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Effect of Some Spice Essential Oils on the Stability of Frying Oils

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In this study, peppers and potatoes were fried in olive and peanut oils. In order to evaluate the oxidative stability of frying oils, essential oils of sage, rosemary, thyme at the concentration of 0.3, 0.6, 0.9 and 1.2 %, separately and 0.01 % butylated hydroxytoluene were added into olive and peanut oils. Chemical properties of frying oils (free fatty acid %, peroxide value, DPPH, total phenolic and fatty acid composition) were determined after frying. Butylated hydroxytoluene showed the best effect on free fatty acid % and peroxide value of olive oils after frying of peppers and potatoes. Free fatty acid % values of frying oils of peppers and potatoes showed variation. The nearest values of oleic, linoleic and linolenic acid contents of frying olive oils of peppers and potatoes were determined with sample addition of butylated hydroxytoluene. Oleic, linoleic and linolenic acid contents of peanut oil with butylated hydroxytoluene and potato frying oil that addition of 0.3 % rosemary essential oil were determined to nearly the initial value of oil. These essential oils were also determined to show high radical scavenging effect. Rosemary essential oil was determined higher the radical scavenging effect and lower total phenolic compounds than thyme essential oils. There were not exact a relationship between radical scavenging effect and the amount of total phenolic compounds. The aim of current study is to establish to the effect of some spice essential oils on the stability of frying oils.

Key Words: Essential oil, Stability, Frying, Olive oil, Peanut oil.

INTRODUCTION

Deep-fat frying process used in the preparation of foods[1]. It is an ancient process probably dated to around the sixth century BC[2]. Recently, the use of foods such as deep-fried potatoes, fried vegetables and fish fries have been significant increases in Turkey[3-5]. Deep frying in oil/fat, both industry and home-made food processing, is widely used[5]. Consumers demand to deep-fried foods (potato chips, french fries, fried chicken, *etc.*) due to its own unique taste and texture[1]. Deep-fat frying is a process of immersing food in a fat or oil heated to 140-180 ºC and is process of cooking[6-8]. Over the course of time and because of oil adsorption by the food being cooked[8]. The purpose of frying is fast cooking, formation of a unique crust, colour, flavour and texture[2]. Frying oil acts as a heat transfer medium and contributes to the development of texture and flavour of fried foods[8]. During frying (basically a drying process), oil replaces the water that has evaporated. When the food is exposed to frying temperatures, water evaporates rapidly, the outer surface becomes dry and a crust forms. Oil viscosity increases considerably with extended frying time[9]. Thereby take place many complex reactions such as colour change and autooxidation, thermal polymerization, thermal oxidation, isomerization, hydrolysis during frying removes edibleness of oil and put down the nutritional value of fried food by transferring a lot toxic substance into fried food[6,7,9,10]. Deep-fat frying is accomplished through simultaneous heat and mass transfer of oil, food and air occurring during the process[8]. Due to the air, oxygen in the food, the moisture content of the food and high temperature, reactions such as hydrolysis, oxidation, polymerization and Maillard reactions take place in oil[8,11]. During deep fat-frying hydroperoxide, which is the major oxidation product, decomposes to secondary products, such as esters, aldehydes, alcohols, ketones, lactones and hydrocarbons. These secondary products adversely affect flavour, taste, nutritional value and overall quality of foods[12]. At elevated temperatures, when the oxygen supply is rather limited, the main reactions lead to polymerization rather than oxidation[2]. Oxidation normally proceeds slowly at the initial stage and then a sudden rise occurs in the oxidation rate[13]. Oxidative degradation products consist of much more intense and rapid manner at thermal oxidation conditions such as frying[14]. The oxygen in frying environment reacts with oil. Increase of the oxygen concentration and free radicals increases the oxidative degradation reactions and affects the overall quality of the oil[7,15-18].

EXPERIMENTAL

In this study, the peppers and potatoes were selected as the frying materials whereas extra-virgin olive oil and crude peanut oil were used as a frying medium. Essential oils of sage, rosemary and oregano were used as the source of natural antioxidants and butylated hydroxytoluene was selected as synthetic antioxidant. Sage, rosemary and oregano were purchased from local spice seller in Konya in Turkey and were stored at room temperature until used for analysis. Crude peanut oil (in 10 L PVC barrels) was provided from Baspinar Fistikcilik Soil Products Ltd. Sti. in Osmaniye in Turkey and extra-virgin olive oil (in 5 L tin) was provided from Sifa Olive oils and Soap San. Tic. Ltd. Sti. in Hatay in Turkey and had been stored in the package or at room temperature during the analysis periods. Peppers and potatoes were purchased from a local market.

Isolation of essential oils: Dried and ground sage, rosemary and thyme plants (about 100 g for each) were subjected to hydrodistillation for 3 h using a Clevenger-type apparatus and the oils obtained were dried over anhydrous sodium sulfate. They were stored in fridge-freezer (4 ºC) until used for analysis.

