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Editorial Board

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Effects of Dietary Supplementation of Glycerol on Performance, Egg Quality and Egg Yolk Fatty Acid Composition in Laying Hens

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Abstract

This study evaluated the performance and the quality and fatty acid profile of eggs from laying hens, fed with diets, containing different levels of glycerol replaced by acidulated sunflower soap stock. A total of 60 44-week-old Hy-Line W36 laying hens were distributed according to a completely randomized experimental design into four treatments, consisting of glycerol substituted of acidulated sunflower soap stock dietary inclusion levels (0, 25, 50, and 75 %), with five replicates of three birds each. Dietary treatments had no significant effect on egg production, feed intake, feed conversion ratio, egg weight and egg mass of laying hens. The inclusion of glycerol in the diet of laying hens had no significant effect on egg specific gravity, egg shell breaking strength, egg shell weight and egg shell thickness, egg shape index, albumen index, haugh unit, albumen pH, yolk pH and egg yolk color values L and b but to add glycerol in diets decreased a values in egg yolk . The inclusion of glycerol in the diet of laying hens had no significant effect on stearic, oleic, linoleic and linolenic acid contents of egg yolk. Palmitic acid content of egg yolk was significantly decreased and palmitoleic acid content of egg yolk significantly increased with the higher levels of dietary glycerol supplementation.

Keywords: Glycerol; Performance; Egg Quality; Laying Hens; Fatty Acid

INTRODUCTION

Lipids are necessary for normal growth and reproduction. The composition of lipids supplied in the diet can have a marked effect on the composition of the lipids within the animal. If the proper fatty acids are not supplied within the diet, or if the proper ratio of various fatty acids is not provided, then problems such as impairments in growth and/or reproduction can occur (Dalton, 2000). The most common lipid supplements in commercial vegetable diets are soybean and corn oils, mostly for economical and nutritional reasons (Meluzzi et al., 2001). Although they are rich in n-6 PUFA (Simopoulos& Robinson, 1998), they are expensive and compete with human nutrition (Pardı'o et al., 2005). Usually vegetable oils are used and the most used oil is soybean oil in broiler diets but also to obtain more profit and to recycle some waste materials can used like glycerol from process of biodiesel the most common energy supplements in commercial. The use of glycerol in a diet for farm animals was first attempted and reported in the 1960s and 1970s. Some studies published in this period describe the use of glycerol in the nutrition of poultry and discuss the effect of glycerol on reproduction (Neville et al, 1970; Westfall & Howarth, 1976, Suchy et al., 2012)

Some studies on glycerol for broilers (Simon et al., 1996, Cerrate et al., 2006), turkey, hens (Rosebrough et al., 1980) and pigs (Kijora et al., 1995) have shown that glycerol from biodiesel production can be used as a source of energy. Cerrate et al., (2006) reported that

glycerol can be used in broiler diets up to 5.0%. Some researchers (Mourot et al., 1994, Kijora et al., 1997, Lammers et al., 2008) investigated the effects of dietary glycerol on cholesterol and fatty acid profile of pork lipid and meat. In previous experiments, dietary supplementation of crude glycerol has been reported to improve Growth performance of broiler chickens (Mclea et al., 2011) and pigs (Shields et al., 2011; Zijlstra et al., 2009). However, the reason for this improvement is not clear (Kim et al., 2013).

A study on glycerol for hens (Yalçın et al., 2010) has shown glycerol obtained from biodiesel production from soybean at the level of 5 and 7.5% in diets had increased egg yolk cholesterol content but no adverse effects were seen in other parameters. Soap stock is a by-product of the vegetable oil refining process formed by treating crude vegetable oils with alkali to produce a sodium soap, which is then separated by centrifugation (Cmolı'k & Pokorny, 2000 ; Pardı'o et al., 2005)

Soap stocks are increasingly being used as an animal feed additive, particularly in pig and poultry diets. It has no harmful effects (beyond gossypol) and can be used in a similar way to fat since it contains a high concentration of fatty acids. When soapstock is added into meal, it can improve the palatability, increase the energy density of the diet, reduce dust, help heat stress conditions, and improve pelleting of feed products by reducing feed particle separation. It also minimizes the build-up of feed particles on equipment used for feed mixing at the mill. However, long chain fatty acids are difficult to digest in animals (Johnson & McClure 1973), therefore soap stock must be added in small amounts (approximately 3.5%)(Bock et al., 1991, Dumont&Narine, 2007).

Pardı'o et al., (2003) has studied the effect of different soap stocks (corn, sunflower, canola, and soybean) on production performance and broiler skin pigmentation. Among the soap stocks studied, addition of soybean soap-stock (SSS) improved (P = 0.005) live BW gain of birds and produced the highest percentage of broiler skin pigmentation. Because SSS is a source of fatty acid, its inclusion in laying diets was considered (Pardı'o et al., 2005).

The aim of this study was to evaluate the effects of different levels of glycerol and acidulated soap stock on performance, egg quality and yolk fatty acid composition in laying hens egg.

MATERIAL and METHODS

A total of 60 44-week old Hy-Line W36 hens were distributed according to a completely randomized experimental design into four treatments, consisting of four levels of dietary glycerol with five replicate cages of three hens each. Layers were fed with a complete feeding mixture in a mash form. The difference between experimental diets and the control diets (100 % sunflower acidulated soap stock) was that 25, 50 and 75 % of acidulated soap stock (ASS) was replaced with glycerol. Glycerol used in this experiment was containing 3800 kcal metabolizable energy/kg. Ingredient and nutrient composition of experimental diets are shown in Table 1. The control diet was formulated to meet or exceed nutrient recommendations (NRC, 1994). Cage dimensions were 40 × 50 cm equalling 2,000 cm2 of total floor space. The laying hens diet and water were offered for ad libitum consumption (16.5% crude protein, 2,750 kcal ME /kg, 3.60% Ca, and 0.42% available P) during the experimental period. The experiment lasted 84 days and was divided into three 28-day period.

Table 1. Composition of experimental diets

	Experimental diets			
Ingredients (%)	**100 % ASS**	**75% ASS / 25 %Glycerol**	**50 % ASS / 50% Glycerol**	**25 % ASS / 75 %Glycerol**
Corn	51.20	51.50	51.50	51.00
Barley	11.00	10.00	8.60	6.00
Soybean meal	24.50	24.60	24.90	25.60
Sunflower acidulated soapstock	2.60	2.40	2.15	1.67
Glycerol	---	0.80	2.15	5.02
Limestone	8.25	8.30	8.30	8.30
Di-Calcium phosphate	1.75	1.70	1.70	1.70
Salt	0.35	0.35	0.35	0.35
Premix[1]	0.25	0.25	0.25	0.25
Methionine	0.10	0.10	0.10	0.10
TOTAL	100	100	100	100
Calculated nutrients				
Metabolizable Energy (Kcal/kg)	2754	2753	2753	2751
Crude protein (%)	16.56	16.52	16.51	16.51
Calcium (%)	3.60	3.61	3.61	3.61
Available phosphorus (%)	0.42	0.42	0.42	0.41
Lysine (%)	0.90	0.89	0.90	0.91
Methionine (%)	0.37	0.37	0.37	0.37
Methionine +Cystine, %	0.61	0.61	0.62	0.63

[1] Premix provided the following per kg of diet: vitamin A, 8.800 IU; vitamin D_3, 2.200 IU; vitamin E, 11 mg; nicotinic acid, 44 mg; Cal-D-Pantothenate, 8.8 mg; riboflavin 4.4 mg; thiamine 2.5 mg; vitamin B_{12}, 6.6 mg; folic acid, 1 mg; D-Biotin, 0.11 mg; choline, 220 mg; manganese, 80 mg; copper, 5 mg; iron, 60 mg; zinc, 60 mg; cobalt, 0.20 mg; iodine, 1 mg; selenium, 0.15 mg. ASS (Sunflower acidulated soapstock)

Feed intake (FI) and Egg weight (EW) were recorded biweekly. Egg production (EP) was recorded daily and Egg mass (EM) was calculated from collecting data of EP and EW at biweekly via: EM= (EP x EW) / Period (days). Feed conversion ratio (FCR; g of feed g of egg) was calculated via: FCR = FI (g of feed/hen/period) / EM (g of egg/hen/period).

The eggs were subjected to determine characteristics of eggshell quality parameters (shell breaking strength, shell weight and shell thickness) on all collected eggs produced at the last two days of each period during the experiment. Eggshell breaking strength was measured using a cantilever system by applying increased pressure to the broad pole of the shell using an instrument (Egg Force Reader, Orka Food Technology, Israel). Eggs were then broken, and eggshell, albumen, and yolk were separated and weighed. Eggshells were rinsed running water and dried in oven at 60 °C for 12 h, to determine eggshell thickness (including the membrane) in three points on the eggs (one point on air cell or the randomized two points of equator) using a micrometer (Mitutoyo, 0.01 mm, Japan). Eggshells were weighed using a 0.001g precision scale. Eggshell weight was calculated via: Eggshell weight (g/100 g egg) = [Eggshell weight (g) / Egg weight (g)]. A colorimeter (Minolta Chroma meter CR 400 (Minolta Co., Osaka, Japan) was used to assess the egg yolk color and the CIELAB colorimetric (Romero et al., 2002). At the end of the experiment, 15 eggs per group (3 eggs from each replicate) were randomly chosen to determine yolk fatty acid composition. Triacylglycerides were methylated using the ISO 5509 method (ISO, 1978) and fatty acid methyl esters were collected. The methyl esters of the fatty acids (1 µl) were analysed in a gas chromatography (Agilent 7890A), equipped with a flame ionising detector (FID) and a fused silica capillary column (100 m × 0.25 mm i.d; film thickness 0.20 micrometer). It was operated under the following conditions.

Oven temperature program: holded at 140 ^{0}C for 5 min. and raised to 240 ^{0}C at a rate 4^{0}C /min and then, kept at 240 ^{0}C for 15 min. Injector and detector temperatures were 260 and 280 ^{0}C, respectively. Carrier gas was helium, and the flow rate of helium was 1.51 ml/min. Split ratio was 30/1 µl/min.

Data were subjected to ANOVA by using MINITAB. Duncan's multiple range tests were applied to separate means. Statements of statistical significance are based on probability of $P<0.05$.

RESULTS and DISCUSSION

Dietary treatments had no significant effect on egg production (EP), feed intake (FI), feed conversion ratio (FCR), egg weight (EW) and egg mass (EM) of laying hens. (Table 2).

Table 2. Effect of different levels of glycerol addition to diets on performance in laying hens from 44 to 56 weeks of age. Results are expressed as mean ± standard error.

Performance Parameters	Diets			
	100 ASS %	**75 ASS %/ 25 G%**	**50 ASS % / 50 G%**	**25 ASS % / 75 G%**
Egg production (%)	94.19± 1.61	96.06±2.24	93.60±1.09	93.50±0.89
Feed intake (g/hen/day)	125.96±2.32	126.44±2.85	125.74±2.17	129.50±1.94
Feed conversion ratio (g feed/g egg)	2.10±0.06	2.00±0.03	2.05±0.04	2.07±0.02
Egg weight (g)	63.77±0.75	65.66±1.44	65.46±0.34	66.94±0.87
Egg mass (g/hen/day)	60.06±1.12	63.00±1.38	61.26±0.52	62.59±1.03

ASS :Sunflower acidulated soapstock , G: Glycerol

İn terms of performance parameters of this study are consistent with the findings of researches involving acidulated soap stock and glycerol in laying hens (Pardı'o et al., 2005, Yalçın et al., 2010). The results of the present study are similar to those reported by Bregendahl et al., (2008), in experiment with Single Comb White Leghorn hens, found that EP, EW, EM and FI were not affected when 5, 10, or 15% crude glycerol was incorporated into the diet. Coşkun et al., (2007) observed that feed intake in laying hens was significantly increased by the usage of 5% pure glycerol, but the usage of 5% and 10% crude glycerol had no significant effect on FI of laying hens. Yalçın et al., (2010) reported that the study hens fed diets with 7.5% glycerol consumed significantly less feed than those of other groups but the inclusion of 2.5 and 5% glycerol in diets had no significant effects on feed intake during the 16 week experimental period. Swiatkiewicz and Koreleski (2009), reported that the inclusion of 2, 4, or 6% crude glycerine had no significant effect on laying performance parameters as compared with the control group. Duarte et al., (2014), reported that egg production and feed conversion were not affected by mixed crude glycerine inclusion. The results of this study consistent previous research that used acidulated soap stock in laying hens. Mızrak et al., (1999), reported sunflower oil as an energy source was replaced by different levels (0, 25, 50, 75, and 100 %) of sunflower soap-stock in the experiment) and egg weight, feed consumption, feed efficiency and body weight gain were not significantly affected by the treatments. The inclusion of glycerol in the diet of laying hens had no significant effect on egg specific gravity, egg shell breaking strength, egg shell weight and egg shell thickness, egg shape index, albumen index, and haugh unit, albumen pH, yolk pH value. L and b values of egg yolk had no significant affected by the glycerol levels in diet. The highest egg yolk a value was determined in 75 % ASS/ 25 % G of group, the lowest value determined in 25 % ASS / 75 % G of group (Table 3).

Table 3. Effect of different levels of glycerol addition to diets on egg quality parameters in laying hens from 44 to 56 weeks of age. Results are expressed as mean ± standard error.

Egg Quality Parameters	Diets			
	100 ASS%	**75 ASS%/ 25 G%**	**50 ASS% / 50 G%**	**25 ASS% / 75 G%**
Egg specific gravity (g/cm^3)	1.0809±0.00	1.0811±0.00	1.0800±0.00	1.0803±0.00
Eggshell breaking strength (kg)	3.78±0.07	3.91±0.04	3.80±0.08	3.67±0.04
Eggshell weight (g/100 g egg)	5.83±0.08	5.86±0.10	5.86±0.07	5.97±0.15
Eggshell thickness (mm)	0.3534±0.05	0.3520±0.00	0.3484±0.00	0.3490±0.00
Egg shape index (%)	73.08±0.93	73.34±0.44	73.86±0.18	73.58±0.41
Albumen index (%)	5.28±0.08	5.27±0.24	4.95±0.04	5.09±0.14
Haugh unit	89.96±0.46	90.17±1.44	87.92±0.43	88.60±0.95
Yolk pH	5.33±0.10	5.36±0.07	5.35±0.09	5.35±0.05
Albumen pH	7.08±0.17	7.07±0.13	7.12±0.14	7.05±0.11
Egg yolk color value				
L	54.74±0.29	55.17±0.26	55.11±0.68	54.72±0.37
a	3.35^{bc}±0.20	4.15^{a}±0.18	3.56^{b}±0.13	2.93^{c}±0.14
b	42.00±0.33	42.59±0.48	42.18±0.17	41.75±0.28

ASS :Sunflower acidulated soapstock , G: Glycerol $^{a, b, c}$: Values in rows are statistically different; P<0.05

Mızrak et al., (1999), reported sunflower soap-stock replaced soybean oil in the diet improved egg yolk pigmentation. In terms of other data similar results were reported by Swiatkiewicz and Koreleski (2009), observed no effect of the inclusion of 2, 4 and 6% crude glycerol in the diets on egg quality parameters (albumen height, haugh unit, egg shell thickness, and egg shell breaking strength). In the study of Coşkun et al., (2007) the values of yolk index, albumen index and haugh unit of eggs were not affected by the inclusion of glycerol at the levels of 5 and 10% in the diets but the shell thickness of egg was decreased with the usage of 10% glycerol. Duarte et al., (2014) reported that egg quality parameters were not affected by mixed crude glycerine at any of the inclusion levels.

The effects of dietary supplementation of glycerol on yolk fatty acids composition are shown in Table 4.

Table 4. Effect of different levels of glycerol addition to diets on egg yolk fatty acid compositions in laying hens from 44 to 56 weeks of age. Results are expressed as mean ± standard error.

