Investigation of Physicochemical Properties of Bowl and Packet Margarines Produced by Interesterification Technology

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ABSTRACT

The physiochemical properties and the values of free fat acid (FFA), peroxide, water, pH, color, solid fat content (SFA), slip melting point (SMP), total saturated fat acid (SFA), total monounsaturated fat acid (MUFA), total polyunsaturated fat acid (PUFA), and total trans fatty acid (TFA) in fat acid compositions of 38 breakfast margarines sold in cups and 39 packet margarines produced in Turkey were analyzed. While FFA, pH and color analysis results were observed at normal values required to be found in margarine, water value of 10 out of all samples were observed above legal limits.In6 out of all samples, peroxide was observed in 5 which is the maximum value allowed. In cup margarines, SMP values were detected to be 30.40-36.00% and SFC values were 5.50-15.27 while in packet margarines SMP values were 36.00-41.40 and SFC values were 22.90-35.75. TFA contents of the samples were under 1%.

Keywords: esterification, fatty acid, margarine, melting point, SFC, trans fatty acids

1. Introduction

Margarine is an emulsion of hardened oil, water, milk and additives phase. The water phase is dispersed in the oil phase in the margarine. The spreading oils or margarine is described by the Codex Alimentarius Committee and World Health Organization (WHO) as follows: Margarines/fat spreads/blends and blend spreads are water-in-oil emulsions, derived from vegetable/animal fats, with a milk fat content of not more than 3% for margarines/fat spreads. For blends and blended spreads, the milk fat is between 10% and 80%.In our country, according to the Turkish Food Codex, spreadable margarine fats and intense oils/fats include the following:

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-Margarine-Three-quarter-fat margarine: The products have a fat content by weight at least 60%, at most 62%;

-Margarine- Half-fat margarine: The products have a fat content by weight at least 39%, at most 41%;

-Margarine- Percent of fat: The products have a fat content by weight;

-Fat content by weight at least 10% and less than 39%; and

-Fat content by weight more than 41% and less than 60%

-Fat content by weight more than 62% and less than 80% (1).

According to TS 2812 (2), vegetable margarine standard, margarine is divided into three categories depending on places used: Breakfast (table) margarine, kitchen (cooking) margarine, and industrial type of margarine. Margarine history has been developed all over the world. Development history of margarine is shown in Figure 1.