Frying process: Before every frying peppers were prepared fresh by washing, drying and they were cleaned from seeds and were cut of equal size as possible. Potatoes were prepared fresh by peeling potatoes, washing, cutting and drying too. As the source of natural antioxidants sage, rosemary and oregano essential oils were used for each in concentrations of 0.3, 0.6, 0.9 and 1.2 %. Butylated hydroxytoluene was used the concentration of 0.01 % as synthetic antioxidant. 100 mL oil was heated and both peppers and potatoes were added and fried for about 4-6 min for each frying operation. A pan that the mouth open and 19 cm × 3.5 cm in size and a resistance heater 34 cm × 9 cm × 19 cm in size was used for the frying process. Each the frying operation was carried out as two replications and fresh oil was used for each the frying. Immediately after frying operation frying oils were filtered on filter paper. Peroxide value and free fatty acid % of oil at room temperature were determined. Each oil sample was put into glass jars and they were tightly closed and stored in the refrigerator for total phenol, 2,2-diphenyl-1-picrylhydrazyl (DPPH) and fatty acid composition analyses.

Free fatty acid: Free fatty acid is expression as a percentage of free fatty acids in oils and the results are expressed as oleic acid %.

Peroxide value: Peroxide value is a measure of the amount of active oxygen in oils and is calculated on the basis of the amount oxygen in 1 kg of oil as meq[19].

Fatty acid composition: Fatty acid methyl esters were made according to the methods of analysis of the International Olive Oil Council[20]. Fatty acid methyl esters (1 µL) were analyzed by gas chromatography device (Shimadzu GC-2010) using flame ionization detector (FID).

Working conditions of the device: Injection block: 260 ºC; The detector: 260 ºC; Mobile phase: nitrogen; Total flow rate (mL/min): 80; nitrogen flow rate (mL/min): 1.51; Split ratio (mL/min): 1/40; Used in the column: Fused silica capillary column (Teknokroma TR-CN100, Barcelona, Spain, 60 m × 0.25 mm i.d.; film thickness 0.20 µm); Temperature program: Hold 90 ºC for 7 min, rise 240 ºC increasing 5 ºC/ min, this temprature is hold for 15 min.

Oil sample esters were injected under the above conditions where into chromatography. Qualitative identifications of the main fatty acids were made comparing the relative retention times and their percentage were obtained from the corrected data of integrator outputs[21].

Amount of total phenolic compounds: The amount of total phenolic compounds of phenolic extracts of oil samples were determined by the Folin-Ciocalteu colorimetric analysis method. Spectrophotometer (Shimadzu UV-visible mini spectrophotometer 1240) at 760 nm was taken a reading[22] and the results were calculated by taking advantage of the calibration curve was made up with take a reading certain concentrations of gallic acid[23].

DPPH radical-scavenging activity: Change in absorbance of the samples was read on spectrophotometer at 517 nm. The results were reported as µg/mL through amount of concentration required for causing a 50 % reduction (IC_{50}) in the DPPH[24].

Statistical analysis: Research results were analyzed by analysis of variance as regards statistical significance[25].

RESULTS AND DISCUSSION

Free fatty acid and peroxide value: Free fatty acid and peroxide values of olive and peanut oils after pepper and potato frying are given in Tables 1 and 2, respectively. When pepper frying oils had been made with extra-virgin olive oils examined; peroxide values of frying oils 0.3 % sage and 1.2 % rosemary essential oils added are 16.51 and 17.25 meq O_2/kg, respectively. As for potato frying oils; peroxide values of frying oils with butylated hydroxytoluene, 0.3, 0.6 and 1.2 % rosemary essential oils added are 17.73, 18.53, 18.67 and 18.69 meq O_2/kg, respectively. The results showed that all concentrations of rosemary essential oils reduced the free fatty acid while 0.6, 0.9 % sage and 1.2 % thyme essential oils showed a lower effect on the free fatty acid of pepper frying oils. It determined that rosemary essential oils more reduced the free fatty acid of potato frying oils than sage and thyme essential. While peroxide value and free fatty acids of pepper frying oils 0.3 % sage essential oil added determined as 16.51 meq O_2/kg and 1.47 %, respectively. The peroxide value and free fatty acids of pepper frying oil butylated hydroxytoluene added determined as 18.26 meq O_2/kg and 1.50 %. 0.3 % sage more reduce the peroxide value and free fatty acid of pepper frying oils than butylated hydroxytoluene. But it does not show the same effect on potato frying oils. Almost all concentrations of rosemary essential oils (0.9 % excluding) had an effect on peroxide value and the free fatty acids of pepper and potato frying oils. But this effect was determined to be less than butylated hydroxytoluene. The addition of thyme essential oil had an impact on the peroxide value and free fatty acid of peppers frying oils. But it was not effective on the peroxide value and free fatty acid of potato frying oils and the same

TABLE-1
EFFECT OF DIFFERENT ANTIOXIDANTS ON FREE ACIDITY AND PEROXIDE VALUE OF PEPPER AND POTATO FRY MADE WITH EXTRA VIRGIN OLIVE OILS