Fatty acids profile (%)	Diets			
	100 ASS%	**75 ASS%/ 25 G%**	**50 ASS% / 50 G%**	**25 ASS% / 75 G%**
Palmitic acid (16:0)	21.49^{a}±0.69	21.58^{a}±0.32	20.20^{b}±0.35	19.94^{b}±0.34
Palmitoleic acid (16:1)	2.21^{A}±0.40	2.62^{B}±0.28	3.45^{AB}±0.12	4.40^{A}±0.49
Stearic acid (18:0)	7.17±0.88	5.53±0.58	6.19±0.74	6.51±0.58
Oleic acid (18:1)	48.67±1.03	50.90±0.63	50.23±0.84	50.26±0.34
Linoleic acid (18:2)	20.46±0.96	19.34±0.55	19.93±0.60	18.70±0.69
Linolenic acid (18:3)	Nd	0.157±0.00	nd	0.377±0.17
ΣSFA	28.66±3.38	27.11±1.47	26.39±2.10	26.45±0.73
ΣMUFA	50.88^{b}±2.32	53.52^{ab}±1.64	53.67^{ab}±2.01	54.66^{a}±1.52
ΣPUFA	20.46±2.15	19.36±1.23	19.93±1.33	18.88±1.73

ASS :Sunflower acidulated soapstock , G: Glycerol nd:not detected
$^{a, b, c}$: Values in rows are statistically different; P<0.05
^{A,B,C}: Values in rows are statistically different; P<0.01

The inclusion of glycerol in the diet of laying hens had no significant effect on stearic, oleic, linoleic and linolenic acid contents of egg yolk. Palmitic acid content of egg yolk was significantly decreased with fed diet containing levels of 50 and 75 % glycerol.

The highest values of palmitic acid was determined in the groups fed diets containing levels of 0 and 25 % glycerol (P<0.05).

Palmitoleic acid content of egg yolk was higher in the group fed diet containing levels of 50, and % glycerol ($P<0.01$). Glycerol supplementation had no significant effect on total saturated fatty acid (SFA) and polounsaturated fatty acid (PUFA) content of egg yolk. Total monounsaturated fatty acid (MUFA) content of egg yolk fed with 100 % acidulated sunflower soap stock of group was significantly increased than fed with the other groups ($P<0.05$).

The fatty acid profile of eggs is highly dependent on the diet of laying hens (Yannakopoulos et al., 2005, Sosin et al., 2006). Mizrak et al., (1999) reported that replacement of sunflower oil by its acidulated soap stock increased oleic acid content of the egg yolk, however, decreased the linoleic acid.

Some researchers (Kijora et al., 1995; Mourot et al., 1994) reported that crude glycerol supplementation has slightly increased the oleic acid content and decreased the proportions of the linoleic and linolenic acids. Boso et al., (2013) reported that the percentage of PUFAs and omega-6 fatty acids in egg from laying hens fed with glycerol increased as the levels of inclusion. Duarte et al., (2014) reported that alpha linoleic acid and polyunsaturated fatty acid (PUFAs), percentages, as well as ω-6/ω-3 ratio, linearly increased with increasing glycerine levels in laying hens. The differences in fatty acid profile among literatures may be due to the differences in the amount and profile of fatty acids remaining in crude glycerol or the reduction in crude oil or soap stock due to the addition of glycerol.

The reason of increase in palmitic acid and decrease in palmitoleic acid in the egg yolk may be attributed to acidulated sunflower soap stock contains higher palmitic acid and lower palmitoleic acid than glycerol.

CONCLUSION

In conclusion, the results of this study show that it is possible to replace 75 % of glycerol with acidulated sunflower soap stock (4,5 % in diet) that serves as the major energy source of feeding mixtures intended for utility layers, without any significant effects on egg production and egg quality. And also, by the increase of the glycerol level in diet of hens, a slight decrease in palmitic acid content and increased monounsaturated fatty acids (MUFA) percentage was observed.

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Mathematical Modeling of Apricot Drying

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Abstract

Apricot is highly appreciated temperate fruit with taste, smell, visual and nutritional properties. Apricot fruits are mostly consumed as fresh but because of their perishable nature and short storage opportunity they are generally dried. Drying is apparently one of the oldest methods in food preservation technique, used by human and commonly used for preservation of fruits and vegetables. In this study, tray drying and also microwave pretreated tray drying were applied on apricot. The drying was performed at a constant air velocity of 0,5 m/s and temperature of 60°C. For microwave pretreated hot air drying, microwave was applied to apricot at 350 W power intensity and then samples were dried in tray dryer. Moisture content trends for both tray and microwave pretreated tray drying was the same, because of the studying constant temperature, as normal and similar to literature. The fit quality of 6 thin-layer drying models: Newton, Page, Logarithmic, Henderson and Pabis, Two Term and Wang and Sing were applied to the experimental data of apricot drying. Two term model was the best fitting model for tray dried apricot. For microwave pretreated tray dried apricot, best fitting models are Logarithmic and two term.

Keywords: apricot, drying, microwave, mathematical modeling

INTRODUCTION

Apricot is highly appreciated temperate fruit with taste, smell, visual and nutritional properties. It has been widely consumed for over years by various cultures. Apricot botanically named as Prunus armeniaca L. (Huang et al., 2013). Apricot has an important place in human nutrition because of not only the attractive color and taste but also the rich mineral and vitamin contents and antioxidant properties. Apricot fruits are mostly consumed as fresh but because of their perishable nature and short storage opportunity they are generally dried (Hacıseferoğulları et al, 2007).

Apricot has health benefit properties due to presence of bioactive compounds. Apricots are important essential nutrient sources for human such as minerals, vitamins like A, C, riboflavin, niacin, thiamine and pantothenic acid; fibers, bioactive phytochemicals, organic acids, phenolic compounds and carbohydrates (Orsat et al., 2007). Carotenoids, phenolics and antioxidants are important phytochemicals for their biological value. In the later years, interest in carotenoids and polyphenols of apricots has increasing for their antioxidant properties and ability to scramble towards chronic disease. Apricot contains high amount of carotenoids which contribute to fruit color, taste and nutritive value (Huang et al., 2013). In apricot 60-70% of the total carotenoids is represented as β-carotene (Sass-Kiss et al., 2005). Apricots are important source of phenolic compounds. They have antioxidant potential and act as anti-allergic, anti-microbial, anti-carcinogenic, anti-flammatory and anti-mutagenic role.

Drying is apparently one of the oldest methods in food preservation technique, used by human and commonly used for preservation of fruits and vegetables (Lewicki, 2006). Fresh fruits and vegetables are classified as highly perishable commodities because of the moisture content is more than 80%. Moisture in the foods is one of the important factor in microbiological deterioration and chemical and physical changes. For the dehydration of

foods and bio-materials, there is a lot of processing technique. Each drying technique has specific effect on product by means of product functionality and quality. Over the years, a number of new and innovative drying methods have been developed.

Tray drying systems use trays to expose the food product to heated air in an enclosed space. In microwave drying electromagnetic energy with the frequency between 300 MHz and 300 GHz is used. It is demonstrated that using microwave energy for drying reduce the energy consumption. The microwave energy is an attractive thermal energy source by the reasons of reduced processing time and volumetric heating. For fully complete drying process microwave is recommended to combine with other drying techniques.

The drying kinetics of the product are the most important data required for the design and simulation of dryers and estimate the drying time. Thin layer drying equations are used to estimate the drying time for several products and also to generalize the drying curves. In food drying studies semi-theoretical and empirical models are widely used such as Newton, Page, Henderson and Pabis, Logarithmic, Two term and Wang and Sing (Table 1.).

Table 1. Thin layer models in food drying

Model Name	Model
Newton	MR = exp (-kt)
Page	MR = exp ($-kt^n$)
Henderson and pabis	MR = a exp (-kt)
Logarithmic	MR = a exp (-kt) + c
Two term	MR = a exp ($-k_0t$)+ b exp ($-k_1t$)
Wang and Sing	MR = 1 + at + bt^2

In this study hot air and microwave pretreated hot air drying were applied on apricot and kinetic parameters were determined.

MATERIAL and METHODS

Apricot samples were obtained from traditional bazaar in Gaziantep. Apricot fruits were selected of nearly uniform size and maturity, free from diseases. All samples were brought to laboratory immediately and washed with distilled water for removal of dust and other pollutants. After washing, the excess water was dried on the drying paper.

The drying of apricot has been performed in a pilot plant tray drier (VOP 8 Tray Dryer, Armfield, UK). Apricot seeds were taken and all samples were cut into small pieces, and stored at -40°C. Samples stored at -40°C freezer were weighted nearly 200 g and placed to refrigerator for thawing. After 5 hours, samples put into special aluminium dish for tray dryer as a thin layer and replaced in the driers middle shelf. The drying was performed at a constant air velocity of 0,5 m/s and temperature of 60°C. Hot air flows parallel to the drying surface of the sample. Weight loss was recorded at 15 minutes interval by a digital balance connected to the dryer. Drying was continued until the moisture content of samples fall under 25%.

For microwave pretreated hot air drying frozen samples were thawed in refrigerator and nearly 200 g sample was put into squared glass dish and MW was applied for 1 minute at 350 W power intensity. After MW pretreatment, samples were dried in tray dryer in the same conditions with other samples, which dried only in hot air drying.

Six empirical and semi-theoretical models (Newton, Page, Henderson and Pabis, Logarithmic, Two term and Wang and Sing) were tested to fit the moisture ratio versus time. All data were analyzed by one-way analysis of variance (one-way ANOVA) to test for significant differences by using IBM SPSS Statistics 21. Differences among sample means were reported to be significant when $p<0.05$.

RESULTS and DISCUSSION

Drying Kinetics

The initial moisture contents of apricot was about 85 (wet basis). Drying of samples continued until the final moisture contents of about 25 % (by wet basis). Variations of the moisture contents of apricot samples with drying time in tray and MW pretreated tray drying are given in Figure 1. Moisture contents of all samples decreased with similar trends.

Moisture content trends for both tray and microwave pretreated tray drying was the same, because of the studying constant temperature, as normal and similar to literature (Marquez et al., 2006).

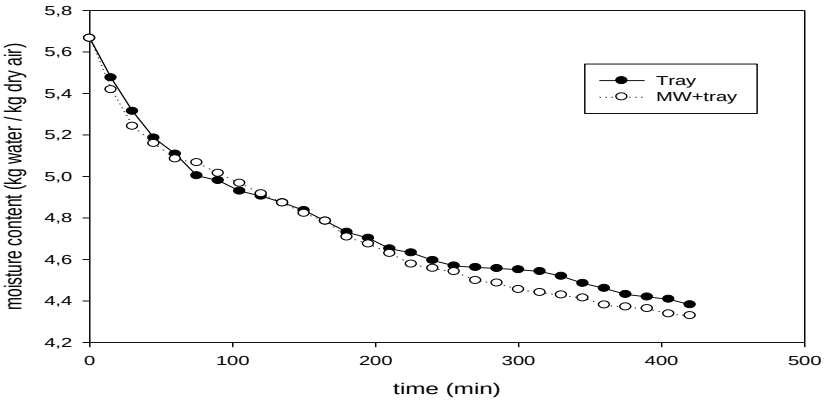

Figure 1. Variation of moisture content versus drying time of samples in tray and MW+tray drying

Modelling of Drying Curves

The moisture content data obtained from experimental drying were converted into moisture ratio (MR). Natural logarithm of moisture ratio plotting versus time (Figure 2). For apricot, only one falling rate period was observed. Then drying models was applied to the experimental data of apricot samples. The statistical values and constants of each model for all samples are shown in Table 2.

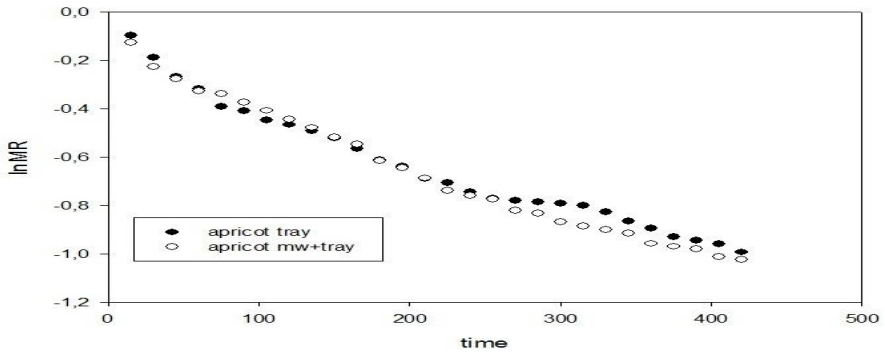

Figure 2. Natural logarithm of moisture ratio versus time graph for apricot

The coefficient of determination (R^2) was one of the primary criterions for selecting the best equation to define the drying curves of apricots and also root mean square error (RMSE) was used to determine the quality of the fit (Delgado et al, 2014).

Table 2. Thin Layer Model Fitting for apricot samples dried with tray and MW+tray drier

Sample	Model	R^2	RMSE	k	n	a	b	k_0	k_1	c
Apricot Tray	Newton	0.7634	0.0678	0.0030						
	Page	0.9926	0.0120	0.0278	0.5921					
	Handerson and Pabis	0.9546	0.0297	0.0021		0.8343				
	Logaritmic	0.9893	0.0144	0.0060		0.5739				0.3446
	Two Term	0.9950	0.0098			0.2809	0.7139	0.0215	0.0016	
	Wang and Sing	0.9029	0.0435			-0.0035	5.1481 E-006			
Apricot MW+Tray	Newton	0.8335	0.0596	0.0030						
	Page	0.9934	0.0119	0.0228	0.6336					
	Handerson and Pabis	0.9818	0.0197	0.0023		0.8462				
	Logaritmic	0.9945	0.0109	0.0044		0.6350				0.2577
	Two Term	0.9945	0.0109			.06350	0.2577	0.0044	4.1429 E-019	
	Wang and Sing	0.9228	0.0406			-0.0035	4.8732 E-006			

Two term model was the best fitting model for tray dried apricot. For mw+tray dried apricot best fitting models are Logarithmic and two term. The performance of the best models are illustrated in Figure 3. and Figure 4. The predicted data generally banded around the straight line which showed the suitability of mathematical model in describing drying behavior of apricots.

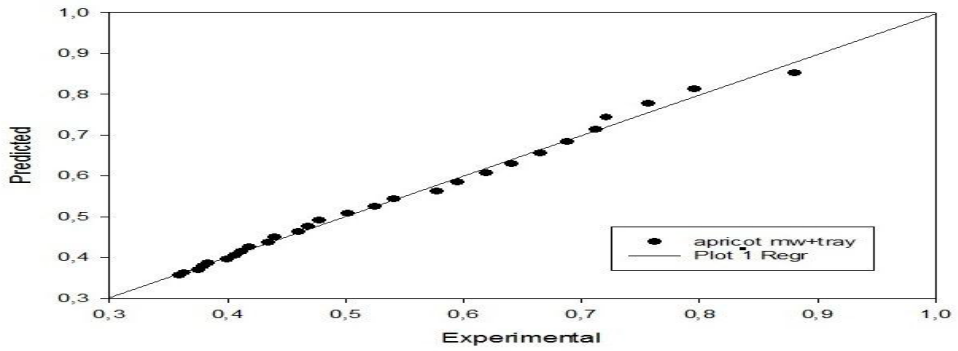

Figure 3. The performance of the logarithmic model for MW+tray dried apricot

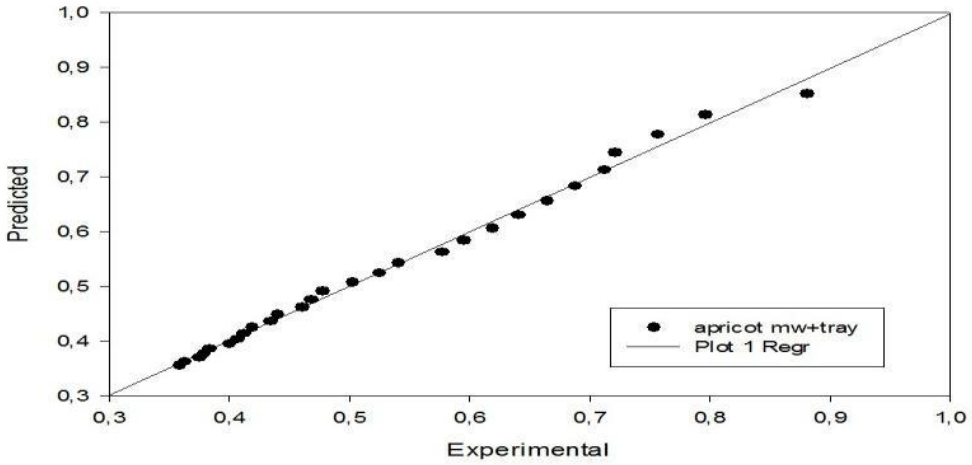

Figure 4. The performance of the two term model for MW+tray dried apricot

Toğrul and Pehlivan (2003) were studied about modeling of drying kinetics of single apricot. They described the logarithmic drying model is best for the drying behavior of single apricot (within 99.9%).

CONCLUSION

Hot air drying and microwave pretreated hot air drying were found to be suitable for drying of apricot. Drying curves for apricot samples only showed falling rate period. These results indicated that moisture movement mechanism in apricot could be by diffusion. The fit quality of 6 thin-layer drying models (Newton, Page, Logarithmic, Henderson and Pabis, Two Term and Wang and Sing) to experimental data were evaluated. Good results according to the coefficient of determination (R^2) and root mean square error (RMSE) were obtained with the Logarithmic and Two Term models.

