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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

THE RESEARCH OF QUALITY INDICATORS OF CHOCOLATE PRODUCTS ON THE BASIS OF THE CHEMICAL STRUCTURE OF FATS AND THE ASSESSMENT OF THE ECOLOGICAL ASPECTS OF PRODUCTION OF THEM

Speciality: 2391.01- Ecological chemistry"

Field of science: Chemistry

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INTRODUCTION

The Relevance of the Research Topic and the Degree of its Elaboration. The chemical and physical properties of fats contained in chocolate sample have been studied in various research papers[1]. Based on research conducted, it has been established that the thermal properties of fats are related to the physicochemical properties of the finished product, which allows to regulate a variety of issues related to its production, storage, transportation and consumption. Hazard assessment on each stage of this cycle and defining critical control points, determination of the origin and extent of raw materials provide a comprehensive approach to production, including consumption. Along with this, in accordance with the international standards for life cycle assessment of each product, it is of great importance, both theoretically and practically to quantitatively and qualitatively determine, to predict and classify its impact on the environment and the human body at all stages from production to consumption.

The study of the authenticity of the food constituents and the application of appropriate standards in production are the basis for monitoring food products in the modern times. Thermal methods - thermogravimetry, differential thermogravimetry and differential scanning calorimetry are reliable instrumental methods applied in this direction. Therefore, determining the role of each stage of production in the formation of a consumer product and the change in its physical properties lays the foundation for the use of these methods. Additionally, nowdays, the use of software in assessing the environmental aspects of many areas of production has expanded. Consequently, calculating the impact on the environment and the human body in the life cycle of a product requires the application of software[2].

[1]Materazzi, S. Thermogravimetric characterization of dark chocolate / S.Materazzi, S.De Angelis Curtis, S.Vecchio Ciprioti [et al] // J Therm Anal Calorim., – 2014, 116, –p. 93–98.

[2]Miah, J.H. Environmental management of confectionery products: Life cycle impacts and improvement strategies / J.H. Miah, A. Griffiths, R. McNeill [et al] // Journal of Cleaner Production, – 2018, 177, – p. 732-751.

Thermogravimetric analysis of chocolate products at different stages of production was studied under different experimental conditions. In the framework of the conducted research, thermogravimetric analyzes performed in a flow of nitrogen and oxygen at appropriate heating rates are of great importance in deftermination the authenticity of the constituents of chocolate products at various stages of production.

Furthermore, the determination of the melting points of fats extracted from finished chocolate products by differential scanning calorimetry at different heating rates is very relevant for defining the polymorphic form of fat content of the product.

Nowadays, determining critical control points by assessing risks at production stages and calculating the impact on the environment and the human body during the product life cycle using software capabilities allows to determine the environmental aspects of production of chocolate products.

Thus, according to the thermal characteristics of the constituent components of chocolate samples in the direction of solving the listed issues, determination of authenticity criteria, application possibilities of thermogravimetric analyzes as a method for determining the authenticity of the constituent components of chocolate samples in various experimental conditions, determination of melting points by differential scanning calorimetry method which allows determination of polymorphous forms of fats, calculation of environmental aspects as a result of application of software in life cycle assessment for all stages from production to consumption clearly prove the relevance of the presented work.

Object and subject of research. The experiments were carried out on the basis of the following research objects of the dissertation work:

- Cocoa butter,
- Milk fat,
- Sugar,
- Cocoa liquor,
- Dark chocolate powder,
- Chocolate Milk Powder,

- Sample of dark chocolate,,
- sample of milk chocolate,
- 14 samples of milk fat,
- 36 pcs dark chocolate (conditionally, D1 - D36),
- 23 pcs milk chocolate (conditionally, M1 - M23),
- 8 pcs white chocolate (conditionally, W1 – W8),
- 4 pcs chocolate powder, including 2 pcs milk and 2 pcs dark chocolate powder (conditionally, DP1 - DP2 və MP1- MP2),
- 44 pcs chocolate sample,
- Statistics of cocoa, chocolate and sugar confectionery produced and consumed in Azerbaijan between 2014 and 2020.