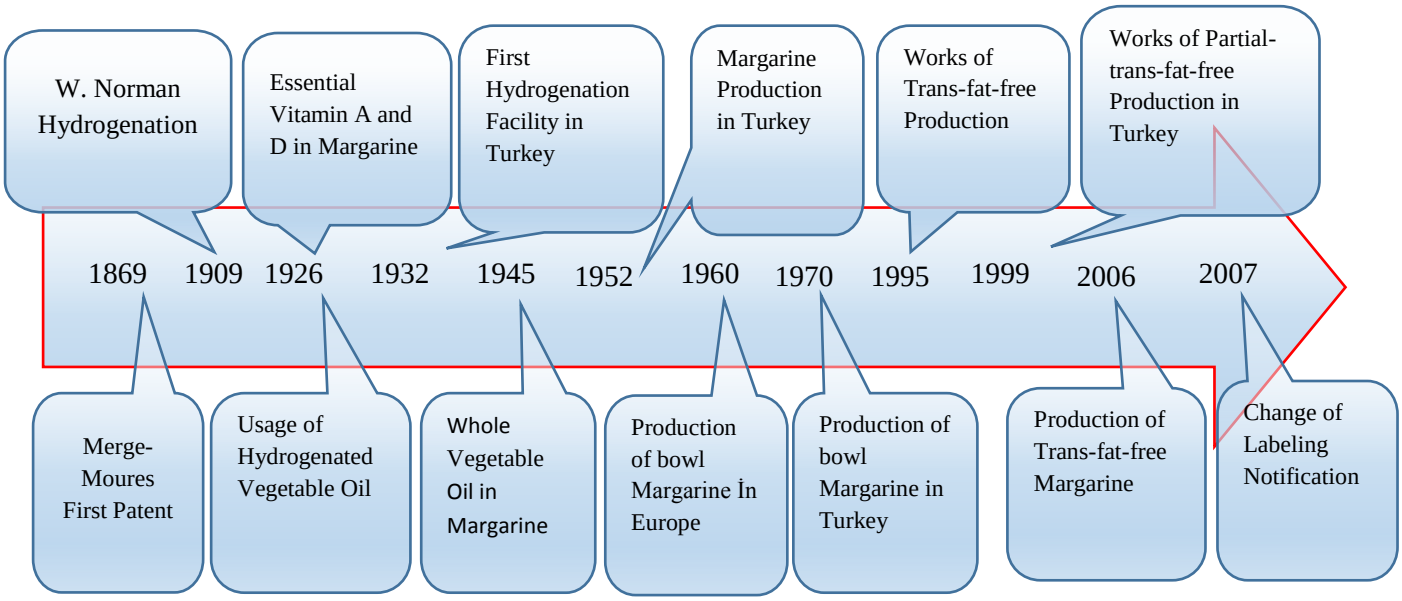

Figure 1. Historical Development of Margarine

Palm, sunflower, soybeans, cotton, canola oil are crystallized in different proportions according to the characteristics of the formulation of these oils, and are used in the margarine industry in Turkey. In order to determine the overall quality of margarine, the fatty acid profile identification and quantification are important. Saturated fatty acids (SFA) and trans fatty acids (TFA) consumption are associated with an increased risk of cardiovascular disease by raising the total cholesterol to HDL-cholesterol ratio (3,4, 5). Metabolic studies indicated that TFA increases plasma concentrations of low-density lipoprotein (LDL) cholesterol and reduce concentration of high-density lipoprotein (HDL) cholesterol (3). The effects of trans fatty acids were more harmful than saturated fatty acids. For this reason, traditionally, the solid fat content of margarine obtained by hydrogenation of liquid oils are replaced with different processes for the production of zero-trans solid fats in the food industry including chemical (6), orenzymatic transesterification(7,8).As a result of studies on the increase of trans fats on health-related issues, the total amount of trans fats have been imposed in Turkey and the world. Hydrogenation technique was used in the manufacture of margarine until 1995 in Turkey and throughout the world. Total trans-fat studies were started in 1999 and margarine production containing less than 1% trans-fat began in our country in 2006. The phrase, “There is no trans-fat” was used legally on label packaging in 2007. The hydrogenation technique used in hardening of the oil was transferred to the esterification technology due to this restriction (9).

Free Fatty Acids (FFA), peroxide, pH, the moisture, color, melting point and solid fat contents are among the most important parameters of margarine quality, and are important to industry.FFA, peroxide value and slip melting point value have maximum limit at TS 2812 (2)vegetable margarine standard (FFA: 1.5%; peroxide 5 mEq/kg; SMP: 36 °C).

Color values have no legal limitations. When imitation butter used in margarine production the precursor (such as vitamin A, β-carotene) is used as a colorant. The percentage of fat values is grouped according to the Turkish Food Codex spreadable margarine and intense fats/oils. Although there are no legal limitations for solid fat, its values are highly important as an indicator when margarine is taken out of the refrigerator for spreadability and taken into the mouth for solubility on the tongue.

Kitchen Products and Margarine Manufacturers Association (MUMSAD) reported that in 2015, 84164 tons packet margarine, and 30015 tons cup (bowl) margarine were produced in our country in 2014. Among several available tests to measure the oxidative stability of oils, the peroxide value test to measure the amount of hydroperoxides at the end of the first stage of lipid oxidation has been used widely. Similarly, a common measure of hydrolytic rancidity is the free fatty acid test or acid value test (10, 11).Most of the studies report physiochemical parameters of margarine such as moisture, free fatty acid content, and fatty acids (12, 13), sterols and tocopherols (14).

Using gas chromatographic (GC) separation of fatty acid methyl esters (FAME) provides important information about oil quality in food science and industry (15,16, 17). However, GC samples must be derivatized to fatty acid methyl esters (FAMEs), requiring the use of solvents. Several researchers have analyzed oil properties using nuclear magnetic resonance (NMR) (17). This technique has also been implemented to study oil components such as mono- and di-glycerides (18),free fatty acids (19, 20)or antioxidant compounds (18,21) and tocopherols (22),the composition in acyl groups of vegetable oils (23, 24 25).The usefulness of ^{1}H NMR spectroscopy offers many advantages over existing analytical methods because of the simplicity of the sample preparation, speed of the analysis, and the quantity of information that can be obtained in the least amount of time. Some studies report the use of ^{13}C NMR to study the triacylglycerol composition of margarine, distribution of fatty acids in the glycerol structure and/or the content of trans fatty acids (26,27). Currently, time domain (TD)-NMR analyzer method for the solid-to liquid ratio analysis of fat compositions is widely adapted and well known as solid fat content (SFC) determination (28).

The study is focused on the determination of the physicochemical properties of different types of margarines sold in the Turkey in 2015. The primary objective of this study is to identify and quantify the fatty acid composition of commercial margarines with special emphasis on TFA.

2. Materials and Methods

2.1. Materials

In this study, the materials used were 60% fat cup margarines of 18 different companies and 60-82% fat packet margarines of 17 different companies making 77 products in total. According to the analysis group, melting processes were performed in laboratory ovens at 45°C. Samples were kept at -18°C until analysed.