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Effects of Cultivar, Maturity Index and Growing Region on Fatty Acid Composition of Olive Oils

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Abstract

Olive oil is an important food for people the countries surrounding the Mediterranean Sea and the presence of biologically important minor constituents such as high content of healthy monounsaturated fatty acid (FA). Virgin olive oil (VOO) is valued for its organoleptic and nutritional characteristics, and is resistant to oxidation due to presence of high monounsaturated fatty acid (MUFAs) and low polyunsaturated fatty acid (PUFAs) content. The fatty acid composition of olive oils is influenced by many factors including, climate conditions, geographic area, cultivar, fruit ripeness and agricultural practices. The health benefits of extra virgin olive oil (EVOO) consumption have been related to its well-balanced FA composition. Major FAs in olive oils are oleic (55–85%), palmitic (7.5–20%), linoleic (7.5–20%), stearic (0.5–5%), palmitoleic (0.3–3.5%), and linolenic (0.0–1.5%) acids, and traces of myristic, arachidic, and margaric acids have also been found. Oleic acid is one of the most important FAs in olive oils due to having the nutritional wealth and support for oxidative stability. In consequence, the olive oils differ in composition of fatty acid mainly depending on variety, maturity index and growing region. Therefore, this review may contribute good information about the effect of these principal factors on the fatty acid composition of olive oils.

Keywords: Cultivar, Fatty acid, Growing region, Maturity index, Olive oil

INTRODUCTION

The olive oil production has extended in recent years beyond the Mediterranean basin to non-traditional regions in the southern hemisphere. Turkey is one of the most important virgin olive oil producing countries in the world, coming after Spain, Italy, Greece, Tunisia, Morocco and Syrian Arab Republic.

According to olive oil quantity data released in FAO (2014). Spain (1.738,600 tonnes), Italy (294,914 tonnes), Greece (208,900 tonnes), Tunisia (179,700 tonnes), Morocco (137,400 tonnes), Syrian Arab Republic (100,638) and Turkey (73,915 tonnes) are the most leading countries, respectively.

Among oils, virgin olive oil, a unique crop owing to its elevated nutritional value and sensory properties, is formed by mechanical tools directly from olive fruits in crude form without any other refining processes with regard to further vegetable oils. The olive oils obtained from different cultivars which are from different environments and have different maturity index could differ in quality properties (Rondanini et al., 2014; Borges et al., 2017). In addition to cultivar, geographic area and maturity index many other factors, such as climatic conditions (rainfall, temperature, humidity), agricultural practices and isolation techniques, may also influence the composition and quality of olive oils (Rondanini et al., 2011; Borges et al., 2017).

Olive oil is a fundamental food ingredient recognized for its nutritional qualities and potential health benefits owed not only to its high oleic acid and antioxidant contents but also to its uniquely high level of squalene, which is known to have an anticancer activity (Waterman & Lockwood, 2007), as well as oleocanthal, a secoiridoid phenolic compound with potential therapeutic properties against inflammation, cancer, and neurodegenerative diseases (Parkinson & Russell, 2014). It is well established that the organoleptic properties of olive oil, which are strongly correlated to its geographical and varietal origins, are behind its wide commercialization and elevated market value (Borges et al., 2017).

Virgin olive oil (VOO) is valued for its organoleptic and nutritional characteristics, and is resistant to oxidation due to presence of high monounsaturated fatty acid content (MUFAs) and low polyunsaturated fatty acid content (PUFAs) (Rigane et al., 2012).

The health benefits of olive oil can be related with its chemical composition which has effect on olive oil oxidative stability and quality such as fatty acid composition of olive oil includes palmitic (C16:0), palmitoleic (C16:1), stearic (C18:0), oleic (C18:1), linoleic (C18:2), and linolenic (C18:3) acids. The proportions of fatty acids found in olive oil are the most important factors affecting the nutrition value and quality of the olive oil. While the oleic and linoleic acids are the main fatty acids in the olive oils, linolenic acid is found in small amounts. Oleic acid is a monounsaturated fatty acid and its ratio in olive oil varies according to the ecosystem and season (45-85%). Linoleic acid is a polyunsaturated fatty acid and constitutes 9% of the olive oil (Figure 1) (Bendini et al., 2007).

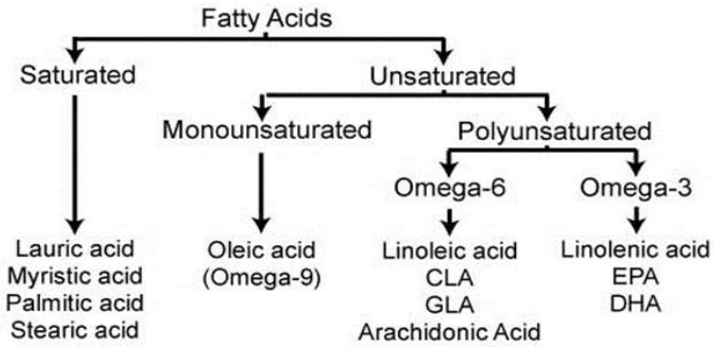

Figure 1. Classification of fatty acids of olive oil

A fatty acid is said to be saturated if each carbon is joined to its neighboring carbons by a single bond. If one or more double bonds is present, the fatty acid is said to be unsaturated. If a fatty acid has only one double bond in the carbon chain, the fatty acid is termed monounsaturated, if a fatty acid has more than one double bond in the carbon chain, the fatty acid is termed polyunsaturated (Figure 2a-2b).

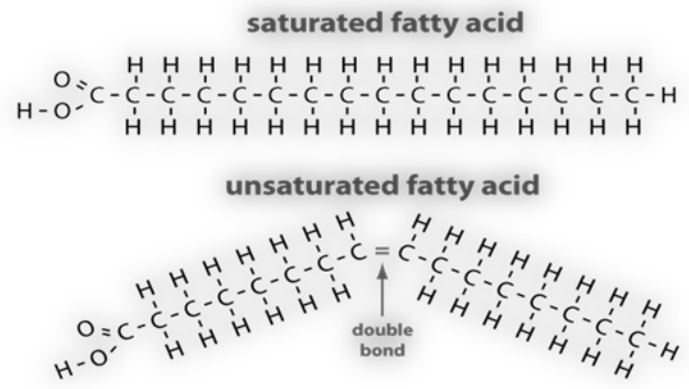

Figure 2a. Types of fatty acids according to presence of double bond

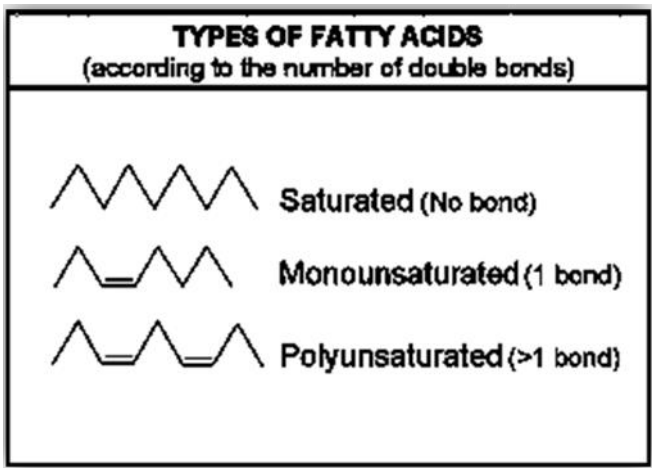

Figure 2b. Types of fatty acids according to number of double bonds

Olive oil extraction using healthy fruits harvested at the right stage of ripening by using proper methods have influence on chemical characteristics of olive oils (Olias et al., 1993). Olive oil is resistant to oxidation because of its low polyunsaturated fatty acid composition and high contents of α-tocopherol and phenolic contents (Sevim et al., 2013).

Among chemical parameters affecting the quality of olive oils, the fatty acid profile is one of the most significant, and this condition may be greatly affected by environmental factors (Borges et al., 2017). The chromatographic analysis of fatty acid methyl esters is applied for the characterization of olive oil and determination of its quality (Zarrouk et al., 2008).

Therefore, due to the importance of fatty acid profile on the oil quality, this review aims to good understand the composition of the fatty acids, and affecting factors (olive variety, maturity index and olive growing region) on these compounds.

Effect of Olive Cultivar On Fatty Acid Composition of Olive Oils

The most important factor affecting oil quality is olive variety. Fatty acid composition may alter among olive oil obtained from different olive cultivars. The effect of olive cultivar on fatty acid composition was studied by different researchers. For example, in Picual, Cornicabra, Manzanilla, Arbequina and Local oils from Spain (Pardo et al., 2007), in Gemlik,

Ayvalik, and Memecik from Turkey (Kelebek et al., 2015), in Throumbolia and Koroneiki from Greece (Vekiari et al., 2010) and Mari from Iran (Amanpour et al., 2016). It is known exactly that the main monounsaturated fatty acid in olive oil is oleic acid. High amount of oleic acid in olive oil is of great significance owing to promoting the nutritional wealth by reducing the breast cancer hazard and diminishing the low density lipoprotein (LDL) cholesterol and triglycerides which decline blood pressure and cardiovascular illness as well as enhancing the oxidative stability (Benito et al., 2010). Therefore, as a consequence the high tolerance to oxidation in olive oil is especially because of the high amount of oleic acid.

Ilyasoglu and Ozcelik (2011) determined oleic acid as the most dominant fatty acid in olive oil obtained from Ayvalık and Memecik varieties and quantified as 71.08% and 75.17% for Ayvalık and Memecik variety, respectively.

Douzane et al. (2012) studied fatty acid composition of olive oils obtained from 6 different olive varieties grown in Algeria, they emphasized that varietal difference was an effective criterion on oleic acid and linoleic acid.

Pardo et al. (2007), evaluated the fatty acid composition of virgin olive oils obtained from different olive cultivars in the Campo de Montiel area. The oils of the studied area stood out for their high contents of oleic and stearic acids, and for their low contents of linoleic and palmitic acids. Means and standard deviations for the significant fatty acids composition (%) in the olive oil samples were shown in Table 1.

Table 1. Significant fatty acid composition of virgin olive oils obtained from different olive cultivars in the Campo de Montiel area

Fatty acids	Variety				
	Picual	**Cornicabra**	**Manzanilla**	**Arbequina**	**Local**
Oleic acid (C18:1)	80.7 ± 1.21^{a}	80.0 ± 0.74^{a}	73.5 ± 3.30^{c}	70.6 ± 0.78^{d}	77 ± 0.92^{b}
Palmitic acid (C16:0)	10.5 ± 0.66^{c}	10 ± 0.89^{c}	13.2 ± 0.90^{b}	14.9 ± 0.50^{a}	10.0 ± 1.13^{c}
Linoleic acid (C18:2)	3.51 ± 0.85^{c}	4.09 ± 0.61^{c}	8.34 ± 1.77^{ab}	9.05 ± 0.35^{a}	7.60 ± 0.00^{b}
Stearic acid (C18:0)	2.93 ± 0.29^{a}	3.32 ± 0.43^{a}	2.30 ± 0.34^{b}	1.70 0.00^{c}	1.95± 0.00^{a}

In our previous study (Kelebek et al., 2015), Ayvalik, Gemlik, and Memecik olive varieties cultivated in their respective growing areas were evaluated and compared due to differences in the fatty acids. Thirteen fatty acids were identified and quantified in all samples. Oleic acid was the highest concentration and this acid was more dominant in Gemlik oils. There were significant differences in the mean values of FA composition of the olive oils in relation to varieties. Oleic acid was highest concentration in all oil samples followed by palmitic and linoleic acids. According to the results, the highest amount of oleic acid was found in GEM oil (75.85%) and the lowest in AYV oil (68.95%). However, the amount of palmitic acid was found to be the highest in AYV oil (14.51%) and the lowest in GEM oil (11.42%) (Table 2).

Table 2. Significant fatty acid composition of virgin olive oils obtained from different olive cultivars in Turkey

Fatty acids	Cultivars		
	Ayvalık	**Gemlik**	**Memecik**
Palmitic acid (C16:0)	14.51±0.34^{a}	11.42±0.96^{b}	12.31±1.08^{b}
Stearic acid (C18:0)	2.39±0.02^{b}	3.35±0.08^{a}	2.12±0.08^{c}
Oleic acid (C18:1)	68.95±0.42^{b}	75.85±0.89^{a}	69.57±1.07^{b}
Linoleic acid (C18:2)	11.40±0.05^{b}	6.49±0.04^{c}	13.14±0.10^{a}

Ruiz-Dominguez et al. (2013) examined the effects of varietal differences in fatty acids obtained from different olive varieties grown in Valencia, Spain, on fatty acid composition. In the study 45 different olive varieties were used. According to the findings obtained, the varietal difference was statistically significant ($p \leq 0.05$) on all other fatty acids except palmitoleic and margoleic acids. It was found that the predominant fatty acid was oleic acid in all varieties and the amount varied between 56.8-84.2%. The amount of palmitic acid in the second importance was in the range of 7.37-20.38%.

Effect of Maturıty Index on Fatty Acid Composition of Olive Oils

The second factor that is effective on oil quality is the maturity index. Fatty acid composition of olive oils may vary depending on the maturity stage of the olive fruits. The maturity indexes are calculated according to International Olive Oil Council method (IOOC, 2011). Maturity index color scale is used for this purpose. 100 olive samples were randomly selected and classified according to their skin color. This scale has 0-7 colors (Figure 3a) and classification is shown in Figure 3b. The number of olives in each group is multiplied by coefficient and the calculated values are summed and divided by 100. The value found is the maturation index.

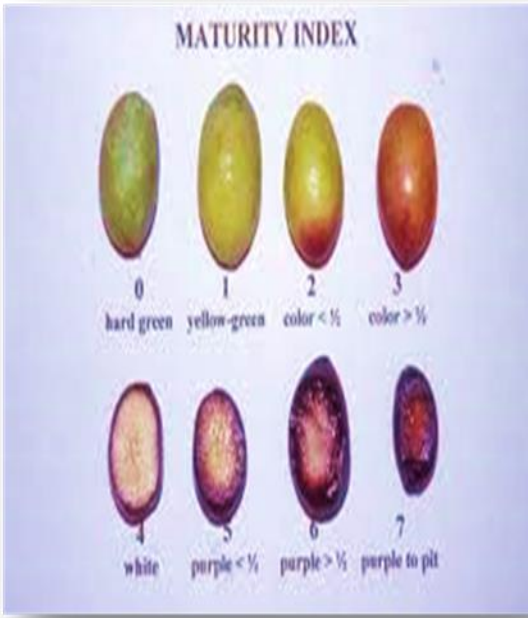

Figure 3a. Coefficients of maturity scale index **Figure 3b.** Classification of olives

There are a lot of studies that have shown the formation of fatty acids and their relationship with each other and also effect of maturity index on fatty acid composition.

Ninni (1999) studied of the biosynthetic route of the fatty acids in Greek virgin olive oil during the ripening period of the olive. They pointed out that oleic acid is formed first in the fruit and there is a strong antagonistic relationship between oleic and palmitic, palmitoleic and linoleic acids.

Though the palmitic acid level may remain permanent during the maturation, the ratio of palmitic acid decreases, and the level of oleic acid enhances for the sake of active triacylglycerol biosynthesis. The level of linoleic acid may raise over the maturation because of the production of oleic acid and the activation of enzyme oleate desaturase, which converts oleic acid into linoleic acid. But, in another study fatty acids, such as palmitoleic, stearic and linolenic, remain relatively constant over the normal harvesting stage (Ayton, 2006).

Morello et al. (2004) studied effect of harvesting periods on fatty acid composition. Oils collected from the first week of November to the second week of January were classified as the first harvesting period, and oils collected from the second week of January onwards were classified as the last harvesting period. There was an increase in the percentage of oleic acid as a consequence of the maintenance of the percentage of the saturated fatty acids and decrease of the polyunsaturated ones, linoleic and linolenic acids (Table 3). The unsaturated fatty acids are very important for the stability of oils because of the chemical reactions occurring at the double bonds. The rates of those oxidation reactions depend on the number of double bonds in the carbon chain.

Table 3. Significant fatty acid composition of virgin olive oils obtained from different harvesting period

Harvesting Period	Fatty Acids				
	Palmitic	**Stearic**	**Oleic**	**Linoleic**	**Linolenic**
First harvesting period	13.4	2.39	70.1	10.9	0.76
Last harvesting period	12.3	2.23	74.0	9.1	0.55

Changes in fatty acids were investigated on two different types of Greek olives (Throumbolia and Koroneiki) depending on harvest time. In the study, it was reported that the predominant fatty acid was oleic acid and this acid was changed between 61.07-62.92% in Throumbolia and 74.97-76.33% in Koroneiki variety. In both types, the highest amount was detected in the third maturation phase (black crust color) (Vekiari et al., 2010).

