	19.47 ± 0.10 ^{dF}	9.50 ± 0.23 ^{aF}	10.93 ± 0.05 ^{bF}	15.50 ± 0.05 ^{cF}
Yellow color (Lovibond)	0	19.60 ± 0.08 ^{dA}	10.30 ± 0.12 ^{aA}	14.40 ± 0.09 ^{bA}	18.29 ± 0.07 ^{cA}
	1	19.90 ± 0.08 ^{aA}	19.30 ± 0.14 ^{aB}	23.53 ± 0.05 ^{bB}	31.90 ± 0.08 ^{cB}
	2	20.03 ± 0.03 ^{aA}	29.97 ± 0.02 ^{bC}	31.23 ± 0.10 ^{cC}	39.53 ± 0.05 ^{dC}
	3	26.63 ± 0.07 ^{aB}	39.07 ± 0.03 ^{cD}	31.63 ± 0.11 ^{bC}	44.17 ± 0.14 ^{dD}
	4	29.60 ± 0.05 ^{aC}	39.57 ± 0.07 ^{bD}	43.37 ± 0.07 ^{cD}	50.17 ± 0.14 ^{dE}
	5	39.63 ± 0.15 ^{aD}	41.23 ± 0.12 ^{bE}	53.53 ± 0.05 ^{cE}	54.63 ± 0.07 ^{dF}

Each value in the table represents the mean of three replicates ± SE.

Values within a row with the same lowercase letters are not significantly different at $P < 0.05$.

Values within a column with the same uppercase letters are not significantly different at $P < 0.05$.

3.6 Changes in Thermal Properties

Changes in thermal properties were evaluated by DSC at different frying times on PO and CO and their blends (Figures not shown). Due to the complexity of the recorded thermal events, all melting and crystallization points are read at the maximum/minimum of either endo-or exotherm peaks as reported earlier [35].

Cooling curve of fresh CO showed a broader exotherm peaking at -37.60°C whereas PO showed a sharp and tall peak (at 1.02°C) with a small one (at -24.63°C). Addition of PO to CO altered the shape of CO peak and became sharp; might be due to the change of fatty acid composition. During frying the peaks of pure oil and their blends were found to be broader and shorter in most case, as the treatment time increased. Crystallization enthalpy of CO and PO decreased and then increased with frying periods; probably as consequence of the broadening of temperature range of the phase transition [36]. Enthalpy of crystallization decreased in the blends PC1 and PC2 and then increased, as previously observed for substrate oils. Fresh CO melting profile exhibited a well distinct endothermic event, peaking at -17.90°C with a small shoulder peak peaking at lower temperature (at -27.63°C) whereas fresh PO displayed a major endothermic peaked at 4.31°C with some broader/shoulder peaks. The fresh PC1 showed one major peak at -12.67°C with smaller one peaked at lower temperature (at -27.68°C). After 1st day of frying, PC1 heating thermograms exhibited four peaks; being shorter and broader with increasing frying times. The major one peaked at -6.02°C . The sample PC1 showed a significant decrease of the overall enthalpy starting from 1st day of frying. Four endothermic events were exhibited by heating profiles of fresh PC2 with major one peaked at -6.10°C and

became broader and shorter dramatically as the treatment time increased. At the end of frying, two broader peaks at -32.92°C and -5.68°C were found with one small sharp peaked at higher temperature (-1.30°C). CO seemed to be more extensively altered by frying, as both primary and secondary lipid oxidation products markedly increased compared to its blends. All these changes may be related to the higher unsaturation degree of lipid molecules present in CO with respect to those found in PO or blends.

4. CONCLUSIONS

In this study, most of the chemical and physical degradation indicators suggested that the degradation was the fastest in CO as compared to its blends with PO. Overall, based on the results reported herein, it can be concluded that addition of PO to CO slowed down the thermooxidative degradation rate of the CO. However, some degradation indicators such as free fatty acid content and color, increased faster in the blended oils compared to CO. Therefore, further research is needed to find out additional factors that are responsible to enhance the level of such indicators in the blends. In view of this finding, it can be inferred that use of CO blends as frying oil is a promising possibility. It is hoped that the data obtained from this study may facilitate food manufacturers to decide on the suitable oils for their frying operation.

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