2.2. Methods

2.2.1. Fat Acids Composition and Determination of Trans Isomers

Fatty acid composition of oleogel samples was determined by using GC-FID (Agilent 6890 GC) equipped with HP-88 column (100 m x 0.25 mm ID x 0.2 µm). 0.1 gr of sample was taken, poured into 10 ml of n-Hexane and shaken for 30 seconds with a vortex mixer. 100 microliters of 2 N potassium hydroxide

(KOH) (prepared in methyl alcohol) was added and shaken for 30 seconds using a vortex mixer. After centrifugation of whole mix, 1-2 ml of the liquid phase was poured into vial and injected into GC-FID equipped with auto sampler. Temperature and oven program of the device were as follows: Inlet temperature: 250°C; Injection volume: 1 µl; Split Ratio: 1/50; Carrier gas: Helium; Pressure flow: 2 ml/min; Oven Temperature: 120°C, 1 min, 10°C/min to 175°C, 5°C/min to 210°C, 5 min 5°C/min 230°C, 5 min; Detector temperature: 280°C; Detector gases. Hydrogen: 40 ml/min, Air: 450ml/min, Helium: 30ml/min (29).

2.2.2. Solid Fat Content Determination

The brand name and model of the NMR device: Bruker/Minispec 7.5 MHz. 3.5 ml of samples which do not contain water are put into NMR glass tubes. They are kept at 60°C for 5 minutes and then at 0°C for 1 hour. Afterwards, they are kept in 20°C water-bath for 0.5 hour. The conditioned sample is then put into the device (30).

2.2.3. Melting Point Determination

The sample is melted by heating. It is filtered through filter paper and the water, if any, is evaporated. Capillary tube is immersed into the filtered sample. 4 capillary tubes are prepared so that they each contain sample to the height of 1cm. They are connected to the thermometer with a clamp and kept in the refrigerator at 0°C. The water-bath is filled with water not warmer than 10°C, capillary tube and the thermometer is immersed in it. Melting point designation device is turned on (at 8-10°C lower than the melting point, to increase 0.5°C per minute). When the fat column in the capillary tube gets transparent and rises, the temperature is read on the thermometer. The average temperature of 4 capillary tubes is calculated (31).

2.2.4. Peroxide Determination

5 g of sample is weighed and put into screw cup Erlenmeyer flask. It is dissolved in 10 ml of chloroform. 15 ml of acetic acid and 1 ml of saturated KI are added and the cap of Erlenmeyer flask is closed and shaken for 5 minutes. Then it is kept in dark for 5 minutes. 75 ml of distilled water and 0.2 ml of starch indicator (1% solution) are added over the samples kept in dark and they are shaken strongly. If the colour of the solution is white, peroxide is zero. If it is blue-grey, it is titrated with 0.01 N $Na_2S_2O_3$until it turns white. The amount of the solution used for titration (ml) is read and the calculation starts. Calculation:

Peroxide value (meq O_2/kg):N X f X S X $\frac{1000}{5}$

N: the normality of $Na_2S_2O_3$ solution; f: 0.01 N $Na_2S_2O_3$ factor; V: Volume of the used 0.01 N $Na_2S_2O_3$ (ml)(32).

2.2.5. Water Determination

A glass container which has a fixed weight at 105^{o}C is tared. Approximately 5 g of sample is put into the container, and it is dried in the laboratory oven for 1hour at 105 ±2^{o}C. It is cooled down and weighed in desiccator. When the final mass reaches a fixed weight, the weight is recorded. The amount of water in the sample is calculated with the following formula:

Water Amount (%):$(m_2-m_3) / (m_2-m_1)$ X 100

$m_{1:}$ mass of the glass container, g

$m_{2:}$ glass container + mass of the sample, g

$m_{3:}$ glass container + mass of the dried sample, g(33).

2.2.6. pH Determination

pH values of the prepared samples are measured directly or by percentage with a pH meter which was previously calibrated. The measurements are recorded (34).

2.2.7. Colour Determination

Sample is put into the sample container as much as 2/3 of the container's volume, it is then placed on the device. On the two separate divisions of the device (Lovibond, F series), colour scales of Red-Yellow-Blue are adjusted until the colours are the same, and the values are read (35).

2.2.8. Acidity Determination

10 g of sample is put into an Erlenmeyer flask with a capacity of 250ml. The sample is dissolved in 100 ml of previously neutralised Diethyl ether and Ethanol (95% v/v) mixture prepared to be a 1+1 solution by volume. The solution is mixed, then 0.5 ml of indicator solution (1% of Phenolphthalein) is added. It is titrated until the turning point with adjusted 0.1 N sodium hydroxide solution. The acidity of the sample (A) is calculated as percentage by mass with the following formula according to the type of the fat:

$$A = (V \times c \times M) / 10 \times m$$

V: Volume of the adjusted sodium or potassium hydroxide solution, ml
c: Concentration of the adjusted sodium hydroxide solution, mol/l
M: Molecular mass of the Oleic acid which is used to express the acidity, 282 g/mol
m: Mass of the sample, g(34).