Effect of Growing Region on Fatty Acid Composition of Olive Oils

Fatty acids in olive oil vary depending on the region where the olive tree is located. Due to previous study a significant effect ($P < 0.05$) of the geographic area was observed in the fatty acid profile. The oils from different locations presented the diverse content in MUFA and the PUFA and, consequently, varying MUFA/PUFA ratio (Reboredo-Rodriguez et al., 2015). According to studies of Arbequina olive oils recently produced in Australia, Argentina and Tunisia, different cultivation and environmental conditions may have a strong effect on the fatty acid composition of oils, with oleic and palmitic acids being especially affected (Mailer et al., 2010). Among the environmental factors considered, temperature plays an essential role in the fatty acid composition of oils, by regulating fatty acid desaturases (Hernandez et al., 2011).

It has been shown that low temperatures increase the polyunsaturated fatty acid content of plants, thus maintaining the fluidity of biological membranes. Corroborating this relationship, in the present study a significant association ($P < 0.05$) was recorded between minimum temperatures and the C18:2 and C18:3 content of the oils analysed, whereas maximum temperatures were mainly correlated with the percentages of saturated fatty acids. In Arbequina oils from Argentina, it has been observed that the oleic acid content is dependent on the mean temperature during fruit growth, and can decrease by up to 2% for each ^{o}C of increased temperature (Rondanini et al., 2011).

According to results of some other studies, while Spanish, Italian and Greek olive oils contain a high level of oleic acid and low level of linoleic and palmitic acids, Tunisian olive oils involve a lower level of oleic acid and high level of linoleic and palmitic acids. Based on the data released from different countries, olive oils are categorized in two diverse classes, one is composed of a high oleic acid extent and low linoleic-palmitic acids, and the further entailed a lower oleic acid extent and high linoleic-palmitic acids. Therefore, the low oleic acid content found in those oils, compared with the Spanish, has been attributed to high temperatures (Torres et al., 2009).

Ceci and Carelli (2007) examined the growing region effect on the composition of fatty acids in the oils. For this purpose olive cultivars were obtained from different locations of Argentina. In the study, fatty acids varied according to the region where the olives were cultivated. Borges et al. (2017) analyzed fatty acid profile of Arbequina virgin olive oils produced in different regions of Brazil. The major fatty acid found was oleic acid (C18:1), followed by palmitic acid (C16:0) and linoleic acid (C18:2) (Table 4). A significant effect ($P < 0.05$) of the geographic area was observed in the fatty acid profile. The results obtained provide useful data on the characteristics of Arbequina olive oils from Brazil show that the geographic area of cultivation may affect the physicochemical properties and composition of olive oils. The fatty acid composition of oils was strongly related to environmental factors, particularly with altitude. Thus, findings of the present study reveal that geographic and climate aspects of producing areas may significantly influence the fatty acid composition of Arbequina olive oil.

Table 4. Significant fatty acid composition of Arbequina virgin olive oils obtained from different regions of Brazil

Fatty acids	**Regions**				
	Granada	**Jaén**	**Málaga**	**Cádiz**	**Sevilla**
Stearic acid (C16:0)	11.99 ± 0.10	17.43 ± 0.05	14.14 ± 0.03	16.98 ± 0.68	17.34 ± 0.18
Oleic acid (C18:1)	75.22 ± 0.20	64.09 ± 1.36	71.66 ± 0.07	63.12 ± 0.72	63.85 ± 0.09
Linoleic acid (C18:2)	8.04 ± 0.02	13.17 ± 1.19	9.51 ± 0.00	14.76 ± 0.01	13.77 ± 0.13

Salvador et al. (2003) described the influence of the production area on the fatty acid composition of Cornicabra virgin olive oil. Major fatty acids presented significant statistical differences ($P \leqslant 0.001$) with respect to the production area (five production areas of Toledo and Ciudad Real). The results appear to confirm the general consensus on the quality of Cornicabra virgin olive oils from Castilla-La Mancha, namely that oils from mills located in the south and southeast of the province of Toledo are generally of higher quality (Table 5).

Table 5. Major fatty acid of Cornicabra virgin olive oils obtained from different production areas

Fatty acids	Production Areas				
	Toledo (TO)			Ciudad Real (CR)	
	N	SE 1	SE 2	N	S
Palmitic acid (C16:0)	9.33[b, c]	8.61[a]	8.85[a, b]	9.13[b, c]	9.34[c]
Stearic acid (C18:0)	3.29[a]	3.60[c]	3.47[a,b,c]	3.35[b]	3.56[b, c]
Oleic acid (C18:1)	80.0[a]	80.8[b]	80.7[b]	80.6[a, b]	80.1[a]
Linoleic acid (C18:2)	4.81[b]	4.63[b]	4.49[a, b]	4.36[a]	4.50[a, b]

Piravi-Vanak et al. (2012) studied that the effect of geographical difference of olive cultivation. They reported that fatty acids of oils obtained from twenty seven Iranian olives grown in northern and southern Iran varied according to the olive-growing regions. The samples were collected from different geographical locations that varied in altitude, temperature, humidity and rain fall. According to results oleic acid content of oils in the northern regions was high, but linoleic and stearic acid contents were low than those of southern regions.

CONCLUSIONS

In this review, the effects of several factors including olive cultivar, maturity index and growing region were tried to reveal based on the different studies on fatty acid compositions of olive oils. These works showed that olive oils consist of diverse fatty acids entailing myristic, palmitic, palmitoleic, margaric, margoleic, stearic, oleic, linoleic, arachidic, linolenic, gadoleic and behenic acids. Among them, oleic acid was the most prevailing fatty acid. According to many previous studies on fatty acids of olive oils, it can be said that the composition of fatty acids varies depending on the variety, maturation index and region where the olive grows.

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Temperature dependency of sweet cherry concentrate colour: A kinetic study

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Abstract

The present study was undertaken to study degradation kinetics of visual colour of sweet cherry concentrate over temperature range of 60-80 °C during 480 minutes heat treatment. The visual colour was evaluated using a HunterLab Colourflex Colourimeter and change in visual colour was expressed in terms of total colour difference (*TCD**) which is a combination of *L** (lightness), *a** (redness/greenness) and *b** (yellowness/blueness). *TCD** was fitted to zero-order, first-order and combined kinetics model by non-linear regression iterative procedure. Correlation coefficients (R^2) ranging between 0.9040-0.9763 for zero order kinetics, 0.8232-0.9520 for first order kinetics and 0.9765-0.9898 for combined kinetics, respectively. It could be concluded that change in sweet cherry color during heating at 60, 70, 80 °C for 480 minutes can be described by either first, zero and combined kinetics, but rather better to describe with combined kinetics. Furthermore, it might be inferred that as the temperature increased, change in *TCD** could be predominantly caused by Maillard reaction rather than pigment destruction in sweet cherry concentrates.

Keywords: Colour, Concentrate, Kinetics, Sweet cherry, Thermal Degradation

Introductıon

Cherries (*Prunus* spp.) are the smallest members of the stone fruit family of Rosaceae and, *Prunus avium* L., is known as "sweet cherry"(Ferretti et al., 2010). Sweetness in the cherry fruit is mainly due to glucose and fructose, while sourness is primarily due to the presence of organic acid (malic acid). Sweet cherries are characterized by a higher content of simple sugar with respect to sour cherries (Ferretti et al., 2010). Intrinsic sweet taste of sweet cherry juice related to its sugar composition, sweet cherries contains highest amounts of glucose, followed by fructose, sorbitol and sucrose (Kelebek & Selli, 2011). Cherries contain vitamins (C, B, A, E, K), minerals (such as calcium, magnesium, phosphorous and potassium), and some carotenoids, in particular beta-carotene, and to a lower extent lutein and zeaxantine. Cherry phenolics are flavonoids (anthocyanins), non-flavonoids, flavan-3-ols and flavanols (Kelebek & Selli, 2011). Anthocyanins include cyanidin 3-glucoside, cyanidin 3-rutinoside, cyanidin 3-sophoroside, pelargonidin 3-glucoside, pelargonidin 3-rutinoside, 3-glucoside, and peonidin 3-rutinoside; non-flavonoids include phenolic acids (hydroxycinnamic and hydroxybenzoic acids) flavonols and flavan-3-ols include catechin, epicatechin, quercetin 3-glucoside, quercetin 3-rutinoside, kaempferol 3-rutinoside (Ferretti et al., 2010). Major anthocyanins in sweet cherry is cyanidin-3-rutinoside (Patras et al., 2010). Antioxidants and phenolics of cherry fruits have antioxidant, anticancer and anti-inflammation properties (Ferretti et al., 2010).

Since the colour is a major determinant for quality in red coloured fruits and vegetables, it is quite important to minimize color deterioration during processing of these

fruits. The objective of this study was to determine degradation kinetics of visual colour of sweet cherry concentrate at selected temperatures (60, 70 and 80 °C) during 480 minutes heat treatment in order to test their temperature dependency.

MATERIAL and METHODS

Materials

Sweet cherry (*Prunus avium* L.) fruits were collected in Gaziantep, Southeast Anatolia, Turkey. Pectolytic enzyme, Panzym XXL, was kindly gifted by Sinerji A.Ş., Mersin, TURKEY. All the other reagents were of analytical grade.

Preparation of concentrates

All the foreign materials such as pieces of branches and leaves and also unripe and damaged fruits were removed by hand. The cleaned fruits were washed under cold tap water, stalks and seeds were removed. Fruits were ground by using a laboratory blender. Juice was immediately filtered through muslin to remove pulp from the juice. Then the juice was depectinized with 1.0 % (v/w) Panzym XXL at 50 ^{o}C for 2 h. The depectinized juice was allowed to rest at 4^{o}C for 24 h. The juice was again filtered through five layer muslin and finally double layer filter paper to obtain a clear juice. Clear juices were concentrated using BÜCHİ Rotary Evaporator (Rotavapor R-3 model, BÜCHI Loborthechnik AG, Flawil, Switzerland) at 40 ^{o}C. The total soluble solids and pH of sweet cherry concentrate were 45.02 °Brix and 3.75, respectively.

Colour measurements

The visual colour was evaluated using a HunterLab Colourflex (A-60-1010-615 Model Colourimeter, Hunter Associates Lab. Inc. Reston VA, USA). The instrument was standardized each time with a black and a white (L = 91.10, a = 1.12, b = 1.26) tile. The colour values were expressed as *L** (lightness), *a** (redness/greenness) and *b** (yellowness/blueness). Total colour difference (*TCD**) parameter was calculated and modeled. Colour values were the means of triplicate measurements.

Degradation kinetics of visual colour

The complexity of fruit juices and derivatives implies a wide range of enzymatic and non-enzymatic browning reactions caused by thermal treatments. Consequently it is difficult to establish a reaction mechanism and to obtain a kinetic model describing the global process adequately(Ibarz et al., 1999). There are numerous references on the kinetics of colour of food materials in the literature. The majority of these works report zero-order kinetics (Eq. (1)) (Chutintrasri & Noomhorm, 2007; Tiwari et al., 2009), first-order kinetics (Eq. (2))(Ahmed et al., 2000; Shao-gian et al., 2011).

$$C = C_0 \pm k_o * t \quad (1)$$

$$C = C_o * \exp\ (\pm k_1 * t) \quad (2)$$

Sometimes the relatively simple models described do not adequately represent colour change mechanism. That is why a combined kinetics has been developed, in which the non-enzymatic colour change reactions are considered to consist of two stages. A first stage of coloured polymeric compound formation following zero order kinetics, the second stage supposes decomposition of the coloured polymers into non-coloured compounds following a

first order kinetics. According to this combined kinetics, the colour change mechanism can be expressed by (Garza et al., 1999; Ibarz et al., 1999):

$$C = \frac{k_0}{k_1} - \left[\frac{k_o}{k_1} - C_0\right] exp(\pm k_1 * t) \quad (3)$$

The terms C_o is the initial contents and C is the contents after time t (min) of heating at the given temperature while k_0 is the zero order and k_1 is the first order rate constant in Eqs. (1), (2) and (3). The parameters of zero (Eq. (1)) order, first order kinetic model (Eq. (2)) and combined kinetics model (Eq. (3)) were estimated by non-linear regression iterative procedure of the SigmaPlot (SigmaPlot 10.0 Windows version, SPSS Inc.). Total colour difference (*TCD**) was calculated by using L^*, a^*, b^* values (Eq. (4)) (Loughrey, 2002).

$$TCD^* = \sqrt{(L_0^* - L^*)^2 + (a_0^* - a^*)^2 + (b_0^* - b^*)^2} \quad (4)$$

where, L_0^* , a_0^* and b_0^* refer to initial values, and L^*, a^* and b^* refer to colour values at various times during heat treatment.

Statistical Analysis

All measurements were performed in triplicate and are reported as means and standard deviations. The parameters of kinetic models were estimated by non-linear regression iterative procedure of the SigmaPlot (SigmaPlot 10.0 Windows version, SPSS Inc.).

Table 1. Change in total colour difference (*TCD**) value of sweet cherry concentrate during heating at 60, 70, 80 °C for 480 minutes.

	Temperature (°C)		
	60 °C	70 °C	80 °C
Time (min)	*TDC**±*SE*	*TDC**±*SE*	*TDC**±*SE*
0	0.0000±0.0000	0.0000±0.0000	0.0000±0.0000
60	0.2768±0.0138	0.5025±0.0251	0.6388±0.0319
120	0.3850±0.0192	0.6761±0.0338	0.8193±0.0410
180	0.5276±0.0264	0.7938±0.0397	0.9778±0.0489
240	0.6097±0.0305	0.9394±0.0470	1.2458±0.0623
300	0.7325±0.0366	1.1989±0.0599	1.3945±0.0697
360	0.8867±0.0443	1.3919±0.0696	1.5380±0.0769
480	1.0602±0.0530	1.5062±0.0753	1.6873±0.0844

SE: Standard error

RESULTS and DISCUSSION

There are numerous references on the kinetics of color of food materials in the literature. The majority of these works report zero-order kinetics (Eq. (1)) (Chutintrasri & Noomhorm, 2007; Tiwari et al., 2009), first-order kinetics (Eq. (2)) (Ahmed et al., 2000; Shao-gian et al., 2011) and combined kinetic model (Eq. (3)) [4], [9]. Combined model consist of two stages: the first one includes color formation based on Maillard reactions and it follows zero order kinetics and the second includes the color destruction (pigment destruction) which follows a first order kinetics (Garza et al., 1999; Ibarz et al., 2000).

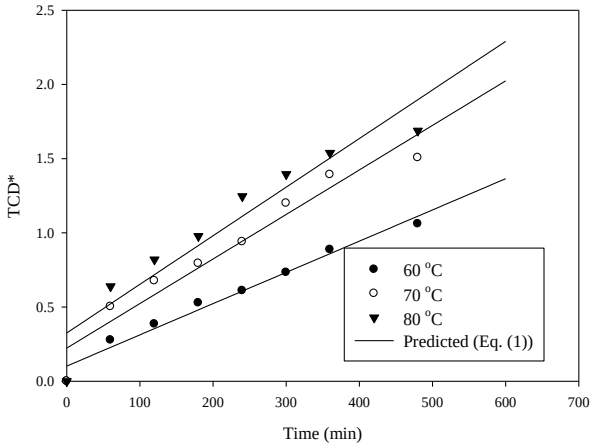

Figure 1. Change in total colour difference (*TCD**) value of sweet cherry concentrate during heating at 60, 70, 80 °C for 480 minutes fitted to zero order (Eq. (1)) kinetics.

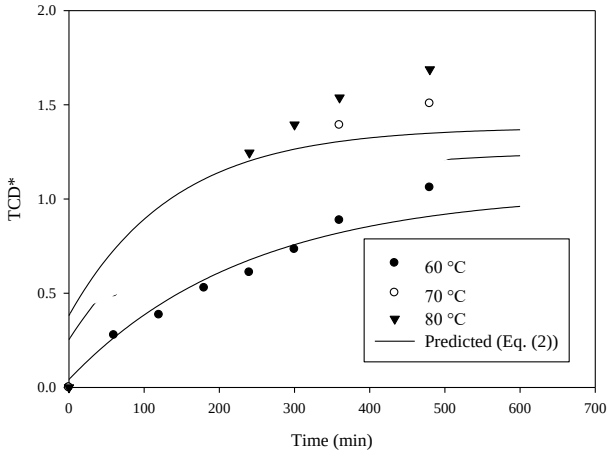

Figure 2. Change in total colour difference (*TCD**) value of sweet cherry concentrate during heating at 60, 70, 80 °C for 480 minutes fitted to first order (Eq. (2)) kinetics.