It is included in the subjects of the research conducted in the dissertation

Dissertasiya işində aparılmış tədqiqatların predmetlərinə daxildir:

- Application of thermogravimetry (TG) and differential thermogravimetry (DTA) methods to determine the authenticity of ingredients in chocolate products;
- Application of a differential scanning calorimeter in studying the properties of oxidation and melting of milk fat samples based on the dependence of oxidation time with regard to heat flow and the attitude of enthalpy values to heating rates;
- Application of differential scanning calorimetry method to detect polymorphic forms of these fats based on the melting properteries of fats extracted from chocolate products;
- Application of Inductively Coupled Plasma Optical Emission Spectroscopy method in determination of metal contents in various chocolate samples and studying the interaction of Hazard Analysıs And Crıtıcal Control Poınt (HACCP) and Life Cycle Assessment (LCA);
- Application of software to identify and evaluate environmental impacts in life cycle assessment (LCA) of production and consumption of cocoa, chocolate and confectionery products in Azerbaijan during the period from 2014 to 2020.

Research aims and objectives: The main aim of the submitted dissertation is to study the impact of various stages of processing on the thermal properties of dark and milk chocolate samples, study the thermal properties of the composition of chocolate, and assess the environmental aspects of its production.

Having in regard with these goals, the following studies are planned to be conducted:

- Analysis of thermal properties of cocoa liquor, cocoa butter and milk fat in chocolate samples that were at different stages of processing, in the flow of nitrogen and oxygen, in the temperature range of 50-700 °C at heating rates of 2, 5 and 10 °C min-1 by using thermogravimetry (TG) and differential thermogravimetry (DTG) methods;
- Determination of the melting point of fats extracted from different types of chocolate in a nitrogen flow at heating rates of 2.5, 4, 5, 7.5, 10, 12.5, 15 °C min-1 by using differential scanning calorimetry (DSC);
- Study of oxidation of milk fat samples in oxygen flow at heating rates of 2.5, 4, 5, 7.5, 10, 12.5, 15°C·min-1 by applying differential scanning calorimetry (DSC);
- Calculation of metal contents in various chocolate samples in inductively Coupled Plasma Optical Emission Spectroscopy method by using ultrasonic scattering technique;
- Interaction of concepts of metal contents of product in chocolate production with the Hazard Analysıs And Crıtıcal Control Poınt (HACCP) and Life Cycle Assessment (LCA);
- Modelling of life cycle assessment (LCA) of cocoa, chocolate and confectionery products producted and consumpted in Azerbaijan during the period from 2014 to 2020 by application of Simapro Demo software.

Research methods. The following methods were used in the reasearch work:

Thermogravimetry (TG), Differential Thermogravimetry (DTG), Solvent Extraction method, Differential Scanning Calorimetry (DSC) technique, Inductively Coupled Plasma Optical Emission spectroscopy method, Eco-Indicator '99 method.

Basic provisions to be defended in dissertation thesis:

I. A thermogravimetry is a convenient method of proving the authenticity of the composition of chocolate samples.

II. A differential scanning calorimetry can be used to determine the polymorphic forms of fats extracted from different types of chocolate samples.

III. Differential scanning calorimetry is the optimal method for determining the oxidation temperatures of milk fats at different heating rates.

IV. The metal content of chocolate samples corresponds to the results of the determination of Hazard Analysıs and Crıtıcal Control Poınt (HACCP) and the assessment of Life Cycle (LCA) during their production.

V. A life cycle assessment of cocoa, chocolate and confectionery products produced and consumed in Azerbaijan in 2014-2020 was simulated using Simapro Demo software.

Scientific novelty of the research. Below mentioned works have been carried out in the frame of dissertation works for the first time:

- Thermogravimetric analysis of cocoa liquor, cocoa butter, and milk fat in chocolate samples that were at different stages of processing was carried out in the flow of nitrogen and oxygen at a heating rate of 2, 5, and 10°C min^{-1}
- The optimality of the thermogravimetric method has been proven in the analysis of the authenticity of the ingredient composition of chocolate samples.
- The differential scanning calorimetry method has been widely used in determining the polymorphic forms of fats extracted from different types of chocolate and in defining the extend of oxidation of milk fat samples.
- The concepts of metal contents of product in chocolate production with the Hazard Analysıs And Crıtıcal Control Poınt (HACCP) and Life Cycle Assessment (LCA) has been interacted.
- Life cycle assessment of cocoa, chocolate and confectionery products produced and consumed in Azerbaijan in 2014-2020 was simulated using Simopro Demo software.

Theoretical and practical significance of the research. Thermal analysis of cocoa liquor, cocoa and milk fat in chocolate products that were at different stages of processing by using the thermogravimetric method has both fundamental and applied significance. It has fundamental significance in the determination of polymorphic forms of fats extracted from different types of chocolate on the basis of their melting points by using the method of differential scanning calorimetry and defining the oxidation temperatures of milk fats. In the frame of the dissertation, simulation of life cycle assessment was carried out on the basis of the Eco-Indicator 99 method the environmental aspects of production and consupmtion of cocoa, chocolate and confectionery products in Azerbaijan in the period of 2014 - 2020.