		Pepper frying		Potato frying	
		Free acid (Oleic acid %)	Peroxide value (meq O_2/kg)	Free acid (Oleic acid %)	Peroxide value (meq O_2/kg)
Fresh oil		1.45 ± 0.007	15.37 ± 0.23	1.45 ± 0.007	15.37 ± 0.23
Control		1.47 ± 0.13	20.61 ± 1.99	1.41 ± 0.12	19.71 ± 0.86
0.01 % Butylated hydroxytoluene		1.50 ± 0.05	18.26 ± 0.81	1.43 ± 0.10	17.73 ± 0.25
Sage (%)	0.3	1.47 ± 0.07	16.51 ± 0.60	1.43 ± 0.05	20.56 ± 1.79
	0.6	1.41 ± 0.06	21.56 ± 0.23	1.42 ± 0.11	21.67 ± 0.47
	0.9	1.44 ± 0.01	20.42 ± 0.63	1.34 ± 0.06	22.60 ± 0.84
	1.2	1.50 ± 0.05	20.24 ± 1.08	1.32 ± 0.05	21.63 ± 0.68
Rosemary (%)	0.3	1.38 ± 0.34	19.68 ± 0.52	1.27 ± 0.04	18.53 ± 0.40
	0.6	1.22 ± 0.08	18.40 ± 0.72	1.34 ± 0.09	18.67 ± 0.27
	0.9	1.36 ± 0.04	22.90 ± 0.88	1.34 ± 0.005	22.82 ± 0.29
	1.2	1.30 ± 0.06	17.25 ± 1.08	1.40 ± 0.05	18.69 ± 0.19
Thyme (%)	0.3	1.45 ± 0.09	19.15 ± 0.30	1.45 ± 0	20.80 ± 0.71
	0.6	1.46 ± 0.05	19.67 ± 1.11	1.49 ± 0.06	21.43 ± 0.38
	0.9	1.47 ± 0.05	19.65 ± 0.13	1.39 ± 0.16	24.16 ± 1,50
	1.2	1.40 ± 0.05	20.64 ± 0.82	1.33 ± 0.09	23.66 ± 0.75

TABLE-2
EFFECT OF DIFFERENT ANTIOXIDANTS ON FREE ACIDITY AND PEROXIDE VALUE OF PEPPER AND POTATO FRY MADE WITH RAW PEANUT OILS

		Pepper frying		Potato frying	
		Free acid (Oleic acid %)	Peroxide value (meq O_2/kg)	Free acid (Oleic acid %)	Peroxide value (meq O_2/kg)
Fresh oil		16.67 ± 0.007	9.41 ± 0.97	16.67 ± 0.007	9.41 ± 0.97
Control		17.09 ± 0.91	4.69 ± 0.94	28.53 ± 0.35	8.24 ± 0.80
0.01 % Butylated hydroxytoluene		16.42 ± 0.15	9.84 ± 0.48	29.79 ± 0.09	8.09 ± 0.41
Sage (%)	0.3	16.26 ± 0.63	5.54 ± 1.12	16.67 ± 0.08	7.46 ± 0.06
	0.6	16.70 ± 0.32	5.89 ± 0.40	16.83 ± 0.18	8.23 ± 0.54
	0.9	16.97 ± 0.15	5.78 ± 0.76	16.86 ± 0.12	10.46 ± 0.66
	1.2	30.77 ± 0.83	9.85 ± 0.14	28.71 ± 0.52	8.58 ± 0.71
Rosemary (%)	0.3	16.28 ± 0.12	6.0 ± 0.87	16.43 ± 0.16	9.79 ± 0.35
	0.6	16.24 ± 0.13	9.55 ± 0.52	16.62 ± 0.13	8.88 ± 0.50
	0.9	16.49 ± 0.23	10.08 ± 1.09	16.65 ± 0.18	9.40 ± 0.52
	1.2	29.94 ± 0.24	11.32 ± 0.68	28.56 ± 0.44	8.12 ± 0.27
Thyme (%)	0.3	16.40 ± 0.61	5.19 ± 0.3	16.74 ± 0.04	6.93 ± 0.70
	0.6	16.67 ± 0.51	5.56 ± 0.59	29.37 ± 0.08	6.62 ± 0.66
	0.9	16.04 ± 0.26	6.08 ± 0.44	28.76 ± 0.46	7.37 ± 0.47
	1.2	29.96 ± 0.38	11.55 ± 1.22	29.83 ± 0.66	9.96 ± 2.12

situation was also obtained for sage essential oils. While the effect of rosemary on frying oils are consistent with Che Man and Jaswir's[26] studies, the effect of sage are determined as different from the same study. The effect of butylated hydroxytoluene is consistent with Nacaroglu's[27] study, but the effect of thyme was found different. Free fatty acids of potato and pepper frying oils were different. Free fatty acids of potato frying oils were reduce than pepper frying oils. This situation is explained with potato starch to absorb the free fatty acids[28]. According to the results, it can be said that phenolic components of essential oil of rosemary have more antioxidative effect than sage and thyme essential oils. According to Andrikopoulos *et al.*[29] fried 500 g of potatoes in 0.3 L (270 g) of oil into the Pan-frying, for 6 min at 180 ± 10 °C and fried about 500 g of potatoes in 2.0 L (1.8 kg) of oil for 12 min at 170 ± 10 °C in deep-frying. They used extra virgin olive oil and vegetable oil for frying. They determined peroxide values of the fresh, deep-frying and pan-frying virgin olive oil are 2.8, 26.0 and 30.6 meq O_2/kg, respectively. In this study, the determined peroxide value of the fresh olive oil as 15.37 meq O_2/kg and the determined peroxide value of olive oil (control) after frying was 19.71 meq O_2/kg. There is a difference between peroxide values of these two studies. This is due to the fact that the quality of olive oil depending on fruit type, degree of fruit maturity, environmental conditions, growth area, processing and storage techniques, *etc.*[30].