2.2.9. Statistical Analyses

Peak identification of the fatty acids in the analysed margarine samples was carried out by the comparison with retention times and FAMEs Analytic StandardsStandard methyl esters of SFA, MUFA, PUFA and TRA were used for the confirmation of GC-FIDFAMEs Analytic Standards. Physicochemical analysis and fatty acid profile of three samples of each brand were collected and each sample was analysed three times. The data obtained were put into SPSS 20.0 software program and reported as mean (n = 3X3).Correlation of SFA, SFC and SMP analysis were performed.

3. Results and Discussion

Physicochemical analyses of cup margarines and packet margarines sold in 2015, and the amounts of total saturated fat, total monounsaturated fat, total polyunsaturated fat, and total trans fatty acids related to their fat acidity are given in Table 1 and Table 2.

Table 1: Physicochemical analysis and % total saturated, total monounsaturated and polyunsaturated and total trans fatty acid for bowl margarine in 2015

Bowl margarine											
#	SMP / (°C)	SFC/NMR (20°C) %	Peroxide meq O_2/kg	FFA %	Water %	Color	pH	∑SFA %	∑MUFA %	∑PUFA %	∑TRANS %
1	33.20	9.66	4.60	0.53	38.96	5.6 - 70	4.6	28.64	34.60	36.44	0.33
2	33.40	7.61	7.60	0.47	39.28	7.1 - 70	5.2	29.11	23.13	47.21	0.55
3	31.00	5.95	13.20	0.25	39.57	4.2 - 70	5.2	21.96	26.74	50.74	0.56
4	32.60	8.31	12.64	0.58	39.91	8.5 - 70	4.4	25.76	28.19	45.77	0.28
5	32.00	6.34	12.80	0.42	39.13	4.5 - 70	4.6	22.23	26.19	51.17	0.41
6	32.00	6.66	6.80	0.42	38.20	4.3 - 70	4.6	24.85	29.02	46.03	0.10
7	34.60	8.73	11.20	0.32	39.87	7.0 - 70	4.9	27.52	24.54	47.37	0.57
8	31.80	10.59	0.60	0.46	38.3	7.9 - 70	4.9	43.15	23.70	32.60	0.00
9	35.60	10.42	3.30	0.36	38.50	3.8 - 70	4.6	28.63	37.92	33.35	0.10
10	31.40	7.46	0.40	0.39	39.24	4.8 -70	4.6	23.27	31.83	44.80	0.10
11	31.80	7.11	2.70	0.40	37.85	4.1 - 70	4.6	22.84	37.98	39.09	0.10
12	31.60	7.52	0.20	0.47	39.42	7.8 - 70	5.2	28.97	28.14	42.58	0.31
13	32.00	6.19	0.20	0.32	39.84	5.2 - 70	5.6	22.95	37.18	39.78	0.09
14	31.20	5.50	2.00	0.32	39.66	4.5 - 70	5.5	22.30	37.43	40.27	0.00
15	32.00	11.48	1.10	0.31	37.58	7.8 - 70	4.8	39.66	23.82	36.52	0.00
16	33.40	10.70	1.20	0.39	38.10	4.1 - 70	4.8	30.03	39.34	30.63	0.00
17	33.00	10.26	0.80	0.507	38.09	4.8 - 70	4.6	29.02	39.65	31.34	0.00
18	36.00	8.41	1.60	0.225	40.09	7.5 - 70	5.25	28.24	24.62	47.14	0.00
19	32.60	7.99	2.74	0.507	39.04	8.5 - 70	4.2	28.21	26.13	45.66	0.00
20	31.40	7.00	1.18	0.564	39.35	6.1 - 70	5.3	26.51	27.88	45.61	0.00
21	31.00	9.17	1.74	0.464	38.38	6.0 - 70	5.2	33.12	34.00	32.88	0.00
22	32.80	12.24	1.00	0.465	37.71	7.0 - 70	4.8	44.47	28.55	26.97	0.00
23	32.00	8.69	1.56	0.425	37.85	6.8 - 70	4.7	28.31	28.74	42.96	0.00
24	33.40	15.27	1.65	0.446	37.69	5.9 - 70	4.8	45.63	28.72	25.65	0.00
25	35.60	11.43	2.10	0.366	39.84	4.1 - 70	4.5	32.35	35.67	31.98	0.00
26	36.00	10.15	1.00	0.423	37.84	4.8 - 70	4.5	29.24	37.60	33.16	0.00
27	32.20	6.61	1.60	0.394	38.55	4.8 - 70	4.5	23.96	29.06	46.98	0.00
28	31.60	7.32	2.00	0.479	39.00	6.2 - 70	5.1	28.30	28.08	43.62	0.00
29	33.40	12.47	0.80	0.479	39.45	9.0 - 70	4.9	42.67	23.92	33.41	0.00
30	31.00	7.72	2.20	0.456	39.12	6.1 - 70	5.1	27.88	26.12	46.00	0.00
31	31.20	7.62	2.00	0.324	39.43	4.5 - 70	5.6	24.59	35.43	39.98	0.00
32	34.00	8.66	1.40	0.380	39.50	5.1 - 70	5.6	23.97	32.79	43.24	0.00
33	32.00	6.46	1.10	0.394	38.31	5.1 - 70	4.9	22.95	29.55	47.45	0.00
34	30.40	6.67	2.20	0.464	38.12	4.2 - 70	4.9	23.02	32.05	44.93	0.00
35	31.80	6.16	1.80	0.394	38.64	6.0 - 70	4.5	22.02	27.48	50.50	0.00
36	33.40	11.38	1.80	0.366	39.26	4.2 - 70	4.6	31.90	36.12	31.98	0.00
37	34.00	9.62	1.20	0.423	38.42	4.8 - 70	4.5	28.86	34.09	37.05	0.00
38	33.40	10.96	1.10	0.423	38.70	7.9 - 70	4.9	41.29	26.92	31.79	0.00