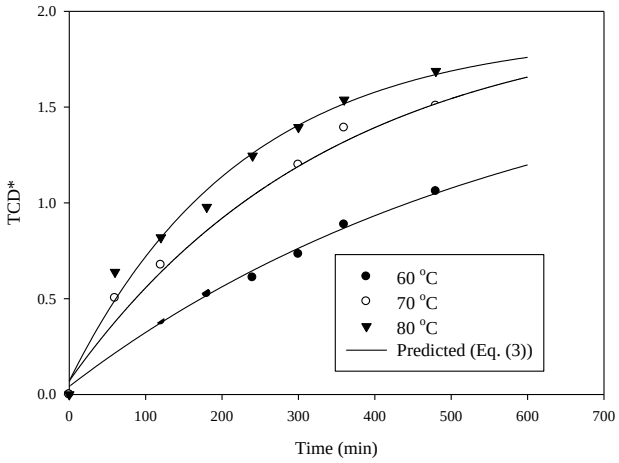

Figure 3. Change in total colour difference (*TCD**) value of sweet cherry concentrate during heating at 60, 70, 80 °C for 480 minutes fitted to combined model (Eq. (3)) kinetics.

Change in total colour difference (*TCD**) value of sweet cherry concentrate during heating at 60, 70, 80 °C for 480 minutes were given in Table 1.Variation in *TCD** value of sweet cherry concentrate was 1.0602, 1.5062 and 1.6873 at the end of 480 minutes heating at 60, 70, 80 °C, respectively (Table 1). Experimental data for change in *TCD** were fitted to zero-order (Eq. (1)), first-order (Eq. (2)) and combined kinetic model (Eq. (3)). Kinetic parameters of zero, first and combined model were given in Table 2, Table 3 and Table 4, respectively. Model graphs of zero, first and combined kinetic model were given in Figure 1, Figure 2 and Figure 3, respectively.

Table 2. Kinetics parameters of zero-order model (Eq. (1)) for *TCD** values.

Concentrate type	Temperature (°C)	$C_o \pm SE$	$ko \pm SE$	R^2
Sweet cherry	60	0.1020±0.0354	0.0021±0.0001	0.9763
	70	0.2233±0.0834	0.0030±0.0003	0.9377
	80	0.3254±0.1151	0.0033±0.0004	0.9040

SE: Standard error, R^2: correlation coefficients.

Table 3. Kinetics parameters of first-order model (Eq. (2)) for *TCD** values.

Concentrate type	Temperature (°C)	$C_o \pm SE$	$k_1 \pm SE$	R^2
Sweet cherry	60	1.0418±0.0728	-0.0042±0.0010	0.9520
	70	1.2536±0.1777	-0.0062±0.0040	0.8455
	80	1.3813±0.1965	-0.0072±0.0054	0.8232

SE: Standard error, R^2: correlation coefficients.

Table 4. Kinetics parameters of combined model (Eq. (3)) for *TCD** values.

Concentrate Type	Temperature (°C)	$C_o \pm SE$	$ko \pm SE$	$k_1 \pm SE$	R^2	ko / k_1
Sweet cherry	60	0.0420±0.0347	0.0031±0.0004	0.0017±0.0006	0.9898	1.82
	70	0.0709±0.0792	0.0058±0.0010	0.0029±0.0010	0.9765	2.00
	80	0.0702±0.0759	0.0083±0.0011	0.0044±0.0010	0.9835	1.89

SE: Standard error, R^2: correlation coefficients.

Correlation coefficients (R^2) ranging between 0.9040-0.9763 (Table 2) for zero order kinetics, 0.8232-0.9520 (Table 3) for first order kinetics and 0.9765-0.9898 (Table 4) for combined kinetics, respectively. It could be concluded that change in sweet cherry color during heating at 60, 70, 80 °C for 480 minutes can be described by either first, zero and combined kinetics due to having good correlation coefficients (R^2) and reasonable C_o values. Contrarily, it is known that there is no significant difference between zero and first order kinetics when a reaction describing any quality attribute (Labuza & Riboh, 1982). So, combination of these two models could be a good alternative to express colour change in sweet cherry concentrate. According to Ibarz et al. (2000), when the ratio of kinetic constants k_o (color formation) and k_1 (pigment destruction) is greater than unity, Maillard reaction predominates over pigment destruction. In this respect, as temperature increased, change in *TCD** may predominantly caused by Maillard reaction in sweet cherry concentrates at each temperature (Table 4). This result is correlated with the previous studies (Garza et al., 1999; Ibarz et al., 1999, 2000).

CONCLUSION

Temperature dependency of colour of sweet cherry concentrate was tested over the temperature range of 60-80 °C during 480 minutes heat treatment. Change in visual color was expressed in terms of total colour difference (*TCD*)* and *TCD** was fitted to zero-order, first-order and combined kinetics model by non-linear regression iterative procedure. Regression

analysis revealed that experimental data well fitted to all models due to having good correlation coefficients (R^2) and reasonable C_o values. So, change in sweet cherry color during heating at 60, 70, 80 °C for 480 minutes can be described by either first, zero and combined kinetics, but rather better to describe with combined kinetics. Finally, it might be inferred that as the temperature increased, change in *TCD** could be predominantly caused by Maillard reaction rather than pigment destruction in sweet cherry concentrates.

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Physicochemical and Nutritional Properties of Bitter Melon at Four Maturation Stages

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Abstract

The purpose of the present study was to investigate the physicochemical characteristics of bitter melon fruit at four maturation stages. Results showed that during the maturation period, ascorbic acid, carotene, total phenolic content and antioxidant capacity of the bitter melons were changed between 5.16±0.03-7.26±0.03 mg/g dry weight, 78.91±0.86-190.28±2.23 µg/g dry weight, 5.62 ±0.2-8.25 ±0.1 mg gallic acid equivalent/g dry weight and 653.84±20.53-822.81±19.75 mg ascorbic acid equivalent /g dry weight respectively. Moreover, the values of Ca, Cu, Fe, K and Mg ranged between 172.33±7.2-196.82±5.1, 14.33±0.1-16.32±0.2, 11.38±41.8-16.58±16.3, 1670.38±84.4-1922.67±95.3 and 106.79±16.0-145.41±28.1 mg/100 g dry weight respectively. Results indicated that maturation stages highly affected nutritional and functional value of bitter melon.

Keywords: Antioxidant activity; nutrient; total phenol

INTRODUCTION

The bitter melon or bitter gourd (*Momordica charantia*) belongs to the family of Cacurbitaceae. This plant is widely cultivated in many tropical and subtropical regions. Bitter melon fruit is widely used for medicinal purposes in developing countries Myojin et al. (2008) and Ullah et al. (2011). Physicochemical properties of the fresh bitter melon are able to affect the sensory and nutritional properties of cooked food or food derivatives produced by bitter melon. However, no reports have been found about the detailed physicochemical properties of bitter melon fruit during the maturation period in the literature. The purpose of the present work was to determine the physicochemical properties of bitter melon fruit at green, yellow, orange and late orange maturation stages.

MATERIALS and METHODS

Bitter melon fruits grown in greenhouse at Yalova/Turkey were harvested at 4 different maturation stages which were yellow, orange and late orange (when the fruit was opened from end point). Fruits had 15.61±0.4 cm length, 6.4±0.2 cm diameter and 135.4±13 g weight. Before the analysis, seeds and pithy white membranes of the fruit were scooped out. Color values were measured with color meter (Minolta, Japan). pH was measured with a pH meter (Consort P514, Belgium).

Titratable acidity was determined according to AOAC (1975). Moisture, oil and mineral element were determined according to official method of AOAC (1990). Sugar

content was determined by the Lane and Eynon method (Cemeroglu, 2007). Ascorbic acid content was determined by the indophenol method Freed (1966). Carotene content was determined with spectrophotometric method (Cemeroglu, 2007). Total phenolic content was determined by the Folin–Ciocalteu method according to Singleton and Rossi (1965). Total antioxidant capacity was determined according to Dasgupta and De (2004). Analysis of variance using the LSD test of multiple comparisons of the means ($p \leq 0.05$) was used to determine the presence of significant differences among the samples.

RESULTS and DISCUSSION

Color values, pH and titratable acidity of bitter melon fruit were demonstrated in Table 1. The highest L value was detected at yellow maturation stage while the lowest value was detected at green maturation stage. In contrast, Aminah and Anna (2011) reported the highest L value at the late orange maturation stage.

Table 1. Color values, pH and titratable acidity of bitter melon fruit

Ripeness	Color parameters			pH	Titratable acidity (%)
	L	a	b		
Green	41.49±2.90c	4.46±0.1a	0.11c	4.46±0.1a	0.11c
Yellow	51.97±1.32a	4.10±0.06c	0.13b	4.10±0.06c	0.13b
Orange	50.84±2.16a	4.25±0.08b	0.16a	4.25±0.08b	0.16a
Late orange	48.15±0.91b	4.38±0.06a	0.16a	4.38±0.06a	0.16a

Different letters between cultivars denote significant differences (Duncan test, $p < 0.05$)

There was a small fluctuation of pH values and an increase of titratable acidity. pH and titratable acidity of bitter ground were determined between 4.10-4.46 and 0.11-0.16% respectively. The highest titratable acidity was detected at orange and late orange stages but the lowest pH value was detected at yellow maturation stage. These results are similar with that found by Aminah and Anna (2011) and Kulkarni et al. (2005). Chemical characters of bitter melon flesh were presented in Table 2.

Table 2. Chemical characters of bitter melon flesh

Ripeness	Moisture content (%)	Fat content (%)	Reduced sugar content (%)	Ascorbic acid (mg/g dry weight)	Carotene (µg/g dry weight)	Total phenolic content (mg gallic acid /g dry weight)	Antioxidant capacity (mg ascorbic acid /g dry weight)
Green	94.60±0.94a	0.14±0.02a	1.04±0.1c	7.26±0,03a	78.91±0.86d	5.62 ±0.2c	822.81±19.75a
Yellow	94.48±1.12a	0.12±0.01b	1.22±0.05b	5.21±0,04bc	123,64±1.47c	8.25 ±0.1a	775.06±18.62b
Orange	93.73±0.77b	0.09±0.01c	1.37±0.1a	5.48±0,04b	190.28±2.23a	8.22 ±0.3a	719.92±19.78c
Late orange	91.25±1.18c	0.08±0.01c	1.35±0.1a	5.16±0,03c	167.65±2.45b	7.53±0.3b	653.84±20.53d

Different letters between cultivars denote significant differences (Duncan test, $p < 0.05$)

As it is shown moisture and oil content of fruit were slightly decreased whereas the value of reduced sugar content was increased. There is no statistical difference between moisture content of green and yellow maturation stages. Although the highest fat content was determined at green maturation, however the highest reduced sugar content was determined at orange and late orange maturation stages. The findings of the present study showed higher

values of moisture content and lower values of reduced sugar content at all maturation stages compared to that found by Kulkarni et al. (2005). In agreement with the values of moisture content detected in this study are the results found by Yuwai et al. (1991) and Donya et al. (2007).

Fat content of bitter melon was changed between 0.08-0.14% during maturation. This result was similar with that found by Yuwai et al. (1991), but lower than that found by Horax et al. (2005) and Donya et al. (2007). During maturation fat content was increased until orange maturation stage in contrast, Horax et al. (2005) stated that there was no change in the fat content of bitter melon during maturation. Ascorbic acid content was determined between 5.16-7.26 mg/g dry weight. Although in literature there was no report relevant to the change in the ascorbic content of bitter melon during the maturation period however, ascorbic acid content of mature bitter melon fruit was reported by Gopalan et al. (1993), Myojin et al. (2008) and Ullah et al. (2011) as 0.8mg/g fresh fruit, 0.96 mg/ g fresh flesh and 9.41-16.20mg/100g fresh respectively.

Carotene content increased from 78.91±0.86 to 290.28±2.23 between green and orange maturation stages. These values were significantly higher than that found by Gopalan et al. (1993) and Stephen and Duke (1994). The increase in carotene content was able to affect the color of the fruit. The values of the carotene content were the lowest at green maturation stage, showing an increase at yellow maturation stage and reaching its peak at orange maturation stage. Bitter melon has higher total phenolic content at yellow and orange maturation stage than at green and late orange maturation stages whereas Kubola and Siriamornpun (2008) found higher total phenolic content at green bitter melon fruit than that of ripe bitter melon. These results were similar with that found by Kubola and Siriamornpun (2008) but lower than that stated by Myojin et al. (2008). Also similar results were found by Horax et al. (2010). Antioxidant capacity showed a decrease during the maturation period. Similar results were found by reference Kubola and Siriamornpun (2008). The amounts of Ca, Cu, Fe, K and Mg content of bitter melon flesh were given in Table 3. The Mg, Fe, Na and Cu contents were decreased during maturation whereas K content was increased while Ca content was not changed significantly ($p<0.05$).

Table 3. Antioxidant capacity and total phenolic, Ca, Cu, Fe, K and Mg contents of bitter melon flesh (mg/100 g dry weight)

Maturation stages	Ca	Cu	Fe	K	Mg
Green	185.07±3.2bc	16.32±0.2a	16.58±16.3a	1670.38±84.4c	145.41±28.1a
Yellow	196.82±5.1ab	15.17±0.2bc	14.67±16.3b	1835.83±148.9b	129.83±35.5b
Orange	172.33±7.2c	16.28±0.1ab	14.43±25.3b	1922.67±95.3a	106.79±16.0c
Late orange	184.15±6.3bc	14.33±0.1c	11.38±41.8c	1826.33±15.6bb	108.84±24.9c

Different letters between cultivars denote significant differences (Duncan test, $p < 0.05$)

These mineral contents were much lower than that found by references Soomro and Ansari (2005) and Ullah et al. (2011). Moreover, although the results regarding Ca and Fe contents are in agreement with that found by Gopalan et al. (1993), Stephen and Duke (19947) and Horax et al. (2010).

CONCLUSION

According to the results of the present study, the maturation stages cause significant changes on the characteristics of the bitter melon. In particular, bitter melon had the highest

pH value, fat, ascorbic acid, Fe and Mg content and total antioxidant capacity at green maturation stage whereas the highest reduced sugar, carotene and total phenolic content were determined at orange and late orange maturation stages. These changes relevant to chemical content of bitter melon determine not only the changes of aroma and other nutrient content of bitter melon when it is used as a food stuff but also affect other changes concerning its phytochemicals content which are important for medicinal uses. Thus, it is obvious that the appropriate maturation stage should be selected according to the use of this fruit. In some countries fat of bitter melon was used in folk medicine.

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An Overview of Nano-Scale Food Emulsions: A Mini Review

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Abstract

Emulsions with droplet size in the nanometric scale (typically in the range of 20-200 nm, or milky up to 500 nm) are often referred in the literature as miniemulsions, nano-emulsions, ultrafine emulsions, submicron emulsions, emulsoids, unstable microemulsions etc. Due to their characteristic size, nano-scale emulsions appear transparent or translucent to the naked eye. They possess the ability of incorporation into optically transparent products, which gives the great potential of increasing bioavailability of lipophilic functional substances, that is, nano-sized emulsions can be used in encapsulating of bioactive components, being as a carrier for bioactive components, and preventing their degradation. Recently, nano-scale emulsions are also attracting increasing attention due to their characteristic feature of kinetic stability. A kinetic stability that lasts for months, stability against dilution or even against temperature changes, totally unlike the (thermodinamically stable) microemulsions. These properties make nano-scale emulsions of great interest for fundamental studies of food, medical and pharmaceutical industries. The aim of this study is to present a mini-review on properties of nano-scale emulsions, and an overview of nano-scale food emulsion.

Keywords: Applications, Bioactive Components, Encapsulation, Food, Nano-Scale Emulsion

INTRODUCTION

Nano-scale emulsions

Nano-scale emulsions, also referred to in the literature as miniemulsions, ultrafine emulsions, emulsoids, unstable microemulsions, submicrometer emulsions, are a class of emulsions with very small and uniform droplet size, typically in the range of 50-200 nm, or milky up to 500 nm (Porras et al., 2008). Mainly two types of nano-scale emulsions present due the type of continuous phase, namely, oil-in-water (O/W) and water-in-oil (W/O) emulsions (Figure 1a). In oil in water emulsions, oil droplets dispersed in continuous phase of water. In water-in-oil emulsions, water is dispersed in continuous phase of oil.

Due to their smaller droplet size they may appear transparent or translucent (Figure 1 b,c) (Solans et al., 2005; Pey et al., 2006). Such emulsions are of interest primarily because of their droplet size, however their potential has also been investigated in such applications as functional ingredient encapsulation and nano-structured multiple emulsions. Applications studied for nano-scale emulsions include polymerization and other reaction processes, drug delivery, cosmetics, and novel foods (Henry et al., 2009).