Nacaroglu[27] determined that *Thymbra spicata* and butylated hydroxytoluene significantly reduce the oxidation of fat during frying. Che Man and Jaswir[26] studied the effects of rosemary and sage extracts on physico-chemical changes of refined, bleached and deodorized palm during deep-fat frying. They observed that the addition of sage (0.4 %) and rosemary (0.4 %) extracts reduced the peroxide value and free fatty acid content of frying oil. They reported both extract reduced oxidation rate of the oil during frying. Houhoula *et al.*[31] observed that oregano which is added into cottonseed oil inhibited the formation of peroxide during frying of potato chips and the storage stability of the produced chips. They reported that oregano was more effective in decreasing the formation of polar compounds, especially polymers and dimers, during frying. Lalas and Dourtoglou[32] evaluated the effect of using a rosemary extract on the stability of oil used for frying potato chips. They fried sliced potatoes intermittently in soybean oil containing a natural extract from rosemary and determined that the oil containing the extract showed greater antioxidant activity. Naz *et al.*[33] studied deterioration of olive, corn and soybean oils due to air, light, heat and deep-frying. They determined that the addition of various antioxidants was quite effective on the peroxide value of oils.

Maestri *et al.*[34] in a study examining the effect of some essntial oils on oxidative stability of peanut oil, stored peanut oil at 60 ºC after the addition of *Origanum majorana*, *Rosmarinus officinalis*, *Myrcianthes cisplatensis*, *Acantholippia seriphioides*, *Eucallyptus cinerea* and *Tagetes filifolia* essential oils into its. They evaluated the effects on the oxidation of essential oils by determining peroxide values of each peanut oil. They determined that the peroxide value (PV) of the control oil was significantly higher than peroxide values of oils added essential oil. They also determined that *Origanum majorana* and *A. seriphioides* essestial oils, rich in phenolic compounds, protected oil appreciably at concentrations of 0.02 %. The most predominant oil component of *R. officinalis*, *M. cipslatensis* and *E. cinerea* was 1.8 cineole (57, 43 and 70 %, respectively). These essential oils at concentrations of 0.02 % in peanut oil, showed protection action under the conditions used. In this study, it was not evaluated because the peroxide and free fatty acid values of peanut oil are highly variable. This situation is also explained by the low stability of peanut oil[35].

Fatty acid composition: Changes in fatty acid composition of pepper and potatoes frying oil are given in Tables 4-6. In Tables 3 and 4. the fatty acid composition of fresh olive oil, C16:0, C16:1, C18:0, C18:1, C18:2 and C18:3, determined as 6.02, 0.12, 1.89, 78.55, 11.97 and 0.54 %, respectively. The fatty acid composition of fresh peanut oil, C16:0, C18:0, C18:1, C18:2, determined as 8.92, 2.98, 59.37, 25.42 and 2.48 %.

It has been indicated that the oxidation is particularly associated with oleic, linoleic and linolenic acids[36]. Therefore, in this study were assessed by oleic, linoleic and linolenic acids taking into consideration. That are expressed how to show a performance of an oil during deep-frying can be estimated from initial fatty acid compositions[37]. While the level of oleic, linoleic and linolenic acid of fresh olive oil was determined as 78.55, 11.97 and 0.54 %, respectively. The oleic acid level of control olive oil decreased to 78.45 %, the amount of linoleic acid and linolenic acid increased to 13.00 and 0.86 % after pepper frying process. The oleic, linoleic and linolenic acids amounts of oil that butylated hydroxytoluene added were determined as 78.47, 12.76 and 0.86 %, respectively. The oleic acid amounts of all concentrations of olive oil that sage added decreased according to oleic acid of fresh oil. Linoleic acid amount of oil that 1.2 % sage added decreased to 10.95 %, as for other concentrations (0.3, 0.6 and 0.9 %) increased to 12.67, 12.96 and 12.28 %, respectively. Linolenic acid level increased also 0.70 % according to linolenic acid level of fresh oil. The levels of oleic and linoleic acid of oils that 0.3 % sage and 0.9 % rosemary essential oils increased to 79.35, 13.42 and 80.18, 13.58 %, respectively while the levels of oleic and linoleic acid of control oil were determined as 78.45 and 13.00 %, the levels of oleic and linoleic acid of oil that butylated hydroxytoluene added were determined as 78.47 and 12.76 %. The addition of 1.2 % rosemary essential oil reduced linoleic and linolenic acid levels as regards control and butylated hydroxytoluene. Almost all concentrations of thyme essential oil increased oleic, linoleic and linolenic acids level by butylated hydroxytoluene and control sample. The nearest value to oleic, linoleic and linolenic acids value of fresh oil determined in the sample that butylated hydroxytoluene added with 78.47 and 12.76 % while the highest level of oleic, linoleic and linolenic acid among all oil samples determined the samples of thyme essential oil supplement. After potato frying process, compared with fresh oil, the addition of butylated hydroxytoluene increased to oleic and linoleic acids level of oil and 0.3 % sage essential oil increased oleic acid but other concentrations of sage reduced. The addition of 1.2 % sage most increased linoleic (14.69 %) and linolenic (1.74 %) acids level