Approbation and application of research work. Based on this dissertation, 15 works have been published, 7 articles out of them were articles, and 8 were articles and thesis of reports at international scientific conferences and seminars.

The findings of the dissertation were reported and discussed at the following international scientific conferences: 33rd Scientific Conference Oilseed Crops – Advances in genetics, breeding, technology and analytics of lipids (Poznań 2016, 5-6 April, p. 40, 106), Bioeconomy in Agriculture, International Conference (Puławy 2016, 21–22 June, p.89-90), 11th International Seminar on Thermal Analysis and Calorimetry to the memory of Prof. St. Bretsznajde (Płock 2016, 26-29 September, p.86), 3rd International Young Researcher Scientific Conference "Sustainable Regional Development - Challenges of Space and Society in the 21st Century (Gödöllő 2018, 26 April, p. 72-76), V International Scientific Conference of Young Researchers (Baku 2021, 29-30, April, p.1034-1036), Modern problems Of theoretical and Experimental chemistry International Conference devoted to the 90th anniversary of academician Rafiga Aliyeva (Baku 2022, 29 - 30 September, p.116-117, 117-118).

The main product of the research work is the modeling of the environmental impacts of the production and consumption of cocoa, chocolate and sugary confectionery products in Azerbaijan in 2014-2020 via Simapro Demo program.

The name of the institution where the dissertation was completed. The dissertation work was conducted at the Department of Environmental Chemistry, Faculty of Ecology and Soil Science of Baku State University.

The total volume of the dissertation with a sign indicating the volume of the structural parts of the thesis separately. Total volume of dissertation in computer context consists of 216 pages, 167157 symbols (table, figure, list of references and appedix excluded), including 7 pages (10786 symbols) in introduction part, 37 pages (49666 symbols) in Chapter I, 10 pages (13319 symbols) in Chapter II, 13 pages (11905 symbols) in Chapter III, 19 pages (14269 symbols) in Chapter IV, 46 pages (63795 symbols) in Chapter V, 2 pages (3414 symbols) in conclusion part, the reference literature in the 17th page, the Appendix and 1 page of used abbreviations in the 59th page. 2 pictures, 26 tables and 22 graphs were indicated in this research work. The dissertation were referred 131 literary sources.

Personal participation of the author: Collection and synthesis of information on literature review, preparation and conduct of experiments, preparation of samples to be studied, systematic processing of results, elobaration of articles and theses, explanation and synthesis of data obtained as a result of analyzes occurred with direct participation of author.

1. Thermogravimetric analysis and differential thermogravimetry (DTG)

The results of cocoa butter, milk fat, cocoa liquor, and sugar presented in Figure 1 were obtained from TG and DTG analyses in nitrogen and oxygen. The TG curve of cocoa butter in nitrogen is characterized by only one step of decomposition (Figure 1a). The peak in DTG curve at the temperature of 414 °C was observed. On the TG curve for cocoa butter, one transition in the range of 310–440 °C was detected. It was due to thermal degradation of cocoa butter. Cocoa butter TG curve in oxygen is characterized by different course. The TG curve can be divided into four stages. First stage ranged from 50 to 290 °C, second—from 290 to 335 °C, third—from 335 to 420 °C, and fourth—from 420 to 700 °C. Different polymorphic forms, which are typical for cocoa butter, have very different physical properties but, upon melting, give identical liquids. In 1966, a complete study of the polymorphic states in cocoa butter was conducted, and the existence of the following polymorphic forms in order of increasing stability: I (sub-α or γ), II (α), III, IV (β`), V (β), and VI was determined. Form V (β) makes that cocoa butter remains stable for a very long period of time at the proper storage temperature. On the DTG curve, four peaks were observed (Figure 1a`). The first peak in DTG curve was detected at the temperature of 286 °C. The TG and DTG curves of milk fat in nitrogen and oxygen are presented in Figures 1b, b` . The maximum temperature of first-derivative peak of milk fat was 384 °C in nitrogen. The course of milk fat curve was very similar to TG curve of cocoa butter. The profiles of the TG and DTG curves in oxygen showed five stages of decomposition of milk fat, with maximum temperature at 95, 296, 340, 414, and 511 °C. Milk fat due to its structure is polymorphic fat. The fat in the liquid state reached by rapid cooling proceeds in the form of α, slow heating, and then solidifying causes the passage in the form of β`. Form β` is more stable than form α. In an analogous manner, form β from the mold β` is created. Form β is the most stable form of fat. There is also a fourth form γ (sub-α); it is characterized by a lower melting point than the form α and $\beta`_2$ and directly converts in the form of β`. Milk fat may crystallize taking on three different polymorphic forms: γ, α, and β`. The most stable form of the milk fat is a form of b0 and the least— form γ. The next stage phases represent the decompositions of trans isomers of fatty acids and saturated fatty acids. The thermogravimetric data TG and first-derivative data DTG of the cocoa liquor under a nitrogen and oxygen are shown in Figures 1c, c`. The TG curves showed that cocoa liquor was thermally unstable in nitrogen and in oxygen. The course of the TG and DTG curves in nitrogen presented three stages of decomposition for cocoa liquor. First stage ranged from 50 to 325 °C, second—from 325 to 400 °C, and third—from 400 to 700 °C. The maximum temperatures at 289 and 390 °C were observed.