Table 2: Physicochemical analysis and % total saturated, total monounsaturated and polyunsaturated and total trans fatty acid for packet margarine in 2015

Packet margarine											
#	**SMP / (°C)**	**SFC/ NMR(20 °C) %**	**Peroxide meq O_2/kg**	**FFA %**	**Water %**	**Color**	**pH**	**∑SFA %**	**∑MUFA %**	**∑PUFA %**	**∑TRANS %**
1	**36.00**	**26.48**	**0.60**	**0.451**	**38.64**	**6.0 - 70**	**4.74**	**60.90**	**25.12**	**13.2**	**0.74**
2	**36.00**	**25.92**	**0.50**	**0.423**	**28.71**	**5.3 - 70**	**4.74**	**57.54**	**27.65**	**14.3**	**0.44**
3	**40.40**	**30.98**	**3.60**	**0.465**	**28.01**	**5.3 - 70**	**4.80**	**53.99**	**31.81**	**14.0**	**0.14**
4	**39.70**	**25.86**	**0.20**	**0.253**	**18.38**	**5.1 - 70**	**4.76**	**50.61**	**33.97**	**15.2**	**0.15**
5	**39.00**	**24.46**	**3.20**	**0.310**	**41.29**	**5.4 - 70**	**4.80**	**48.84**	**35.05**	**16.0**	**0.10**
6	**39.60**	**24.61**	**2.00**	**0.338**	**28.89**	**8.1 - 70**	**4.85**	**51.40**	**17.16**	**31.4**	**0.00**
7	**37.20**	**24.63**	**1.00**	**0.465**	**28.80**	**8.3 - 70**	**4.95**	**51.06**	**27.03**	**21.7**	**0.19**
8	**39.00**	**24.95**	**1.20**	**0.267**	**19.00**	**7.0 - 70**	**5.22**	**50.15**	**30.98**	**18.6**	**0.18**
9	**41.40**	**35.75**	**1.40**	**0.408**	**39.36**	**5.5 - 70**	**4.63**	**56.06**	**26.92**	**16.8**	**0.16**
10	**37.00**	**23.50**	**1.00**	**0.380**	**43.64**	**7.4 - 70**	**4.85**	**49.42**	**33.13**	**17.0**	**0.36**
11	**39.20**	**30.13**	**1.60**	**0.564**	**30.29**	**9.1 - 70**	**4.75**	**53.04**	**36.48**	**10.4**	**0.00**
12	**37.40**	**24.76**	**0.60**	**0.423**	**38.55**	**7.1 - 70**	**4.50**	**54.91**	**29.39**	**15.7**	**0.00**
13	**37.00**	**25.98**	**0.60**	**0.479**	**28.76**	**6.3 - 70**	**4.45**	**56.72**	**29.72**	**13.4**	**0.16**
14	**37.80**	**25.12**	**0.74**	**0.408**	**26.38**	**5.5- 70**	**4.80**	**50.60**	**31.27**	**18.1**	**0.00**
15	**37.00**	**24.98**	**0.78**	**0.366**	**42.35**	**5.5- 70**	**4.82**	**51.52**	**30.59**	**17.8**	**0.00**
16	**37.60**	**25.98**	**2.50**	**0.296**	**19.01**	**5.1- 70**	**4.78**	**51.82**	**30.50**	**17.6**	**0.00**
17	**37.60**	**25.54**	**2.20**	**0.310**	**29.46**	**8.0 70**	**4.85**	**52.92**	**27.52**	**19.5**	**0.00**
18	**37.00**	**23.51**	**1.86**	**0.465**	**28.88**	**8.1- 70**	**4.85**	**52.20**	**27.33**	**20.4**	**0.00**
19	**41.00**	**28.61**	**1.72**	**0.338**	**30.23**	**9.0- 70**	**4.98**	**50.49**	**37.27**	**12.2**	**0.00**
20	**38.60**	**24.60**	**1.28**	**0.478**	**43.63**	**7.5- 70**	**4.88**	**51.00**	**27.93**	**21.0**	**0.00**
21	**38.00**	**23.61**	**4.60**	**0.451**	**39.67**	**5.5- 70**	**4.64**	**51.45**	**31.73**	**16.8**	**0.00**
22	**38.40**	**22.90**	**2.26**	**0.366**	**42.93**	**5.5 70**	**4.65**	**50.10**	**23.83**	**26.0**	**0.00**
23	**40.00**	**25.09**	**1.92**	**0.195**	**28.83**	**9.0- 70**	**4.95**	**50.59**	**34.47**	**14.9**	**0.00**