TABLE-3
CHANGES IN FATTY ACID COMPOSITION OF PEPPER FRYING OILS MADE WITH EXTRA VIRGIN OLIVE OIL (%)

Sample name		Palmitic acid	Palmitoleic acid	Oleic acid	Linoleic acid	Arachidic acid	Linolenic acid	Stearic acid
Fresh oil		6.02	0.12	78.55	11.97	0.85	0.54	1.89
Control		5.47	0.09	78.45	13.00	-	0.86	1.87
0.01 % Butylated hydroxytoluene		5.70	0.10	78.47	12.76	-	0.86	1.85
Sage (%)	0.3	6.79	0.10	77.73	12.67	-	0.85	1.82
	0.6	6.69	0.12	77.64	12.96	-	0.83	1.74
	0.9	8.14	0.10	76.57	12.28	-	0.86	1.84
	1.2	9.4	-	76.51	10.95	0.66	0.70	1.76
Rosemary (%)	0.3	4.59	-	79.35	13.42	-	0.84	1.79
	0.6	9.42	-	76.86	10.39	0.80	0.68	1.84
	0.9	2.96	-	80.18	13.58	-	0.82	1.77
	1.2	9.08	-	75.57	12.06	0.88	0.65	1.74
Thyme (%)	0.3	4.01	-	79.69	13.25	-	0.82	1.76
	0.6	3.16	-	80.06	13.61	-	1.36	1.79
	0.9	3.95	-	79.51	13.38	-	0.83	1.85
	1.2	4.97	-	78.33	13.16	-	1.06	1.70

TABLE-4
CHANGES IN FATTY ACID COMPOSITION OF POTATO FRYING OILS MADE WITH EXTRA VIRGIN OLIVE OIL (%)

Sample name		Palmitic acid	Palmitoleic acid	Oleic acid	Linoleic acid	Arachidic acid	Linolenic acid	Stearic acid
Fresh oil		6.02	0.12	78.55	11.97	0.85	0.54	1.89
Control		6.83	0.10	77.40	12.75	-	1.07	1.81
0.01 % Butylated hydroxytoluene		6.57	-	79.80	13.01	-	0.85	1.74
Sage (%)	0.3	5.63	0.11	78.87	12.76	-	0.85	1.75
	0.6	7.27	0.09	77.02	12.51	-	1.08	1.72
	0.9	7.67	-	77.27	12.33	-	0.87	1.84
	1.2	7.50	-	68.70	14.69	2.37	1.74	1.80
Rosemary (%)	0.3	4.33	-	78.50	13.16	-	1.18	1.77
	0.6	9.0	-	74.82	10.56	0.49	0.63	1.82
	0.9	4.22	-	78.83	13.34	-	1.07	1.84
	1.2	3.73	-	77.38	14.38	-	0.66	1.44
Thyme (%)	0.3	5.02	-	79.27	13.08	-	0.85	1.75
	0.6	4.23	-	77.78	12.83	-	1.35	1.73
	0.9	14.29	-	71.70	13.46	0.79	0.53	1.76
	1.2	13.93	-	71.07	13.41	1.08	0.48	1.75

TABLE-5
CHANGES IN FATTY ACID COMPOSITION OF PEPPER FRYING OILS MADE WITH RAW PEANUT OIL (%)

Sample name		Palmitic acid	Oleic acid	Linoleic acid	Arachidic acid	Linolenic acid	Stearic acid
Fresh oil		8.92	59.37	25.42	0.81	2.48	2.98
Control		9.27	52.57	31.36	0.92	2.69	3.17
0.01 % Butylated hydroxytoluene		9.06	59.12	25.30	0.90	2.57	3.03
Sage (%)	0.3	9.00	58.87	25.69	0.80	2.52	3.00
	0.6	9.02	59.24	25.36	0.81	2.48	3.07
	0.9	12.15	61.75	21.22	2.27	0.08	2.29
	1.2	9.37	52.48	31.15	1.02	2.68	3.27
Rosemary (%)	0.3	8.94	59.21	25.32	0.87	2.52	3.11
	0.6	8.94	59.34	25.34	0.79	2.47	3.09
	0.9	9.20	60.00	24.87	2.54	0.09	3.27
	1.2	9.52	51.93	31.62	1.01	2.62	3.27
Thyme (%)	0.3	9.11	53.91	31.10	2.65	-	3.05
	0.6	9.28	59.67	25.23	2.53	0.07	3.19
	0.9	8.53	58.78	25.27	2.54	2.03	1.50
	1.2	10.50	48.90	28.77	2.29	0.84	5.39