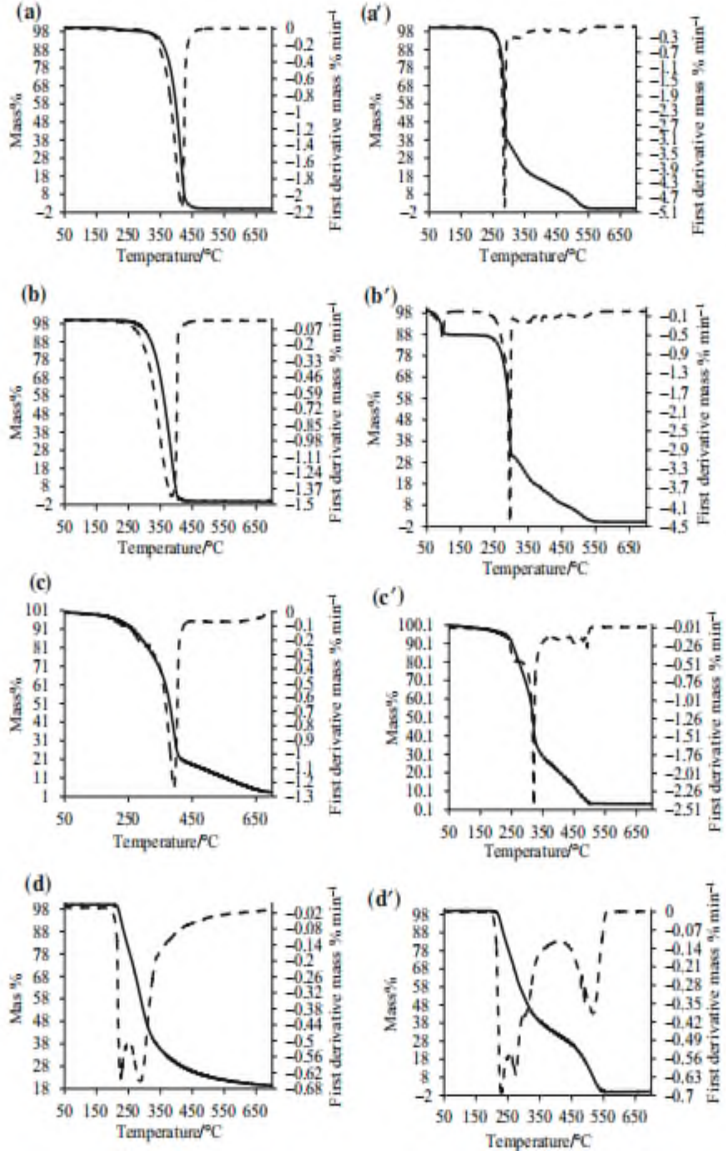


Figure 1. TG and DTG curves of chocolates ingredients: cocoa butter (a) in nitrogen and (a`) in oxygen; milk fat (b) in nitrogen and (b`) oxygen; cocoa liquor (c) in nitrogen and (c`) in