24	**37.00**	**26.80**	**1.10**	**0.394**	**28.56**	**6.0 70**	**4.65**	**56.72**	**29.72**	**13.4**	**0.16**
25	**39.00**	**27.40**	**1.40**	**0.380**	**38.84**	**6.1- 70**	**4.80**	**53.28**	**29.16**	**17.5**	**0.00**
26	**39.20**	**28.56**	**1.20**	**0.549**	**17.37**	**5.5- 70**	**4.78**	**54.14**	**28.91**	**16.9**	**0.00**
27	**38.00**	**32.19**	**1.00**	**0.394**	**29.00**	**8.5- 70**	**4.75**	**61.70**	**28.46**	**9.84**	**0.00**
28	**38.40**	**32.08**	**1.60**	**0.310**	**29.18**	**8.4- 70**	**4.73**	**62.66**	**24.47**	**12.8**	**0.00**
29	**36.80**	**31.71**	**2.90**	**0.423**	**40.23**	**5.9- 70**	**4.65**	**55.24**	**28.04**	**16.7**	**0.00**
30	**37.80**	**30.72**	**2.60**	**0.423**	**43.78**	**6.5- 70**	**4.80**	**60.68**	**29.24**	**10.0**	**0.00**
31	**37.20**	**30.61**	**1.70**	**0.451**	**43.61**	**5.5- 70**	**4.65**	**62.83**	**24.18**	**12.9**	**0.00**
32	**37.60**	**26.29**	**0.70**	**0.380**	**28.88**	**5.9 70**	**4.60**	**53.42**	**28.92**	**17.6**	**0.00**
33	**38.20**	**33.03**	**1.20**	**0.396**	**29.14**	**8.0 70**	**4.82**	**61.82**	**20.43**	**17.7**	**0.00**
34	**38.20**	**33.04**	**1.80**	**0.380**	**29.22**	**8.3- 70**	**4.79**	**61.60**	**24.57**	**13.8**	**0.00**
35	**40.00**	**26.81**	**1.60**	**0.310**	**44.55**	**6.2- 70**	**4,92**	**53.87**	**28.04**	**18.0**	**0.00**
36	**39.80**	**28.59**	**1.60**	**0.451**	**17.55**	**5.7- 70**	**4.88**	**53.28**	**28.78**	**17.9**	**0.00**
37	**39.40**	**35.06**	**1.80**	**0.423**	**40.44**	**5.8- 70**	**4.79**	**58.45**	**27.39**	**14.0**	**0.00**
38	**36.60**	**25.19**	**1.10**	**0.338**	**39.68**	**6.0- 70**	**4.66**	**54.73**	**30.57**	**14.7**	**0.00**
39	**37.40**	**26.70**	**1.00**	**0.479**	**28.91**	**6.1- 70**	**4.58**	**55.61**	**30.02**	**14.3**	**0.00**

According to Table 1, the physicochemical analysis results for cup margarines are as follows: FFA values between 0.225-0.58%, Peroxide values between 0.20-13.20 mEq O_2 / kg, pH values between 4.20-5.60, water values between 37.58-40.09%, colour values between 3.8 K/70 S – 9.0 K/70 S. Physicochemical

analysis results for packet margarines are as follows: FFA values between 0.195-0.564%, Peroxide values between 0.20-4.60 mEq O_2/kg, pH values between 4.45-5.22, water values between 17.37-44.55%, colour values between 5.10 K/70 S – 9.10 K/70 S.

In the related thesis, Tuğal (36) reported the physicochemical analysis results to be Free Fat Acidity (FFA) value between 0.19-0.39% Oleic acid, peroxide value between 0.10-0.91 mEq O_2/kg, water content between 14.00-16.30%, colour value between 2.20-6.30., Laia et al. (37) reported peroxide value to be between 1.28-1.40 mEq O_2/kg., Azizkhani et al. (38) reported peroxide value to be 0.40 mEq O_2 / kg, FFA value 0.03 mg/g – (% Oleic Acid)., Zaeroomali et al. (39) reported water content to be 19.09, peroxide 0.32 mEq O_2 / kg, FFA 0.13% Oleic Acid and colour value to be between 3-4.