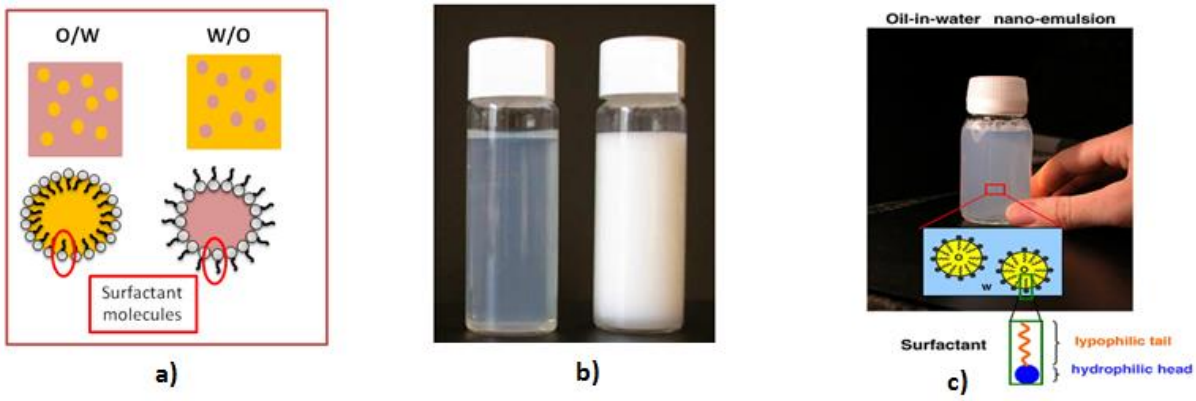

Figure 1.a) Schematic representation of O/W and W/O nano-scale emulsions. **b)** Picture of a nano-scale emulsion (left) and a macro-emulsion (right) with droplet diameters of 35 nm and 1 μm, respectively (Solans et al., 2005). **c)** Visual aspect of an O/W nano-scale emulsion and structural conformation of the droplet (Gutiérrez et al., 2008).

Recently, nano-scale emulsions are also attracting increasing attention due to their characteristic feature of kinetically stability. A kinetic stability that lasts for months, stability against dilution even against temperature changes, totally unlike the (thermodynamically stable) micro-emulsions (Tadros et al., 2004; Anton et al., 2008). Nano-scale emulsions have good stability against coagulation of droplets because the range of attractive forces acting between droplets decreases with increasing droplet size, while the range of steric repulsion less dependent on particle size (Hélder et al., 2012). Nano-scale emulsions highly stable to gravitational separation because the relatively small particle size means that Brownian motion effects dominate gravitational forces which means no creaming and sedimentation occurs on storage (Tadros et al., 2004). Nano-scale emulsions, in contrast to micro-emulsions, are not the thermodynamically stable, i.e. they are not equilibrium phases and their size of droplets tends to increase with time before phase separation (Porras et al., 2008).Nano-scale emulsions are prepared using low-energy, high-energy methods. The high-energy methods include high-shear stirring, ultrasonic emulsification, high-pressure homogenization, microfluidics and membrane emulsification. The most widely used low-energy methods include phase inversion (the phase inversion temperature (PIT), phase inversion composition (PIC)) and the spontaneous emulsification in nonequilibrium systems (Fryd & Mason, 2012; Koroleva & Yurtov, 2012).

Food grade nano-scale emulsions

Nanoemulsions of which all the building components of nanoemulsions are safe for human consumption or ‘‘generally recognized as safe’’ (GRAS) materials are considered as “Food Grade” (Abbas et al., 2013). To obtain food grade nano-scale emulsions, all the components mainly, oil, surfactant and aqueous phase should be food grade. Hélder et al. (2012) classify solvents that can be used in preparation of nano-scale food emulsions. In this context, organic solvents such as sunflower oil, corn oil, olive oil, soybean oil, medium chain triglyceride, sesame oil, paraffin oil, ethanol, octanoic acid and caprylic acid are used without any restriction, acetone, n-hexane, tetradecane and ethyl acetate can only be used up to 50 ppm, while solvents such as n-decane, hexadecane, isohexadecane, and chloroform cannot be used in food-grade nano-scale emulsions.

Emulsions breakdown is usually retarded by using emulsifiers, which are surface-active ingredients that adsorb to the surface of freshly formed oil droplets during

homogenization. Once adsorbed, they facilitate further droplet disruption by lowering the interfacial tension, thereby reducing the size of the droplets produced during homogenization. Emulsifiers also reduce the tendency for droplets to aggregate by forming protective films and/or generating repulsive forces between the droplets. A good emulsifier should rapidly adsorb at the surface of oil droplets formed during homogenization, rapidly lower the interfacial tension by a significant amount and protect the droplets against aggregation during emulsions processing, storage, and utilization (Camino et al., 2011). Typical GRAS emulsifiers suitable for nano-scale food emulsions are surfactants (e.g. Tweens®, Spans®, Brijs®, pluronics, sugar esters, poloxamers), proteins (e.g. whey, casein, soy and gelatin), polysaccharides (e.g. gum arabic, modified starch, pectin) and phospholipids (e.g. lecithin and lyso-lecithin) (McClements,2013).

Many of the previous studies on food-grade nano-scale emulsions involve the preparation of nano-scale emulsion consisting of Food-Grade oil-surfactant-aqueous phase combination by using different emulsification methods (i.e., low-energy or high energy methods) and, are aimed to fabricate, characterize and determine their characteristic properties such as particle size, physical properties and stability. Most previous studies based on high-energy emulsification methods on model systems at ideal conditions by using low density essential oils as oil phase and buffer solutions with neutral pH as an aqueous phase (Rao &McClements, 2011a; Choi et al., 2011; Qian & McClements, 2011; Rao & McClements, 2012a, b; Yang et al., 2012; Kaltsa et al., 2013). The priorities were directed toward to explore applications of nano-scale food emulsions. Subsequent to the discovery of the basic characteristic features of nano-scale emulsion, the nano-scale emulsions studies have been directed toward to the use of these characteristic properties in a way to improve functional properties of foods and to increase their bioavailability. That is, nano-scale emulsions have been developed to encapsulate a number of different lipophilic components (such as *β*-carotene (Tan & Nakajima, 2005; Chu et al., 2007; Yuan et al., 2008; Mao et al., 2009; Hélder et al., 2011), citral (Choi et al., 2009; Mei et al., 2009), flavor oil (lemon oil) (Rao & McClements, 2011b), D-limonene (Li & Chiang, 2012), Vitamin E (Mayer et al., 2013), omega-3 oil (Chalothorn & Warisnoicharoen, 2012) and etc.) and essential oils such as basil oil (Ghosh et al., 2013); cinnamon (Ghosh et al., 2013); peppermint (Liang et al., 2012); thyme (Ziani et al., 2011), lemongrass (Salvia-Trujillo et al., 2014) and etc.

CONCLUSION

In this study, a mini-review on properties of nano-scale emulsions, and an overview of nano-scale food emulsion are presented. Emulsions with droplet size in the nanometric scale (typically in the range of 20-200 nm, or milky up to 500 nm) are often referred in the literature as miniemulsions, nano-emulsions, ultrafine emulsions, submicron emulsions, emulsoids, unstable microemulsions and etc. Nano-scale emulsions are kinetically stable but, they are thermodynamically unstable. Nano-emulsions are unique due to their long term physical stability with no apparent flocculation, coalescence, creaming or sedimentation. Due to their characteristic size, nano-scale emulsions appear transparent or translucent to the naked eye, which gives the ability of incorporation into optically transparent products, which gives the great potential of increasing bioavailability of lipophilic functional substances.

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EURASIAN JOURNAL OF FOOD SCIENCE AND TECHNOLOGY

Increasing Shelf Life of Fruits and Vegetables with Combined System of Modified Atmosphere Packaging and Edible Films Coating

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Abstract

After harvest, fruits and vegetables continue to loss their quality under the influence of their ongoing vitality and physical factors occurred during transport, storage and shipment. To bring an alternative and novel solutions to shelf life problems of foods, modified packaging technology (MAP) was developed both for consumers who conscious about food safety and manufacturers who seek products with longer shelf life. MAP is conducted in two ways as active and passive MAP. The more commonly applied active MAP technology involves the aplication of various combinations of gases (N_2, O_2, and CO_2) suitable to type of the product and packaging material. In recent years, MAP has begun to be used with edible film coating. In this way, the permeability of the packaging material is minimized; the microbial, physical and physicochemical degradation of foods can be prevented or decreased and both the aroma-flavor-structures and the quality of the products can be improved. This will have a significant advantage, especially in exports, because it provides a longer shelf life for crops. In this review, the principle of combined system of MAP and edible coating technology, its applicationin to different type of fruit and vegetables and its effects on the quality of the products are aimed to be explained.

Keywords: Edible films and coating, fruit and vegetables, MAP technology.

INTRODUCTION

Packaging is considered to be the first stage in the shelf life of the product, although it is the last process of production. Packaging protects food from external influences such as moisture, light, oxygen, mechanical deformation and rodents. It is the material that protects against the microbial and chemical deterioration; and used to keep the quality of the product until reaching the consumer. The common used packaging materials include wood, glass, paper, plastic, tin or aluminum selected according to the product variety (Robertson, 2013).

There are many recent technologies available for the food packaging. These technologies include vacuum packaging, intelligent and active packaging, modified atmospheric packaging, and application of nanotechnology in to packaging systems (Robertson, 2013; Ahmed et al. 2017). In the vacuum technology, the gas in the product is completely removed and the product is delivered to the consumer after packaged (Robertson, 2013). In intelligent packaging technologies, gas, temperature, humidity, microbial growth and pathogen indicators are added to the package to provide intelligent functionality to the product and to follow the product throughout its shelf life (Roya and Elham, 2016). With the use of nanotechnology, nanomaterials, suitable for foods and compatabile with the regulation, have been added to food and packaging to achieve a shelf-life-enhancing effect (Mihindukulasuriya and Lim, 2014).

When all this packaging method is examined, the superior and positive features of MAP technology have been also revealed and it has proven that modified atmosphere packaging technology has an effect on the shelf life of fruit and vegetables (Oliveria 2015),

therefore it has been increasingly used worldwide. In the modified atmosphere packaging method, the gas component in the product is removed from the package and CO_2, O_2 and N_2 gases are supplied to the product in appropriate proportion (Oz and Sufer, 2016; Gaikwad and Lee, 2017; Harris et al. 2017). In MAP technology, CO_2 is used to prevent microbial growth in food products, hence prolonging shelf life of foodswhile maintaining its freshness, N_2 gas is used to prevent oxidation and vacuum conditions in the package as an inert gas and O_2 is usually set at a low level to inhibit growing of anaerobic bacteria and prevent oxidation (Oliveira et al, 2015).

MAP can be combined with chemical treatments including calcium chloride and sitric acid to increase the shelf life of crops by prolonging some of the quality parameters. Calcium chloride is reported to increase the firmness of fruit and vegetables (Martin-Diana et al. 2007). In a study, papaya fruits were immersed in calcium chloride and citric acid solution following packaging at modified atmospheric conditions of 5% O_2, 10% CO_2 and 85% N_2 and storing at 5 °C for 25 days. It was reported that shelf life of coated and MAP packaged fruits increased 25 days more compared to fresh fruits (Waghmare and Annapure, 2013).

Resecent years, MAP has also been successfully combined with the edible film coating technology to increase the shelf life of foods. The processed, unprocessed or minimally processed foods are first coated with an edible film. Then the modified atmosphere packaging process is applied. In this way, the permeability of the packaging is minimized; the microbial, physical and physicochemical degradation of foods can be prevented and both the aroma-flavor-structures and the quality of the products can be improved. This will have a significant advantage, especially in exports, because it provides a longer shelf life for crops (Ghidelli and Pérez-Gago, 2016; Wilson et al. 2017).

In this review, the principle of combined system of MAP and edible coating technology, its application in to different type of fruit and vegetables and its effects on the quality of the products are aimed to be explained.

EDIBLE FILM COATING TECHNOLOGY

Edible coatings are defined as *"the thin layers of edible material applied to the product surface in addition to or as a replacement for natural protective waxy coatings and to provide a barrier to moisture, oxygen, and solute movement for the food"* (Dhall, 2012). Edible film coating technology is a technology aimed to extend the shelf life by retarding some quality parameters of fruits and vegetables (Chaple et al. 2017; Bal and Kocak, 2016; Gomes et al. 2017), including browning (Lee et al. 2003) and by compressing the factors needed for growth of microorganism without using chemical preservatives. After coating, a thin layer is formed on the outer part of the food.

In coating technology, many plant and animal originated agents derived from lipids, polysaccharides and proteins are used both as a single material and as a mixture. In terms of their function, lipid derived agents including waxes and glycerides are used to reduce water transfer, while polysaccharide derived agents including starch and its derivatives, cellulose and its derivatives, alizinate, pectin (Sanchis et al. 2017), chitosan (Severino et al. 2015), gums are used to control the passage of gas. Protein derived agents including keratin, collagen, gelatin, egg white protein, casein, whey protein, wheat gluten, soya protein are preferred in order to increase the strength of the films.

In addition, solvents such as water, ethanol, acetone, plasticizer, emulsifier, flovoring, colorant, antioxidant and antimicrobial agents are used (Yildiz and Yangilar, 2016; Tural et al. 2017; Dhall, 2012; Marquez et al. 2017).

There are four main different methods reported in the literature regarding coating techniques. In the dipping method, a layer is formed on the surface of the food following

immersion in to the solution of the coating agent. It cannot be considered as an advantageous method for large surface foods. Spraying method is based on coating of the surface as a thin layer by a sprayer device. Although the method can be considered as advantageous based on the principle of completely covering the surface, it has also disadvantageous since it consumes more coating material than usual. In the dyeing method, the coating of the food is performed by painting its surface with a liquid coating solution. Short drying time and completly covered product can be given as an example to its advantageous features. In the pouring method, a proper solution in a desired thickness is pouredon a smooth surface, and then the film is formed following spreading and drying the solution. The method has disadvantageous of consumption of more coating material. The extrusion method is based on the thermoplastic properties of polymers. In this method, plasticizers such as polyethylene, glycol and sorbitol are added to the polymers at ratio ranging from 10% to 60%. It can be considered more proper for industrial applications than other methods, due to not requiring drying process and solvent addition (Dhall, 2012; Yildiz and Yangilar, 2016; Tural et al. 2017; Guillen et al. 2007).

COMBINED APPLICATION OF MAP AND EDIBLE COATING

The combined effect of mixture of essential oils including eugenol, thymol, and carvacrolas an edible film and MAP on the quality of the product including weight loss, color changes and firmness was investigated for grapes. The samples tretaed with combined system of MAP and edible film coating were compared with the control samples, and it was observed that the stems were green in the samples treated with combined MAP and edible film, whereas they were brown in the control samples. Moreover, it was observed that the microbiological count decreased (Guillen et al. 2007).

Avci (2016) studied the combined system of Aloe veragel coating and MAP packaging as a postharvest treatment for Black Amber plum cultivar, the combined system was compared with fruits packaged under modified atmospheric conditions without coating and control fruits non-treated with neither of the methods. Weight loss, respiration rate, oxygen and carbon dioxide gas concentration, ethylene production, fruit flesh hardness, fruit shell and flesh color and decay rate were investigated as quality parameters, moreover the changes in total pehnolics, antioxidant activity, and total flavonoid content were studied. During cold storage and shelf life of fruits, decrease in weight loss was observed in both coated and uncoated fruits packed under modified atmospheric conditions. On the other hand, weight loss was found higher in fruits just coated with Aloe vera gel without packaging. Compared with the control samples, approximately 70% lower ethylene production was measured during storage of the fruits coated with Aloe vera gel and packaged under modified atmosperic conditions, while approximately 35% lower ethylene production was measured in fruits packed under modified atmospheric conditions but uncoated with Aloe vera gel. It was concluded that all MAP applications in the study showed more positive effect on the preservation of quality characteristics and biochemical content of the fruits during cold storage and shelf life periods.

Despite of the positive expectation on the method including coating fruits with Aloe vera gel alone in the light of the previous reported studies for other type of fruits, the results indicated that the treatment was not advantageous compare to untreated control samples of plum. Therefore, it was recommended to carry out future studies with different concentrations of Aloe vera gel.

When the combined effect of coating with chitosan and sodium chloride and MAP conditions including 10% CO_2 and 10% O_2 on the quality characteristics of minimally

processed Pomelo fruit was investigated, the combined application inhibitated the microbial growth in fruits, reduced weight loss, kept sensorial quality of the fruits (Ban et al. 2015).

