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US Wijewardhana
Department of Food Science and Technology, University of Sri Jayewardenepura, Gangodawila, Nugegoda, Sri Lanka

UGSA Gunathilaka
Department of Food Science and Technology, University of Sri Jayewardenepura, Gangodawila, Nugegoda, Sri Lanka

SB Navaratne
Department of Food Science and Technology, University of Sri Jayewardenepura, Gangodawila, Nugegoda, Sri Lanka

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Correspondence
US Wijewardhana
Department of Food Science and Technology, University of Sri Jayewardenepura, Gangodawila, Nugegoda, Sri Lanka

Determination of changes occurrence in chemical properties of antioxidant incorporated palm olein during deep-fat frying

US Wijewardhana, UGSA Gunathilaka and SB Navaratne

Abstract
Deep fat frying, refers to the process of cooking food by immersing it in hot oil (150 ^{0}C-190 ^{0}C), leads to various chemical changes in an edible oil including oxidation, polymerization and hydrolysis. In this study, dietary antioxidant sources such as garlic, cinnamon and black cumin were introduced to palm olein to monitor the changes in chemical properties during deep-frying. They were added to oil at a rate of 2% w/v and cassava chips were subjected for three consecutive frying cycles. Samples were drawn after each frying cycle and peroxide value, free fatty acid value, conjugated diene and triene content were measured. Results revealed that the addition of dietary antioxidant sources to palm olein before frying reduces the formation of peroxides, free fatty acids, conjugated dienes and conjugated trienes against the control and garlic has the highest potential to be used as a dietary antioxidant reducing the respective values significantly (p<0.05).

Keywords: Deep frying, natural antioxidants, palm olein, cinnamon, black cumin, garlic

1. Introduction

Deep fat frying is one of the oldest and most popular means in preparation of food and of it, food is dehydrated and cooked by immersing in hot oil at a high temperature (150 ^{0}C to 190 ^{0}C) [1, 2]. Since oil is exposed to a high temperature in the presence of moisture and oxygen during deep-frying, oils are subjected to various physical and chemical changes [3]. Major physical changes are; increment of the viscosity, lowering of the smoke point and increment of the darkness [4] while hydrolysis, polymerization and oxidation are the major chemical changes [5]. Apart from that, the fatty acid composition of oil greatly changes with repetitive frying, arising adverse health issues [6]. Therefore, protecting the oil during deep-frying is very important in both industrial as well as domestic levels. Good frying practices and incorporation of antioxidants before frying can significantly delay or prevent the oxidation [7]. The addition of synthetic antioxidants to oil is negatively perceived by people due to health considerations and their inability to meet performance expectations [8, 9]. Thus, naturally-derived antioxidants are continuously assessed by the researchers for their effectiveness in suppressing oil quality changes [10, 11]. Hence, this study aims to determine the effectiveness of natural antioxidant sources such as Black cumin, garlic and cinnamon against quality deterioration of oil during deep frying. In this study, commercial palm olein was used to fry cassava chips along with those dietary antioxidant sources for three consecutive frying cycles and samples drawn from each frying cycle were analyzed in terms of peroxide value, free fatty acid value, conjugated dienes and conjugated triens.

2. Materials and methods

2.1 Material collection

Cassava tubers (*Manihot esculanta* variety MU-51) and Cinnamon bark (*Cinnamomum zeylanicum*) were collected from the Department of Agriculture and Cinnamon Research Station in Peradeniya and Matara, Sri Lanka respectively. Garlic (*Allium sativum*) and Black cumin (*Nigella sativa*) seeds were collected from a registered Ayurvedic-herbal material supplier in Sri Lanka and oil samples (palm olein) were collected from supermarkets. All chemicals used for chemical testing were of analytical grade with the highest purity available (>99.5%).

2.2 Preparation of cassava chips for frying

Collected cassava tubers were washed, peeled off and then sliced into an even thickness (2 mm) using a slicer. The slices were washed with cold water to remove starch particles still intact with the surface and dried at 60 ^{0}C for 30 minutes to remove excess moisture.

2.3 Preparation of spices prior frying

Cinnamon bark and Garlic were pulverized into small pieces (0.5×0.5×0.5 cm^3) and dried them at 60 ^{0}C for one hour using the same oven to dry the commodities well.

2.4 Frying process and sample collection

Fresh oil was added to a frying pan and preheated to 60 ^{0}C and the antioxidant source was added at a rate of 2% (w/v) while stirring and maintaining the temperature at 60 ^{0}C for 10 minutes. Thereafter, the temperature of the oil was bought up to 120 ^{0}C and cassava chips (100g) were added and frying was carried out at 170 ^{0}C for 10 minutes. The oil sample used for frying was reused for two more frying cycles (three frying cycles in total) over three days. Following each frying cycle, oil samples (100ml) were drawn (After the oil reached the room temperature) and stored at -18 ^{0}C until the chemical analysis. Standard samples were prepared following the same procedure by the addition of vitamin E (600mg/L).