TABLE-6
CHANGES IN FATTY ACID COMPOSITION OF POTATO FRYING OILS MADE WITH RAW PEANUT OIL (%)

Sample name		Palmitic acid	Oleic acid	Linoleic acid	Arachidic acid	Linolenic acid	Stearic acid
Fresh oil		8.92	59.37	25.42	0.81	2.48	2.98
Control		8.63	60.23	23.18	-	0.03	3.12
0.01 % Butylated hydroxytoluene		9.54	52.86	31.51	2.78	-	3.28
Sage (%)	0.3	9.13	59.32	24.27	2.61	0.07	3.27
	0.6	9.52	58.30	26.86	2.42	0.09	2.67
	0.9	9.00	58.80	24.78	0.84	2.52	2.98
	1.2	9.44	52.64	31.20	2.65	1.18	1.70
Rosemary (%)	0.3	9.08	59.00	25.25	0.93	2.60	3.11
	0.6	9.25	60.04	24.92	2.59	-	3.18
	0.9	9.27	60.81	24.09	2.59	0.05	3.17
	1.2	9.24	52.82	31.12	0.81	2.72	3.27
Thyme (%)	0.3	9.18	59.95	24.75	2.70	0.09	3.29
	0.6	10.00	53.07	31.26	0.82	2.24	2.58
	0.9	17.82	64.26	17.90	0.20	-	1.20
	1.2	8.92	52.45	32.01	0.84	2.67	3.08

of oil according to other concentrations. The addition of rosemary essential oil increased oleic acid level in general according to control oil but decreased by butylated hydroxytoluene. The 0.6 and 1.2 % rosemary essential oil significantly reduced linoleic acid amount compared with control and butylated hydroxytoluene. Linolenic acid amounts of 0.6, 1.2 % rosemary essential oil, butylated hydroxytoluene and control are 0.63, 0.66, 0.85 and 1.07 %, respectively (Table-4).

Oleic and linolaic acids amount of oil that 0.3 % thyme essential oil added are 79.27 and 13.08 %. Oleic acid amount of control peanut oil decreased to 52.57 % according to fresh oil after pepper frying and linoleic and linolanic acid amounts increased to 32.36 and 2.69 %, respectively. Oleic, linoleic and linolenic acids amount of oil that butylated hydroxytoluene added are determined as 59.12, 25.30 and 2.57 %, respectively. These values are close to the fresh oil values. Oleic acid amount (61.75 %) of peanut oil that 0.9 % sage essential oil added is the highest according to its other concentrations, butylated hydroxytoluene and control. Oleic (60.00 %) and linolenic (2.54 %) acid amounts of peanut oil that 0.9 % rosemary essential oil added is the highest according to its other concentrations, butylated hydroxytoluene and control. Oleic acid amount of oil that 0.6 % thyme essential oil added is lower than butylated hydroxytoluene and control oil. Oleic, linoleic and linolenic acids amount of fresh peanut oil are determined as 59.37, 25.42 and 0.81 %, respectively. Linoleic and linolenic acids amount of control peanut oil reduced to 23.18 and 0.03 % and oleic acid amount increased to 60.23 % after potato frying process. This is explained by degradation of double bonds in unsaturated fatty acids and the formation of saturated or monounsaturated fatty acids as a result of the accelerated oxidation during frying[37]. While linoleic acid amount of oil that butylated hydroxytoluene added increased, oleic acid amount decreased to 52.86 % and as for the amount of linolenic acid is not determined. While all concentrations of sage essential oil reduced the amount of oleic acid of oils according to control and fresh oil but increased in according to butylated hydroxytoluene. It was recorded that decreased amounts of linolenic acid in general. While reduction linolenic acid amounts of oil that 0.6 and 0.9 % rosemary essential oil added are determined compared to linolenic acid amount of fresh oil, increasing oleic acid amount is determined. The amount of oleic acid of oil that 0.9 % thyme essential oil added (64.26 %) is the highest in all oil samples. As for its linolenic acid amount is not defined. Differences were determined between pepper and potato frying oils. These differences can be explained by components such as α-phellandrene, α-pinene, α-terpineol, β-pinene, camphene, capsaicin, caryophyllene, citric-acid, δ-3-carene, eugenol, γ-terpinene, hexenal, hexanoic acid, limonene, myrcene, octanoic acid, oleic acid, *p*-cymene, palmitic acid, piperidine, pulegone, stearic acid, terpinolene, threonine, valine in pepper[38] and potatoes have the protective effect on fatty acids during frying[39]. Gerde *et al.*[40] have expressed that oleic acid levels of soybean oils increased at the end of frying. In another study, this increase are explained by made polyunsaturated fatty acids into oleic acid which are more stable compared to them. Houhoula *et al.*[41] reported oleic acid (C18:1) of oil showed a small but significant decrease after frying of potato chips made with cottonseed oil. It has been reported that oil that has the highest linolenic acid content is more susceptible to degradation. Reducing the linolenic acid content will increase the oxidative stability of the frying oil[42]. This supports oleic acid level of frying oils made with olive oil reduction. Oxidation realized over these two fatty acids for oleic (59.37 %) and linoleic (25.42 %) acids level of peanut oil are high. Che Man and Jaswir[26] reported that there was a significant ($P < 0.05$) difference in the C18:2/C 16:0 ratio between oils with added antioxidants and control. They reported that C18:2/C16:0 ratio for initial value, control, sage and rosemary were 0.29, 0.17, 0.20 and 0.21, respectively during the 6-day frying. Yu[43] in a study the evaluation of the antioxidant effect of oregano on lipid oxidation of a bakery product, evaluated fatty acid compositions of the shortbread incubated at 45 ºC for 36 days. They reported that the decrease in total fatty acid concentration of the representative fatty acids in shortbread without antioxidant was 23.29 %. In shortbread with oregano, was 19.04 %; and in shortbread with butylated hydroxytoluene, was by 17.99 %. The loss of linoleic acid was the highest followed by oleic acid. This is because the bond dissociation energy in unsaturated fatty acids is much lower due to the double bonds, which makes the hydrogen abstraction much easier. Andrikopoulos *et al.*[29], evaluated the performance of virgin olive oil and vegetable shortening during domestic deep-frying and pan-frying of potatoes. As a result of their work, they reported that fatty acid composition of the samples remained relatively unaltered during the frying experiments, the most characteristic changes being the decrease of linoleic acid levels. No significant decrease of oleic acid during frying was detected. In a previous study, before frying and after frying fatty acid composition of peanut oil was determined. C16:0, C18:0, C18:1, C18:2, C20:0 and C22:0 levels of peanut oil before frying were determined as 11.5, 3.5, 48.5, 29.4, 1.5 and 2.8 %; and after frying 11.3, 3.6, 48.8, 29.1, 1.5 and 2.8 %[44].