A study on two different types of avocado fruit was conducted by combining MAP (8% CO_2, 2% O_2) and thyme oil coating technology. Coated and packed fruits were allowed to be maturated for 5-10 days at 25 ºC following the storage period of 10 ºC for 18 days. The effects of the application on quality parameters of fruit including color, firmness, weight loss, sensory properties including taste, texture, aroma and general acceptability, total phenolic compound content, flavonoid content and antioxidant activity were investigated in the study. At the end of the storage period; the applied conditions increaased total phenolic compound content, flavonoid content and antioxidant activity, and decreased weight and firmness loss Moreover,taste, texture and aroma were also maintained (Sellamuthu et al. 2013).

In the study with sliced melon, application of vanillin and cinnamic acid in an aqueous solution and their combinations with active MAP technology were investigated. It was stated that both antimicrobial agents were effective especially against mesophilic bacteria and Enterobactericeae. The use of MAP in combination with cinnamon was recomended to be a new approach for the industry as it would bring a new perspective to obtain safe product (Silveira et al. 2015).

Carrots which is a source of beta carotene were coated with chitosan through the use of spraying and dipping techniques. Following the coating, baby carrots were packaged under modified atmospheric conditios and stored at 4 °C. The study revealed that the combined application postponed the microbial decay while keeping the colour and texture acceptable (Leceta et al. 2015).

The other study on carrot conducted by Guimaraes et al. (2016) included coating fresh cut-carrots with natural smectite montmorillonite (MMT) and starch followed by a passive MAP. The dispersal of MMT clay was dispersed as nanoparticiles into edible coating of starch in order to change its barrier properties to decrease the mass transfer from fruits and vegetables. The study revealed that combined system of coating film with starch nanoparticles and a modified atmosphere preserved the total antioxidant activity, the volatile and organic acids of the carrots.

Severino et al. (2015) studied the antibacterial activity of chitosan based nanoemulsions of essential oils including carvacrol, mandarin, bergamot and lemon essential oils, gamma irradiation, modified atmosphere packaging (MAP), alone or in combinations, against Escherichia coli O157:H7 and Salmonella Typhimurium inoculated in grean beans. To modify citosan, it was N-acylated using palmitoylchloride. The most effective antibacterial agent among these emulsions was reported as carvacrol. It was observed that the combined treatment of antimicrobial coating, gamma irradiation and MAP caused the reduction of microbial population to undetectable levels duringthe whole storage period for E. coli and from day 7 to the end of storage for S. Typhimurium.

Ginseng is consumed as food supplement. Due to sensitivity to environmental degredation, fresh ginseng was studied by Jin et al. (2016) to increase its shelf life by application of edible antimicrobial coating and MAP technology in comination. The study results proved that using chitosan 0.5% with multiple organic acids including lactic, levulinic and acetic acids as edible films extended the shelf life more than thirthy eight weeks if they were packed by MAP.

Oz and Sufer (2016) studied on fungi by immersing it in alginate solutions at different concentrations (1%, 2% and 3%) for 2 minutes. Coated samples were then packed with 100% O_2 (high oxygen modified atmosphere) and store for 16 days at 4 °C. The optimum experimental condition was selected as 2% alginate concentration. The findings showed that

the method decreased the formation of browning reactions; moreover the shelf life of fungi was extended to 16 days.

Sanchis et al. (2017) studied the effect of a pectin-based edible coating and low oxygen MAP on controlling enzymatic browning and reducing microbial growth in fresh-cut persimmon. The treatment included the packing under 5 kPa O_2 (MAP) following dipping in to coating material. It was observed that coating application combined with active MAP significantly reduced the CO_2 emission and O_2 consumption in the package and browning of fruits decreased in addition to inhabitation of the growth of mesophilic aerobic bacteria.

CONCLUSION

Combination of modified atmospheric packaging with edible films has proved to positively affect the shelf life of fruits and vegetables. It was observed that the combined system prevented the deterioration of the fruit and vegetables and prolonged the shelf life compared the application of both technique alone. On the other hand, consumer sensory acceptance test should be carried out and the feasibility of combined applications in terms of cost should be taken in to account for industrial application.

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Characterization of fatty acids composition in Iranian Phishomi extra-virgin olive oil

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Abstract

In this test, fatty acid composition of olive oil obtained from Iranian Phishomi olive cultivar grown in the northern part of country, Gilan province, was determined using a gas chromatography fitted with a flame ionization detector. A total of 12 fatty acids entailing myristic, palmitic, palmitoleic, margaric, margoleic, stearic, oleic, linoleic, arachidic, linolenic, gadoleic and behenic acids were detected. From them, oleic acid was the most prevailing fatty acid, representing the highest content (63.65 %) in the sample, followed by linoleic acid (16.93 %), palmitic acid (14.14 %) and stearic acid (2.73 %); the amount of the rest of the fatty acids detected in trace amounts. Fatty acid composition might vary between olive oils obtained from different cultivars. However, our finding was agreed to the range of those disclosed by the International Olive Oil Council and Codex Alimentarius with elevated resemblance. Apart from fatty acid compositions, percentage of saturated fatty acids (17.48 %), monounsaturated fatty acids (64.82 %), polyunsaturated fatty acids (17.71 %) and the ratios of PUFA to SFA (3.66 %) and oleic to linoleic acids (3.76 %) were also evaluated in oils. Oleic to linoleic acid ratio in studied oils was similar to Greek Throumbolia (2.91–3.19 %) oil.

Keywords: Extra-virgin olive oil, Fatty acids composition, Phishomi olive variety

INTRODUCTION

Olive oil, one of the ancient well-known vegetable oils of the Mediterranean zone elaborated from the fruits of olive (*Olea europaea*), is said to protect against cardiovascular illness and cancer hazard because of its bioactive compositions (Amanpour et al., 2016). Moreover, it prohibits the oxidative stress, which is one of the main causes of aging, for the sake of its balanced fatty acid composition and presence of numerous minor compounds with biological attributes containing phenolic compounds, tocopherols, sterols etc (Kharazi et al., 2012). Also, olive trees are cultivated in a few regions around the world such as USA, Australia and Iran with the similar Mediterranean climate (Homapour et al., 2014).

Among oils, virgin olive oil, a unique crop owing to its elevated nutritional value and sensory properties, is formed by mechanical tools directly from olive fruits in crude form without any other refining processes with regard to further vegetable oils. The request for olive oils has promoted quickly in the last decade, both in oil-producing countries and among

those who are not such as Canada, Japan, Germany, the United Kingdom, and the United States. Iran with more than 22,000 hectares area harvested and 36,000 tons olive production ranked 11th among 43 olive-producing countries in 2013. It is guesstimated that the harvested area will enhance to 40,400 hectares with 121,200 tons production in 2026. More than 80 % of olive cultivation is connected to the northern part of country, Gilan province. The olive oil production of Iran amounted to 4,504 tons in 2011 (Amanpour et al., 2016).

In addition to its health and organoleptic properties, the oxidative stability of virgin olive oil is high because of the high amount of oleic acid, low amounts of linoleic and linolenic acids, and also the presence of biophenols and tocopherols. Thus, the quality and beneficial effects of virgin olive oil intensively belong to its acidic profile and the amount of the minor compounds (Kharazi et al., 2012). Subsequently, quantity and quality of fatty acids composition existing in the virgin olive oil is influenced by different parameters involving the kind of the olive variety, climatic conditions, ripening phase, irrigation management and the isolation techniques. Among these parameters, the variety is one of the most substantial parameters, as each variety has a unique attribute (Hashempour et al., 2010).

Iran is placed in the eastern Mediterranean basin. The history of olive cultivation in Roodbar, the principle olive growing zone of Iran, has been registered for more than nine hundred years. Roodbar is placed in a mountainous area of Iran at 36490N latitude, and 49350E longitude with the same Mediterranean climatic conditions. Phishomi is one of the major olive oil producing cultivar in Iran. In last years, studying in the olive oil composition, as a reliable scale for certified quality and authenticity of virgin olive oil, is of great scientific interest (Kharazi et al., 2012). However, there are limited studies about quality and composition of Iranian virgin olive oils in the Roodbar area. Therefore, due to the importance of fatty acid profile on the oil quality, the present study aims to investigate the composition of the fatty acids, percentage of saturated fatty acids (SFA), monounsaturated fatty acids (MUFA) and polyunsaturated fatty acids (PUFA) as well as the ratio of oleic acid to linoleic acid and MUFA to PUFA in the extra-virgin olive oil obtained from the Iranian Phisomi olive cultivar.

MATERIALS and METHODS

Olive Oil Sample. The monovarietal Phishomi olive oil (70 kg) was elaborated from an olive farming zone (five different olive trees) of Roudbar in the province of Gilan, in the North of Iran. Olive fruits were handpicked in the year 2016 and the relative oils were immediately acquired by cold press techniques (Amanpour et al., 2016). Samples were kept at 10 °C in darkness before analysis.

Fatty Acid Composition Analysis. Gas chromatographic analysis of the fatty acids was carried out applying a Schimadzu 14B GC (Tokyo, Japan) fitted with a flame ionization detector (FID) and a split injection system (split ratio 1:50). For the determination of fatty acid composition, the methyl esters were provided by cold transmethylation. Separation was performed with a DB23 (Agilent Inc., USA) capillary column (60 m × 0.25 mm id). Hydrogen was the carrier gas, and injector and detector temperatures were set to 250 and 300 °C, respectively.

Oven temperature was adjusted to 130 °C for 1 min, increased from 130 to 170 °C at 6.5 °C/min then was programmed to 215 °C at 2.75 °C/min for 12 min and then increased to 230 °C at 40 °C/min for 3 min. The injection volume was 1 µL. The identification of individual FA (myristic, palmitic, palmitoleic, margaric, margoleic, stearic, oleic, linoleic, arachidic, linolenic, gadoleic and behenic) was performed by checking with retention times of known standards and expressed as a percentage of the total (Amanpour et al., 2016).

RESULTS and DISCUSSION

Fatty Acid Composition of Olive Oil

The most conquering compounds in olive oil are fatty acids. Table 1 exhibited the fatty acid composition outcomes of Phishomi olive oil.

Table 1. Fatty acid composition of Iranian Phishomi olive oil

No.	Fatty acid composition	Olive Oil[a]	IOOC regulation[b]	Codex alimentarius[c]
1	Myristic acid (C14:0)	0.04±0.00	<0.05	0.0–0.05
2	Palmitic acid (C16:0)	14.14±0.03	7.5–20.0	7.5–20.0
3	Palmitoleic acid (C16:1)	0.86±0.02	0.3–3.5	0.3–3.5
4	Margaric acid (C17:0)	0.05±0.00	<0.3	0.0–0.3
5	Margoleic acid (C17:1)	0.06±0.00	<0.3	0.0–0.3
6	Stearic acid (C18:0)	2.73±0.01	0.5–5.0	0.5–5.0
7	Oleic acid (C18:1)	63.65±0.08	55.0–83.0	55.0–83.0
8	Linoleic acid (C18:2)	16.93±0.03	3.5–21.0	3.5–21.0
9	Arachidic acid (C20:0)	0.40±0.01	<0.6	0.0–0.6
10	Linolenic acid (C18:3)	0.78±0.00	<1.0	–
11	Gadoleic acid (C20:1)	0.25±0.00	0.24	0.0–0.4
12	Behenic acid (C22:0)	0.13±0.00	<0.2	0.0–0.2
	Saturated fatty acids	17.48±0.02	–	–
	Monounsaturated fatty acids (MUFA)	64.82±0.03		
	Polyunsaturated fatty acids (PUFA)	17.71±0.01		
	Oleic acid/linoleic acid	3.76±0.00		
	MUFA/PUFA	3.66±0.01		

[a]Results are expressed as mean ± standard deviation of relative percentages of the compounds
[b] (IOOC, 2001)
[c] (Codex Alimentarius Commission, 2003)

As can be indicated in Table 1, a total of 12 fatty acids were discovered under study. Findings revealed that the fatty acids existing in the oil samples were myristic acid (C14:0), palmitic acid (C16:0), palmitoleic acid (C16:1), margaric acid (C17:0), margoleic acid (C17:1), stearic acid (C18:0), oleic acid (C18:1), linoleic acid (C18:2), linolenic acid (C18:3), arachidic acid (C20:0), gadoleic acid (C20:1) and behenic acid (C22:0). Among these fatty acids, oleic acid (C18:1) was the most prevailing fatty acid, representing the highest content (63.65 %) in the sample, followed by linoleic acid (16.93 %), palmitic acid (14.14 %) and stearic acid (2.73 %); the amount of the rest of the fatty acids found in trace values are accessible in Table 1. Fatty acid composition may alter among oils from different olive cultivars. Nevertheless, our finding was agreed to those acquired in Racimilla, Bodocal, and Negral oils from Spain (Cerretani et al., 2006), in Gemlik, Ayvalik, and Memecik from Turkey (Kelebek et al., 2015) and in Throumbolia and Koroneiki from Greece (Vekiari et al., 2010) and Mari from Iran (Amanpour et al., 2016).

It is known thoroughly that the main monounsaturated fatty acid in olive oil is oleic acid. High amount of oleic acid in olive oil is of great significance owing to promoting the nutritional wealth by reducing the breast cancer hazard and diminishing the low density lipoprotein (LDL) cholesterol and triglycerides which decline blood pressure and cardiovascular illness as well as enhancing the oxidative stability (Benito et al., 2010). Therefore, as a consequence the high tolerance to oxidation in olive oil is especially because of the high amount in oleic acid. The content of oleic acid (63.65 %) shown in Table 1 is lower than the content disclosed in Coratina (79.70 %) from Pescara of Italy, Picual (78.20 %) from Sevilla of Spain (Luna & Aparicio, 2002) and Ayvalik (67.07 %) and Memecik (73.22 %) from Balikesir and Mugla of Turkey (Kelebek et al., 2015), and higher than the percentage

of Chemlali (ranging between 58.31 and 61.6 %) (Mraicha et al., 2010) as well as very similar to Throumbolia (ranging between 58.31 and 61.68 %) from Southern Greece (Vekiari et al., 2010). Linoleic acid is the second main fatty acid that comes right after the oleic acid as an unsaturated fatty acid with the content of 16.93 % in the total olive oil. The percentage of linoleic acid (16.93 %) in our study was higher than those reported in Coratina (5.80 %) from Pescara of Italy, Picual (4.60 %) from Sevilla of Spain, Koroneiki (4.60 %) from Crete of Greece (Luna & Aparicio, 2002), and lower than the percentage of Thrombolia (ranging between 20.97 to 19.68 %) from Southern Greece (Vekiari et al., 2010). Among saturated fatty acids, palmitic acid (C16:0) was the main compound with a 14.14 % content. As can be seen in Table 1, the percentages of the fatty acid compositions in our study were in the range of those reported and established by the IOOC (IOOC, 2001) and Codex Alimentarius (Codex Alimentarius Commission, 2003) with high similarity.

Apart from fatty acid compositions, the percentage of saturated fatty acids (SFA), monounsaturated fatty acids (MUFA), polyunsaturated fatty acids (PUFA) and the ratios of PUFA to SFA and oleic to linoleic acids were also assessed in our olive oil sample. The oleic to linoleic acid ratio is an important indicator of the oxidative stability in olive oil; thus, the higher value of this ratio, the less prone to oxidation (Cerretani et al., 2006). The percentage of this ratio was 3.76 % in studied olive oil which was similar to that obtained in Greek Throumbolia (2.91–3.19 %) (Vekiari et al., 2010), and lower than that reported in Spanish Bodocal (5.07 %) and Negral (8.04 %) oils (Cerretani et al., 2006), in Turkish Ayvalik (6.68 %) and Memecik (7.09 %) oil (Kelebek et al., 2015).