FFA values reported in this study mostly match the values reported in literature. The reason for the maximum FFA value of 0.96% is the high number of samples and producer companies. However, this value is under the maximum limit of 1.5% according to TSE (Turkish Standards Institute) 2812 (2).

Maximum peroxide values in this study are higher than previously reported peroxide values in literature (37, 38, 36) particularly for cup margarines. One of the reasons for this is that cup margarines tend to oxidize more due to the high amount of unsaturated fat acids. Unsaturated fat acids oxidize much more easily than saturated fatty acids (40). Another reason is that the margarine samples sold at markets are not stored at a stable temperature and cold chain conditions are not met. Storage conditions are important in terms of peroxide values of margarines (41). In addition, the maximum legal peroxide value allowed for margarines is 5 by the expiry date, thus companies keep the peroxide value during the production process between 0 and 1.

Water values are higher compared to other water values given in literature (36, 39). The reason for this is the increase in the production of low fat margarine in our country in recent years. Because, in accordance with the Turkish Food Codex Spreadable and Intensive Margarines Communiqué and TSE 2812 (2), it is allowed to produce margarines with fat content between 90% and 10%.

This shows that the increase in obesity, cardiovascular diseases, etc. reduces the consumption of margarines and high-fat products, especially at breakfast, leading to decrease in annual production each year, which prompts to manufacturers to produce low-fat-containing margarines.

Colour values are higher compared to other colour values given in literature (36,39). The reason for this is that our study covers all of the products of the margarine producers in Turkey (the number of the samples is high).

Since the essential goal of margarine production is to produce a margarine similar to butter as much as possible. Therefore, palm, cotton, or soyoil which have high colour values are used in margarine formulation, on condition that β crystal structure of margarine is not damaged and chemical properties of this oils allow. Depending on the end product, producers generally use natural or artificial β-carotene and food colourings such as annatto, bixin for having a yellowish colour.

In this study, pH values match mostly the values reported in, Tuler's thesis (42). There is not a legal limitation on pH values. However, pH values are important in terms of quality criteria (sensorial and microbiological). In margarine sector, the pH value is largely between 4-4.5, and citric acid is used as pH stabiliser (43, 44).

Values of Total Saturated Fat Acids, Total Monounsaturated Fat Acids, Total Polyunsaturated Fat Acids and Total Trans Fatty Acids are given in Table 1 and Table 2. Accordingly, in cup margarines Total Saturated Fat Acids were detected to be between 25.65-45.63%, Total Monounsaturated Fat Acids to be between 23.13-39.65%, Total Polyunsaturated Fat Acids to be between 20.88-51.17%, and Total Trans Fatty Acids to be between 0.00-0.57%; while in packet margarines Total Saturated Fat Acids were detected to be between 48.84-62.83%, Total Monounsaturated Fat Acids to be between 17.16-36.48%, Total

Polyunsaturated Fat Acids to be between 9.84-31.40%, and Total Trans Fatty Acids to be between 0.00-0.74%. Total saturated, total mono, and poly unsaturated acid composition values given in this study match with the values previously reported in literature by, Brat et al. (45), Kandhro et al. (46), Kroustallaki et al. (12). In this study, the maximum value of total saturated fat acids in cup margarines is almost equivalent to the minimum value in packet margarines. This shows that cup margarines are more spreadable, more prone to melt in mouth, and better spreadable with knife when taken out of refrigerator.

Amount of total trans fatty acids in our study are similar to those determined by, Kroustallaki et al. (12); while they are different from the values given by, Brat et al., (45), Kandhro et al. (46). The reason for the similarity with the total trans fatty acid values given by Kroustallaki et al. (12) is that production of margarines containing less than 1% of trans fat started in our country as of 2007, and that, in accordance with the labelling communiqué, products with less than 1% trans-fat shall legally have an expression on the package saying that it does not contain trans-fat. On the other hand, the reason for the high levels of total trans-fat acids given in the study of Brat et al. (45) is that hydrogenation technique was used those years in margarine production in the world and in our country.

In our study, we designated SMP values for cup margarines between 30.40-36.00 and SFC values (at 20°C) between 5.50-15.27, while in packet margarines SMP values were between 36.00-41.40 and SFC values (at 20°C) were between 22.90-35.75 (Table1, Table 2).

Among 38 samples of cup margarines, all samples had an SMP value under 36.0 which is the maximum level allowed for breakfast margarines by TS 2812 (2). For packet margarines, SMP values of only 2 samples out of 39 were not over the legal limit. There is not a limitation related to SFC values.