Effect of DPPH free radical scavenger and the amount total phenolic compount: Changes in DPPH free radical scavenger and total phenolic content of pepper and potatoes frying oil are given in Tables 7 and 8. Pepper frying oils made with extra virgin olive oil were examined. It was determined that radical scavenger effect (RTE) of oils with added rosemary essential oil (all concentrations) were the highest. While radical scavenger effect of oils with added 1.2 % rosemary is 63.13 %, this value is the nearest to radical scavenger effect of fresh oil (63.63 %). Radical scavenger effect of oils with added 0.9 and 1.2 % thyme essential oils are 55.69 and 60.00 %, respectively. The radical scavenger effect of butylated hydroxytoluene is 36.75 %. All concentrations of rosemary and thyme essential oils and 1.2 % concentration of only sage were more effective than butylated hydroxytoluene on the radical scavenger effect of frying oils. Potato frying oils made with extra virgin olive oil were examined. All rosemary and 0.9 and 1.2 % thyme essential oils were increased the radical scavenger effect of frying oils. Rosemary and thyme essential oils were more effective than butylated hydroxytoluene on the radical scavenger effect of potato frying oils. It is observed that the amount of total phenolic content of pepper frying oils made with extra virgin olive oil ranged from 181 to 703 mg/kg depending on the concentrations of sage, rosemary and thyme essential oils. As for the amount of total phenolic content of potato frying oils ranged from 187 to 529 mg/kg. Pepper frying oils made with raw peanut oil were examined; while radical scavenger effects of oils with added 0.3, 0.6, 0.9 and 1.2 % thyme essential oils were determined as 59.75, 66.81, 68.50 and 70. 56 %, respectively, the effect of thyme essential oils on radical scavenger effect were more effective that the addition of sage, rosemary essential oils and butylated hydroxytoluene. Also

TABLE-7
RESULTS OF ANALYSIS OF TOTAL PHENOLIC AND DPPH-FREE RADICAL SCAVENGER EFFECT (IC_{50}) OF PEPPER AND POTATO FRYING OILS MADE WITH EXTRA VIRGIN OLIVE OIL

		Pepper frying		Potato frying	
		Radical scavenger effect (IC_{50}) inhibition (%)	Total phenol (mg/kg) extract	Radical scavenger effect (IC_{50}) inhibition (%)	Total phenol (mg/kg) extract
Fresh oil		63.63	238	63.63	238
Control		36.50	230	53.81	213
0.01 % Butylated hydroxytoluene		36.75	247	36.50	243
Sage (%)	0.3	35.63	242	36.31	219
	0.6	34.13	236	38.38	217
	0.9	36.12	181	34.19	261
	1.2	40.50	217	36.38	228
Rosemary (%)	0.3	58.25	245	55.13	209
	0.6	61.44	241	56.75	237
	0.9	59.69	244	56.69	211
	1.2	63.13	246	58.00	187
Thyme (%)	0.3	48.88	367	40.69	289
	0.6	52.25	445	44.88	330
	0.9	55.69	511	51.00	529
	1.2	60.00	703	53.88	456

TABLE-8
RESULTS OF ANALYSIS OF TOTAL PHENOLIC AND DPPH-FREE RADICAL SCAVENGER EFFECT (IC_{50}) OF PEPPER AND POTATO FRYING OILS MADE WITH RAW PEANUT OIL