CONCLUSIONS

In this test, fatty acid composition of olive oil obtained from Iranian Phishomi olive cultivar grown in the northern part of country, Roudbar in the province of Gilan, was determined using a gas chromatography fitted with a flame ionization detector. A total of 12 fatty acids entailing myristic, palmitic, palmitoleic, margaric, margoleic, stearic, oleic, linoleic, arachidic, linolenic, gadoleic and behenic acids were detected. From them, oleic acid was the most prevailing fatty acid, representing the highest content (63.65 %) in the sample, followed by linoleic acid (16.93 %), palmitic acid (14.14 %) and stearic acid (2.73 %); the amount of the rest of the fatty acids detected in trace amounts. Fatty acid composition might vary between different olive oil cultivars. However, our finding was agreed to the range of those disclosed by the International Olive Oil Council and Codex Alimentarius with elevated resemblance. Apart from fatty acid composition, percentage of saturated fatty acids (17.48 %), monounsaturated fatty acids (64.82 %), polyunsaturated fatty acids (17.71 %) and the ratios of PUFA to SFA (3.66 %) and oleic to linoleic acids (3.76 %) were also evaluated in oils

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EURASIAN JOURNAL OF FOOD SCIENCE AND TECHNOLOGY

Application of Nanotechnology in Food Packaging

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Abstract

Nanotechnology has been widely used in the fields of medicine, physics, chemistry, biology, molecular biology, food and food packaging. This technology is based on the manipulation of the material used at the atomic and molecular scale. Nanomaterial is defined as a material containing particles in the size range between 1 nm and 100 nm. Investigations have reported that the annual number of nanomaterials used in the market has reached 11 million tonnes. Application of the nanotechnology into food packaging prolongs the shelf life of the food product as well as improving its quality. The studies revealed that nanomaterial applied to packaging material improved its mechanical strength and permeability; therefore the packaging material protected the freshness of the product. While given the increase in human population and food shortages in our developing world, nanotechnology is an important step for the packaging industry. In the scope of this study, the history of the development of nanotechnology is addressed, the structure of nanomaterials and nanocomposite structures developed from these materials are defined, and the application of nanotechnology to foods and food packagings are reviewed. In this context, the use of silver, titanium dioxide, zinc oxide, silicon dioxide, MgO nanoparticles, polimer techonology, an antimicrobial nanocomposite film and nanosensorsis are explained. Moreover, the adverse effects of nanomaterials on human health as well as its legal regulations are also discussed.

Keywords: Food packaging, health risk, nanotechnology, nanomaterial, regulations.

INTRODUCTION

Nanotechnology has been widely used in the fields of medicine, physics, chemistry, biology, molecular biology, food and food packaging, agriculture, aquaculture and fisheries including fish biotechnology, genetics, and its reproduction. This technology is based on the manipulation of the material used at the atomic and molecular scale. Nanotechnology enables to create materials and systems with new features by manipulation of the matter at the level of atoms and molecules (Mura et al., 2014). Nanoparticles are the small object which acts as a whole unit in terms of transport and properties. The classification of the nanoparticles depends on their characteristics, size and structures. The size of nanomaterial ranges between 1 nm and 100 nm. Material science is applied to nanotechnology for developing novel materials with the nanoscale characteristics (Hatzigrigoriou and Papasyrides, 2011; Cushen et al., 2012; Otles and Yalcin, 2013; Chellaram et al., 2014).

According to the “Recommendation on the definition of a nanomaterial” adopted by the European Commission “nanomaterial” means “a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1-100 nm” (EU, 2011a).

It was reported that nanotechnology has been unknowingly applied since the 4th century BC, when gold nanoparticles were used in the manufacture of porcelain in China and Egypt and for medical purposes. Lycurgus cups, which were made during the Roman Empire by using colored glasses containing silver and gold nanoparticles, can be given to an example to the application of their optical properties. In 1959, the famous physicist Richard Feynman recommended applying nanotechnology to work on matter at the atomic and molecular scale, this highlighted its importance, and then many people started to interest (Mura et al., 2014).

Food nanotechnology has been dated back to Pasteurization process in which Pasteur killed the spoilage bacteria with 1000 nanometers size. It stands an important improvement in food processing due to its obvious effect in food quality (Chellaram et al., 2014). Moreover, Watson and Crick's model of DNA structure, which has two helix with in 2.5 nm diameter, was defined. The other reported development in nanoscience included the invention of carbon nanotubes, which is 1 nm in size (Chellaram et al., 2014).

Nanotechnology can deliver significant improvements in terms of reducing waste for global product diversification, increasing food quality to higher levels, and "sustainable intensification" of production in agriculture. The environmental pollution caused by the pesticides and fertilizers used causes the destruction of biodiversity and the development of harmful pathogens in agriculture. Nanoformulations can be created to prevent this. This also reduces harvest damage (Cushen et al., 2012).

Nanofood is defined as the food which is obtained by the application of nanotechnology techniques (Ötleş and Yalçın, 2013). The purposes of using nanotechnology in the food industry is to improve the shelf life, freshness, the quality and safety of food products, to detect pathogens and chemical contaminants, to increase the range of food texture, colour and taste, to improve the efficiency of nutrient supplements and natural health care products, to provide encapsulafion of flavour or odour enhancers and decrease the use of fat (Cushen et al., 2012; Ötleş and Yalçın, 2013; Lopes et al., 2013; Silva and Cerqueira, 2012; Rashid and Khasravi-Darani, 2011; Sözer and Kokini, 2011).

It has been reported that by using nanotechnology, shelf life of seafood products can be prolonged by detecting bacteria in packaging and by increasing the barrier properties of the packaging material. Therefore such a healty food can be benefited by consumer safely (Buzby, 2014).

Nanoparticles can also be used as active and intelligent food packaging materials. According to European regulations 1935/2004/EC and 450/2009/EC, active materials and articles are defined as ‘‘materials and articles that are intended to extend the shelf life or to maintain or improve the condition of packaged food’’. On the other hand, intelligent food contact materials are defined as ‘‘materials and articles which monitor the condition of packaged food or the environment surrounding the food’’ (Mihindukulasuriya and Lim, 2014; EU, 2004; EU, 2009].

There are different types of nanosystem applied in food industry such as nanoencapsulation, nano-emulsion, spontaneous structure, nano-filtration, nanotechnology sprey, nanocoating and nano feed additive, and edible nano coating. Nano-encapsulation includes nanospheres suitable for food hydrophobic materials encapsulated to moisture or pH sensitive bioadhesive microspheres.

Those encapsulation system provides benefits including ease of use, increase stability, protection against oxidation, retention of volatile ingredients, taste masking, moisture and pH controlled release (Lopes et al., 2013). Nano emulsion system consists of a lipid phase dispersed in an aqueous continuous phase surrounded by a thin interfacial layer of emulsifying molecules (Ranjan et al., 2014). The use of nano emulsions in food products provides less oil use without losing cream. As example include low fat nanostructured mayonnaise, spreads and ice creams (Cushen, 2012). A firm is reported to be developing

nanosize emulsion-base dice cream with low fat content but that standardizes texture and flavor (Alfadul and Elnesh, 2010). Spontaneous structures include sturucte of proteins, starches and fats that may change during food processing at the nanometer and micrometer scales. As an example can be given denaturation of milk proteins during yoghurt formation, homogenized milk with sized droplets of 100 nm, ice cream, and whey proteins (Ranjan et al., 2014). Nano-filtration is a membrane separation method between ultrafiltration and reverse osmosis. It is used to remove bacteria, viruses, organic residues and hardness applications in food such as in whey and juice filtration and water purification (Mamin et al., 2013). Nanotechnology sprey is used to enhance the uptake of vitamin B12 and the use of other supplements in foods (Mamin et al., 2013). Nano-coatings and nanofeed additives are used in poultry meats with nano-titanium dioxide (TiO_2) to oxidize and destroy bacteria (Prasad et al., 2014). Edible nano coatings include a nano-laminate with improved moisture and gas barrier properties. Since they are physically or chemically bonded to each other, they can be used to encapsulate different type of substances, active functional agents including antimicrobials, antibrowning agents, antioxidants, enzymes, flavors, and colors, these agents may increase the shelf life and quality of coated foods (Dobrucka, 2014).

In this study, firstly, the development of nanotechnology in the historical process is addressed, the structure of nanomaterials is defined, and nanocomposite structures developed from these materials are investigated, the effects of nanotechnology on packaging and its applications are mentioned. In this context, the use of silver, titanium dioxide, zinc oxide, silicon dioxide, MgO nanoparticles, polimertechonology, an antimicrobial nanocomposite film and nanosensors are explained briefly. Finally, the effects of nanotechnology applications on health and the legal regulations in EU are discussed.

APPLICATION OF NANOTECHNOLOGY INTO FOOD PACKAGING

The packaging process is used to protect the food product from humidity, physical action, heat and light source deteriorations, to prevent microorganism, to protect against external pollution, to provide ease of transportation, to facilitate presentation, and to show content (Robertson, 2012).

There are some important points that should be considered when choosing the packaging materials including glass, paper, metal and plastics. These includes characteristics of the food products, the exact fit between the packaging material and the product, the content of the information given on the packaging material, the cost of the packaging material, and the visual and functional design of the packaging (Robertson, 2012; Silvestre et al., 2011).

Food packaging prevents permeability and acts as a barrier. In addition, the most important aim of food packaging is to prevent unwanted changes, flavor, odor and sensory properties. Application of nanotechnology to the packaging material increases the functionality of the material (Sözer and Kokini, 2014). There are different nanomaterials to be used for food applications, as well as industrial scale atomic measurement.

POLYMER NANOTECHNOLOGY

The polymer nano technology is an industrial activity involving all the processes of producing polymeric materials filled with particles under 100 nm in size. Recently, the use of polymers has increased. Polymer materials with application of nanotechnology have very good properties such as permeability, flexibility, hardness. (Silvestre et al., 2011).

In order to prevent the biodegradability of the packaging materials, inorganic particles such as clay are added to the biopolymer structures. The use of inorganic particles helps

improve the transmission of fragile micro nutrients in edible capsules (Silva and Cerqueira, 2012).

ANTIMICROBIAL NANOPACKAGING

There are nanoparticles that enhance antimicrobial properties of the food packaging. They provide antimicrobial activity by inactivating the microorganisms present in the food (Ötleş and Yalçın, 2013).

Silver nano particles (AgNPs) used in polimeric films are widely benefited in antimicrobial food packaging. Surface area of the nano silver particles to contact with bacteria or fungi is very high. Food packaging, storage containers, chopping boards, refrigerators and health supplements are some of the usage areas of the silver nano particles as antimicrobial agents. The antimicrobial capacity of AgNPs on the meat was investigated, when the meat was packaged with a low density polyethylene (LDPE) based plastics blended with nano antimicrobial masterbatch. Delay in lipid oxidation was also observed (Yang et al., 2016).

Zinc oxide nanoparticles have become a useful material in many areas as UV absorbers. In a study, zinc oxide nanoparticles were prepared as active packaging material for the inactivation of Salmonella typhimurium and Staphylococcus aureus. The film was used as an active packaging material against the same pathogens in poultry meat. It has been observed that the daily bacterial workload is reduced to zero from seven. In another study, a zinc oxide filled bio-nanocomposite film was prepared and the effect of the film against *E. coli* was examined, it was observed that the results were very positive. These properties have shown that ZnO-nanoparticles based bio-nanocomposites are a potential packaging material (Yang et al., 2016).

Titanium dioxide (TiO_2) is an environmentally friendly, non-toxic, inexpensive material with a high refractive index. The photocatalytic reaction of titanium dioxide inactivates microorganisms by causing the oxidation of phospholipids in cell structures of microorganisms. TiO_2 constitutes a basis form any works due to its lower cost. It was reported that a TiO_2-PE film was developed to inactivate *Escherichia coli* or *Staphylococcus aureus*. It has been observed that it exhibits an effective antibacterial activity for the microorganisms. Titanium dioxide is used as an antimicrobial additive in food packaging (Yang et al., 2016).The other research study reveals that *E. coli* activity was stopped after the packaging films were coated with titanium dioxide. However, since it requires UV for disinfection, its use is not preferred (Hatzigrigoriou and Papasyrides, 2011). Also, it has been observed that TiO_2 coated folies subjected to UV can neutralize fecal coliforms in the water (Dasgupta et al., 2015). Disinfection is used with silver to improve the process (Ötleş and Yalçın, 2013).

Magnesium oxide (MgO) nanoparticles have high conductivity and antibacterial effects. A study has shown that *E. coli* and anthraquinone are inactivated by MgO (Yang et al., 2016). In another study, it was observed that (MgO) was most effective in killing microorganisms (Mihindulasuriya and Lim ,2014).

Metal nanomaterials are also of interest. It has its own unique antimicrobial properties like silver and gold (Sözer and Kokini, 2011).

Silicon dioxide and carbon are 100 nm in size, like other nanoparticles, and packaging is also used as a food additive. Gold and platinum nanoparticle biosensors can be used in the packaging material to make up the food. Also, in these contexts, ontmorillonite clay, polyethyene nylon polyvinyl chloride and starch are also used extensively (Lopes et al., 2013).

ANTIMICROBIAL NANOCOMPOSITE FILM

To increase product's shelf life and to control the growth of both pathogenic and spoilage microorganisms, materials with antimicrobial activity can be used. An antimicrobial nanocomposite film can be used for those purposes and it may solve shelf life problems of the foodstuffs by providing acceptable structural integrity and barrier properties. Those properties may be obtained from both nanocomposite matrixes and the natural antimicrobial agents impregnated within the structure (Hatzigrigoriou and Papasyrides, 2011).

NANOSENSORS

Nanosensors are the application area of nanotechnology to intelligent packaging. They can be used either as coating in food packaging. They ensure the integrity of the package, since they can detect leaks; indicate the time–temperature variations, or microbial safety. They can detect some chemical compounds, pathogens, and toxins in food. By application of nanosensors, real-time status of food freshness has provided and then real expiration dates have observed. In addition, studies are being made to develop smart packaging technology (Sözer and Kokini, 2011).

Nanobiosensors are advanced devices that digitally output all the changes of the food. It is used for the detection of materials such as drought, temperature, humidity, pathogen, insect, pollutant. Because of these features, farming in agriculture provides great convenience. Helps farmers have an idea about harvest time (Prasad et al., 2014).

HEALTH RISKS

The nanomaterials in corporation into food present a whole new array of risks for the public, workers in the food industry and farmers (Mamin et al.,2013). Due to the increasing use of products containing NPs, the ecotoxicology of NPs became of an increasing importance in last years. In general, the toxicity of NPs is determined by their particle size, shape and biodegradability. Based on the particle size and biodegradability of NPs these can be classified into four classes: (i) size > 100 nm and biodegradable; (ii)size> 100 nm and non-biodegradable; (iii) size < 100 nm and biodegradable; (iv)size < 100 nm and non-biodegradable (Dasgupta et al., 2015). Particles smaller than 70 nm can enter cell and cause impairment of DNA replication and transcription.

Of course, non-biodegradable materials, which can remain in the body, accumulate and stimulate the immune system, represent an increased risk of toxicity.Therefore long term exposure can cause variety toxic case in human body (Mamin et al., 2013). Morries et al. (2017) states that harmful effects of nanoparticiles still remains an unknown issue, eventhough enorumous studies has been conducted and reported based in the literature.

REGULATION

In European Union, there is not a direct regulations for nanomaterials for food packaging. However, producers should comply with the related regulations on food packaging. In the European Union (EU), Regulation (EC) No 1935/2004 sets up the criteria which aims to provide safely use of food contact material and articles which includes food packaging as well (EU, 2004). The regulation states that materials and articles, including active and intelligent materials and articles, should not release their chemical ingredients in to food in a concentartion which is harmfull to health and the chemical migration should not

change the organoleptic properties of the food. Plastic materials and articles intended to come into contact with food are regulated by Commission Regulation (EU) No 10/2011. Annex I of Commission Regulation (EU, 2011b) No 10/2011 contains the Union list of authorized monomers, other starting substances, macromolecules obtained from microbial fermentation, additives and polymer production aids (EU, 2011).There are two migration limit set for plastic based materials and articles including specific migration limit (SML) for individual authorized substances fixed on the basis of a toxicological evaluation and overall migration limit – 10 mg of substances/dm² of the food contact surface for all substances that can migrate from food contact materials to foods (EU, 2011b). It is reported that titanium nitride is the only nanoparticle which is authorized under the regulation EU 10/2011 (Hoekstra, 2014).

Bumbudsanpharoke and Ko (2015) and Störmer et al. (2017) summarized the studies on migration of nanomaterials from food packaging in to foods. It is stated that there is a probable migration from those type of material in to foods; eventhough the concentration is lower than that is specified in the regulation.

Nanomaterials used as active and intelligient materials are regulated according to Regulation (EC) No 450/2009 (EU 2009). If a nanomaterial is released into food, it requires to be authorised as food additive under Regulation (EC) No 1333/2008 (EU, 2008).

Moreover, if a food contain engineered nanomaterials, it should be stated on the food labeling (EU, 2011c).

CONCLUSIONS

Nanotechnology is a major technology that increases the quality of life in many areas. In this article, the areas used (especially in packaging) are examined. Packaging applications have effects such as being a mechanical barrier, protecting against physical effects, lengthening the shelf life of food, and improving taste-quality, antimicrobial effect. The chemical migration of nanomaterials from packaging materials in to foodstuff is important, when considering the health and safety risks of food and human beings during its application. Like in European Union, the legal limits of this technology in our contry are not obvious, so its application is few in practice. If more risk studies are undertaken to assess the negative effects of this technology, which increases the quality of food, its applicability will be positively increased.

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