2.5 Analysis of oil for oxidative stability

Quality changes of oil were assessed after each frying cycle in terms of peroxide value, free fatty acid value, conjugated dienes and conjugated triens. Peroxide value and free fatty acid levels were determined according to AOAC official methods 965.33 and 940.28 respectively. Conjugated diene (CD) and Conjugated triene (CT) contents were determined according to the method AOCS cd 7-58 which was modified according to the method described by [12], where oil was dissolved in pure hexane followed by the measurement of absorbance at 232 nm and 270 nm respectively.

2.6 Statistical analysis

All tests were carried out in triplicates and obtained data were analyzed using Minitab 17 statistical software and differences were considered statistically significant when $p<0.05$.

3. Results & Discussion

3.1 Peroxide value

Peroxide value (PV) is a common indication of oil deterioration concerning the primary oxidation of oil. It measures the hydroperoxides formed in the early oxidation of fats and oils [13]. Hence, the peroxide value of palm olein after each frying cycle with natural antioxidant sources was measured and results are given in Table 1.

Table 1: Peroxide values (meq/kg) after each frying cycle (P values evaluated at 95% confidence level and results illustrated by a, b, c, and d letters in the same column are significantly different)

Treatment	Frying Cycle		
	1	2	3
Control	17.37 ± 1.343^a	20.48 ± 1.044^a	37.33 ± 4.692^a
Vitamin E	11.84 ± 0.950^b	13.87 ± 0.901^b	15.05 ± 1.445^b
Black cumin	10.92 ± 0.957^{bc}	10.26 ± 1.099^c	14.53 ± 1.400^b
Cinnamon	9.28 ± 0.536^{cd}	12.23 ± 1.066^{bc}	17.47 ± 2.147^b
Garlic	7.56 ± 0.522^d	9.91 ± 0.934^c	13.86 ± 1.710^b

As illustrated in table 1, mean peroxide values have been reduced at all frying cycles against control treatment. When antioxidant sources were added to the oil before frying, the reduction of peroxide value during three frying cycles was significantly different (p value < 0.05) against control treatment. When compared with vitamin E, cinnamon and garlic incorporated samples had a significantly lower peroxide value after the first frying cycle. According to the second frying cycle, black cumin and garlic were able to reduce peroxide value significantly (< 0.05%) than the vitamin E added sample. The effect of all antioxidant sources was the same for the 3rd frying cycle and there was no significant difference in added antioxidant sources with vitamin E at 95% confidence level.

Under this circumstance, the addition of garlic, cinnamon and black cumin before frying has a positive impact on palm olein in terms of retarding peroxide value. Decrease of peroxide value indicates that the incorporation of natural antioxidant sources to palm olein before frying reduces the formation of hydroperoxides in the early stages of oil oxidation by terminating the development of free radicals. In a similar study where turmeric leaf extract was incorporated into soybean oil during deep-frying, peroxide value has been reduced significantly in comparison to the control [14]. A study was done by [15], incorporating Rosemary and Sage extracts to palm olein during consecutive deep frying, which shows a decrease of PV against the control and according to their results PV increases up to 3rd day of frying in all samples and then fall.

3.2 Free fatty acid value

The free fatty acid value is an indication of the amount of hydrolysis of oil [13]. During frying, oil is heated to high temperatures in the presence of water which causes the hydrolysis of triglycerides that results in forming of free fatty acids. In general, the free fatty acid value increases with the number of frying cycles. The effect of antioxidant sources in developing free fatty acids was studied and mean fatty acid values were given in table 2.

Table 2: Free fatty acid level (% oleic) of palm olein after each frying cycle (P values evaluated at 95% confidence level and results illustrated by a and b letters in the same column are significantly different)

Treatment	Frying Cycle		
	1	2	3
Control	0.431 ± 0.085^a	0.645 ± 0.648^a	0.684 ± 0.091^a
Vitamin E	0.393 ± 0.073^{ab}	0.382 ± 0.039^b	0.390 ± 0.074^b
Black cumin	0.455 ± 0.017^a	0.456 ± 0.041^b	0.461 ± 0.059^b
Cinnamon	0.464 ± 0.030^a	0.420 ± 0.025^b	0.379 ± 0.084^b
Garlic	0.271 ± 0.031^b	0.429 ± 0.085^b	0.286 ± 0.016^b

Free fatty acid value provides supporting evidence on the oil deterioration. It is a measure of acidity but that does not differentiate between acids formed by hydrolysis and oxidation [15]. According to the results given in table 2, in the first frying cycle, both black cumin and cinnamon are not effective when compared with the control and vitamin E added sample. Only garlic shows a significant difference comparatively other treatments at a 95% confidence level. Values obtained for the second frying cycle shows a different picture as all antioxidants have been able to significantly reduce the FFA content than the control. Again, in the 3rd frying cycle, all antioxidants were significantly effective when compared with the control. At all frying cycles, the effect of garlic was significant. Similar studies have shown a decrease of FFA content than the control when palm olein is incorporated with Rosemary and Sage extracts during deep-frying [16].