However, the SFC value is an indicator of quality for the customer satisfaction since the spreadability of margarine at refrigerator temperature depends on its solid fat content at 2-10°C. There is a direct relation between the structure, viscosity and plasticity of the end product and solid fat content. The SFC value demonstrates the tendency of crystallisation and the quality of the end product. For this reason, most margarine producers use SFC values at 10, 21.1 and 33.3°C for controlling the viscosity of margarine (46, 47, 48).The results related to the SMP values show that legal controls are not conducted adequately, and that packet margarines are produced with higher SFC and SMP values due to their packaging and the inadequate cold chain conditions in our country. SMP and SFC values obtained in similar studies in the literature are parallel to the values in our study (49, 50, 51, 37,52).Fat acid composition of the samples is given in Table 3. As seen in the fat acid composition, in margarine formulation the highest acids found were palmitic acid (C16:0), oleic acid (C18:1) and linoleic acid (C18:2). Palmitic acid in packet margarines was higher than cup margarines, but linoleic acid (C18:2) was lower. Additionally, linolenic acid (C18:3) was detected higher in bowl margarine. As seen in fat acid composition, different types of oils were used in margarines. Related to the margarine composition, high value of palmitic acid in the formulation shows that palm olein oil is used in higher amounts while lauric acid (C12:0) and myristic acid (C14:0) values show the use of low level of palm kernel oil. Besides, the detection of linolenic acid in the composition (C18:3) shows that canola and soy oil are used. Because, linolenic acid (C18:3) is found in cotton, sunflower, corn, and palm oil with low ratios (< 0.5), while it is found in canola and soy oil with higher ratios (4.5-1.4). Studies of Karabulut and Turan (52) are similar in terms of palmitic acid (C16:0), lauric acid (C12:0) and myristic acid (C14:0) values.

Table 3: Min–max values of Fatty acid compositions for bowl and packet margarines in 2015

Min –max values of Fatty acid compositions for bowl and packet margarines in 2014				
Carbon Number	**Bowl**		**Packet**	
	Min	Max	Min	Max
C6:0	0.00	0.03	0.00	0.14
C8:0	0.00	0.73	0.00	1.97
C10:0	0.00	0.47	0.00	1.64
C12:0	0.00	6.71	0.45	15.08
C14:0	0.72	2.72	1.07	6.34
C16:0	8.76	33.30	27.71	44.37
C16:1	0.00	0.41	0.00	0.36
C17:0	0.00	0.12	0.00	0.21
C17:1	0.00	0.12	0.00	0.25
C18:0	3.80	7.60	4.17	12.38
C18:1-T	0.00	0.41	0.00	0.81
C18:1	22.68	47.06	16.72	46.30
C18:2-T	0.00	0.31	0.00	0.23
C18:2	20.78	50.33	8.64	30.94
C20:0	0.12	0.61	0.12	0.59
C18:3	0.04	8.09	0.07	2.54
C20:1	0.00	0.08	0.00	0.37
C20:2	0.00	0.08	0.00	0.07
C22:0	0.01	0.60	0.00	0.36
C22:1	0.00	0.38	0.00	0.07
C22:2	0.00	0.07	0.00	0.03
C24:0	0.00	0.48	0.00	0.47
C24:1	0.00	0.10	0.00	0.08

According to the correlation analysis of 2015 bowl margarines; SFC values were positively and strongly correlated ($P<0.05$) with SFA values ($r= 0.874$), while SFC were positively and moderately correlated ($P < 0.05$) with SMP ($r= 0.513$). For 2015 packet margarines, there was a strong significant correlation between SFC and SFA ($r= 0.695$), while there was a weak significant correlation between SFC and SMP ($r= 0.331$). In regarding to the correlation data of the bowl and packet margarine in 2015; finding association among SFC, SFA and SMP values confirmed that the increase % fat resulted in the increase total saturated fat and melting point value in the margarine composition.

4. Conclusion

Total trans fatty acid of margarine was found less than 1% since interesterification technology was used for margarine production. Physical and chemical analysis values of the packet margarine were within the legal limits except for some SMP values. These studies gave an impression that in formulations of margarines produced in Turkey palm olein oil, palm kernel oil and sunflower oil are mostly used.

In this study, the products of different brands belong to all margarine producing companies in Turkey were bought from various stores and analysed. As a result of study, Total Trans Fatty acid of all margarines

was found less than 1%. That shows that all producers used interesterification technology instead of hydrogenation technology in margarine production process.Physical and chemical analysis values of the packet margarine were within the legal limits except for some SMP values. Another result displays that especially in packet margarines still contained total saturated fatty acids at risky levels for heart health, therefore new studies should be carried out to reduce total saturated fatty acid in breakfast margarines.These studies give an impression that in formulations of margarines produced in Turkey palm olein oil, palm kernel oil, sunflower oil and cotton oil are mostly used.

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