		Pepper frying		Potato frying	
		Radical scavenger effect (IC_{50}) inhibition (%)	Total phenol (mg/kg) extract	Radical scavenger effect (IC_{50}) inhibition (%)	Total phenol (mg/kg) extract
Fresh oil		58.06	257	58.06	257
Control		49.25	198	49.38	232
0.01 % Butylated hydroxytoluene		50.44	213	48.63	198
Sage (%)	0.3	55.87	282	54.25	237
	0.6	56.63	224	53.88	205
	0.9	56.63	293	31.25	345
	1.2	49.38	286	46.88	190
Rosemary (%)	0.3	56.88	227	55.00	237
	0.6	54.31	207	54.19	251
	0.9	55.44	230	52.81	256
	1.2	50.25	215	48.94	215
Thyme (%)	0.3	59.75	408	58.25	435
	0.6	66.81	516	64.81	387
	0.9	68.50	562	67.67	554
	1.2	70.56	723	67.67	584

the addition of rosemary and sage increased radical scavenger effect of frying oil although not as thyme. Radical scavenger effects of oils with added 0.3, 0.6, 0.9 and 1.2 % thyme essential oils were determined as 58.25, 64.81, 67.67 and 67.67 % in potato frying oils made with raw peanut oil. It was determined that thyme and rosemary essential oils increased more than butylated hydroxytoluene the radical scavenger effects of pepper and potato frying oils. The amount of total phenolic compounds of pepper frying oils made with raw peanut oil ranged from 207 to 723 mg/kg depending on the concentrations of sage, rosemary and thyme essential oils. As for the amount of total phenolic content of potato frying oils ranged from 190 to 584 mg/kg. Differences between the radical scavenger effects of pepper and potato frying oils could be explained by phenolic substances in pepper are more than it. The radical scavenger effect of extra virgin olive oil are higher than peanut oil. This probably relates to the phenolic substances in olive oil are more stable than the phenolic substances in peanut oil during frying. While the radical scavenger effects of olive oils with added rosemary essential oils have been found to be high by comparison with sage and thyme essential oils, the radical scavenger effects of peanut oils with added thyme essential oils have been found to be higher than. The amount of total phenolic content of all frying oils with added thyme essential oils have been found to be higher than rosemary and butylated hydroxytoluene when examined the amount of total phenolic compounds of pepper and potato frying oils made with extra virgin olive oils. The amount of total phenolic content of frying oils with added rosemary essential oils are almost the same value with butylated hydroxytoluene. The oils with added sage essential oils have low amount of phenolic compounds. The amount of total phenolic content of frying oils with added thyme essential oils have been found to be the highest and total phenolic content of frying oils with added sage and rosemary essential oils are lower than that of thyme when examined the amount of total phenolic compounds of pepper and potato frying oils made with raw peanut oils. It was determined that butylated hydroxytoluene did not affect the too much the phenolic amount of frying oils (Fresh oil: 198 mg/kg; butylated hydroxytoluene: 213-198 mg/kg). It was determined that rosemary essential oils have higher radical scavenging activity and lower total phenolic compound amount according to thyme essential oils on olive olive while thyme essential oils which were most effective on the total phenolic compound showed a high radical scavenging activity on raw peanut oil at the same time, too. Silva *et al.*[45] reported that the radical-scavenging activity of extra-virgin olive oil was higher than for other olive oil samples and was also positively correlated with the phenolic content of the oil in the study that examining beef or potatoes were processed in 60 g of each olive oil, peanut oil and several vegetable oils, poured into 15 cm diameter glass beakers, in an oven at 180 ºC until the inner temperature of meat reached 180 ºC (~60 min). In the study observed that there is not a completely connection radical scavenging activity of pepper and potato frying oils made with peanut oil and olive oil with added sage, rosemary and thyme essential oils. It is determined that almost all concentrations of rosemary essential oils (excluding 0.9 %) has been effective on free fatty acid % and peroxide values of pepper and potato frying oils made with extra virgin olive oils but this effect is less than butylated hydroxytoluene. 1.2 % rosemary essential oil reduced more the free fatty acid % and peroxide values of pepper frying oil than butylated hydroxytoluene. It has been determined that the samples with added butylated hydroxytoluene have the highest oleic and linoleic acid levels among the potato frying oils. It has been found that the oleic, linoleic and linolenic acids level of pepper frying oils made with peanut oil are the nearest to the values of fresh oil. Likewise, the oleic, linoleic and linolenic acids level of frying oils with added 0.6 % sage, 0.3 and 0.6 % rosemary essential oils are the closest to fresh oil values. The linoleic and linolenic acids level of oils with added 0.3 % rosemary are determined as the closest values of fresh oil when potato frying oils examined. Radical scavenger effect of pepper frying oil, 1.2 % rosemary added, was found to be closest to value of fresh oil. Rosemary and thyme essentil oils were indicated to be more effective than butylated hydroxytoluene on the radical scavenger effect of pepper frying oil. Thyme and rosemary essential oils were determined to increase more than butylated hydroxytoluene that radical scavenger effect of peppers and potaoes frying oils. It may indicate that frying oils stability different from according to variety of frying oil and fried product.

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