3.3 Conjugated dienes and triens

Conjugated dienes and triens are a good measure of primary oxidation of the oil. Double bonds in lipids are changed from non-conjugated to conjugated bonds upon oxidation [17]. At the early stages of oil oxidation, as a result of reactions of free radicals, hydroperoxides are produced. The formation of hydroperoxides from polyunsaturated fatty acids leads to the conjugation of the pentadiene structure [18]. This causes absorption of UV radiation at 230-234 nm for conjugated dienes. When hydrogen abstraction happens on two active methylenes on C-11 and C-14, it produces two pentadienyl radicals which result in producing a mixture of conjugated dienes and triens [19]. This leads to an increase of UV absorption at 270nm attributable to conjugated triens, apart from 232nm for CD. To study the formation of conjugated dienes and triens in palm olein during deep-frying, the absorbance of oil samples concerning four antioxidant sources along with the control was measured and absorptivity was calculated. Obtained results are given in table 3 and table 4.

Table 3: Conjugated dienes ($Lcm^{-1}g^{-1}$) after each frying cycle (P values evaluated at 95% confidence level and results illustrated by a and b letters in the same column are significantly different)

Treatment	Frying Cycle		
	1	2	3
Control	0.266 ± 0.005^{ab}	0.279 ± 0.008^{a}	0.301 ± 0.020^{ab}
Vitamin E	0.280 ± 0.008^{a}	0.301 ± 0.010^{a}	0.329 ± 0.020^{a}
Black cumin	0.280 ± 0.033^{a}	0.252 ± 0.020^{a}	0.292 ± 0.007^{ab}
Cinnamon	0.222 ± 0.024^{b}	0.253 ± 0.023^{a}	0.281 ± 0.035^{ab}
Garlic	0.247 ± 0.018^{ab}	0.237 ± 0.051^{a}	0.242 ± 0.049^{b}

As illustrates in table 3, the effectiveness of vitamin E is low, providing higher CD contents after all frying cycles. When considering black cumin added palm olein, even though it contains a higher CD content than the control at the end of the first frying cycle, effectiveness has increased in second and third frying cycles. Garlic and cinnamon mixed treatments are cited with the lower CD content compared with the other treatments. When all results are considered, black cumin, garlic and cinnamon reduced the formation of conjugated dienes in palm olein during early oxidation but their contribution is not significant at 95% confidence level.

Table 4: Conjugated triens ($Lcm^{-1}g^{-1}$) after each frying cycle (P values evaluated at 95% confidence level and results illustrated by a, b, c and d letters in the same column are significantly different)

Treatment	Frying cycle		
	1	2	3
Control	0.0651 ± 0.0058^{ab}	0.0880 ± 0.0017^{a}	0.0969 ± 0.0089^{a}
Vitamin E	0.0718 ± 0.0030^{a}	0.0758 ± 0.0039^{b}	0.0759 ± 0.0040^{b}
Black cumin	0.0609 ± 0.0037^{ab}	0.0652 ± 0.0049^{c}	0.0685 ± 0.0011^{b}
Cinnamon	0.0651 ± 0.0003^{ab}	0.0533 ± 0.0044^{d}	0.0678 ± 0.0004^{b}
Garlic	0.0619 ± 0.0029^{b}	0.0697 ± 0.0032^{cd}	0.0696 ± 0.0031^{b}

As data given in table 4, considering the impact of antioxidant sources, all of them have reduced the formation of CT at all frying cycles. Compared with control, except the first frying cycle, cinnamon, garlic and black cumin are associated with a significant decrement of CT (<0.05%). Apart from that, all tested antioxidants have been able to reduce CT more effectively at each frying cycle concerning the vitamin E added sample.

Results obtained for conjugated diene and triene contents move parallel to the results of peroxide value. Thus, results suggest that the antioxidant sources are effective against the primary oxidation of palm olein. Similar studies where garlic extract was incorporated to palm olein during accelerated storage shows a decrease of PV, CD and CT content compared with the control sample [20]. Another study done by [8] reveals that the incorporation of coconut oil with pomegranate extract reduces the formation of conjugated dienes and triens during deep frying.

4. Conclusions

The addition of black cumin, garlic and cinnamon to palm olein during deep-frying has a significant positive impact in maintaining the chemical properties of oil during deep-frying, up to three frying cycles particularly in the formation of peroxides, free fatty acids and conjugated triens at 95% confidence level. Further, conjugated diene content was also reduced however, the reduction was not significant. Among the above dietary antioxidant sources, garlic exhibits the highest potential to be used as a dietary antioxidant.

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