oxygen; sugar (d) in nitrogen and (d`) in oxygen

Four stages of decomposition on TG and DTG curves of cocoa liquor in oxygen at maximum temperature: 253, 320, 447, and 491 °C were shown. The cocoa liquor is a mixture of cocoa butter, cocoa powder, cocoa solid, antioxidant flavor, and mineral compounds. The temperature of decomposition was corresponding with thermal degradation of ingredients of cocoa liquor. The thermogravimetric behavior of crystal sugar is shown in Figures 1d, d`. In the TG curve of sugar in nitrogen, between 220 and 700 °C, continuous mass loss was observed. In TG curve in oxygen, three stages were observed that indicate changes in the rate of mass loss during thermogravimetric drying. This result can be attributed to water elimination from several sources. The DTG curves of sugar in nitrogen and in oxygen were characterized by two peaks at similar temperature for both gases. The first peaks with maximum temperatures of 225 and 228 °C in nitrogen and oxygen, respectively, were followed by the second—at 288 and 271 °C (Figure 1d`). Due to the complex behavior of sugars when melted, thermal decomposition reactions can occur before or close to the melting point, and in the literature a range of values for sucrose melting varies between 185 and 190 °C. The sugar's origin may be responsible for the wide variation of melting points, since there are different sources (e.g., cane and beet sugar) and manufacturing methods. The DTG curve in oxygen showed peak at maximum temperature of 518 °C, which indicates the sugar sample decomposition.

The thermogravimetric data (TG) and first-derivative data (DTG) of the three stages dark and milk chocolates production under heating in nitrogen atmosphere are presented in Figure 2. Milk/dark chocolate powders are the products after refining process, milk/dark chocolate before tempering are the products after conching process, and dark/milk chocolates are the final chocolate bars. The TG curves that characterize samples of dark and milk chocolates at different stages of production can be divided into three steps. First stage ranged from 50 to 210 °C, second— from 210 to 350 °C, and third— from 350 to 700 °C. The analysis of the starting materials (sugar, cocoa liquor, and cocoa butter), it is very easy to assign each TG step in the dark chocolate curve: The first one is related to the sugar contribution, the second step is the release of the cocoa liquor, and the final is related to the mass loss of cocoa butter (Figures 1 and 2).

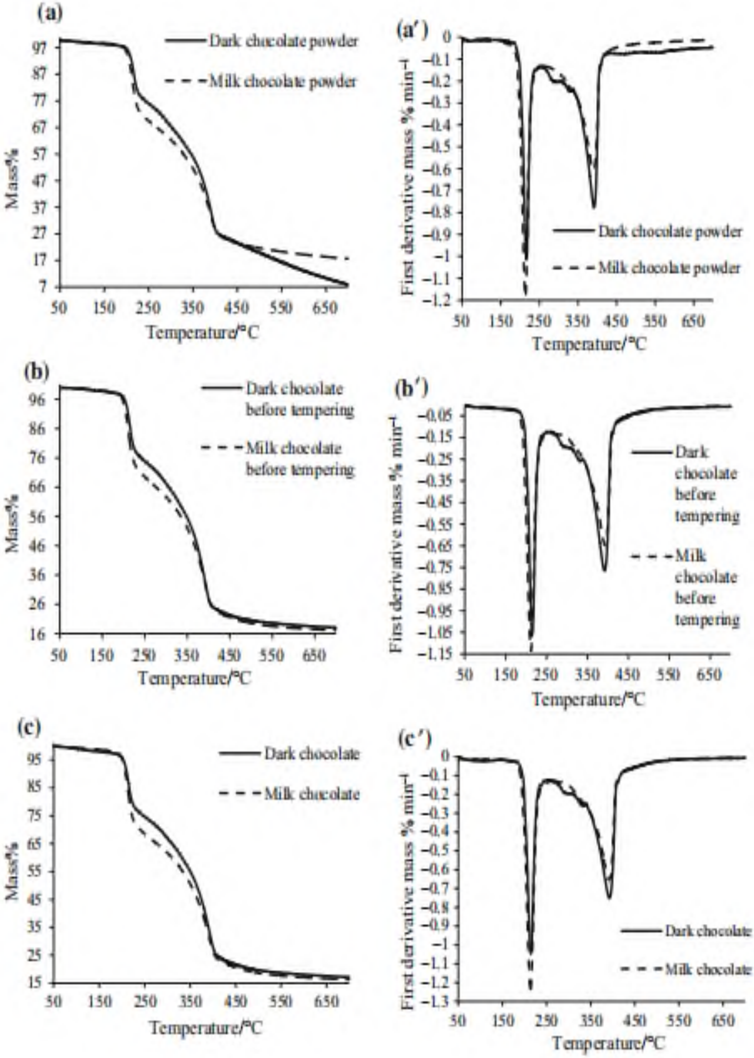


Figure 2. TG (a–c) and DTG (a` –c`) curves of dark and milk chocolates of different processing stages in nitrogen

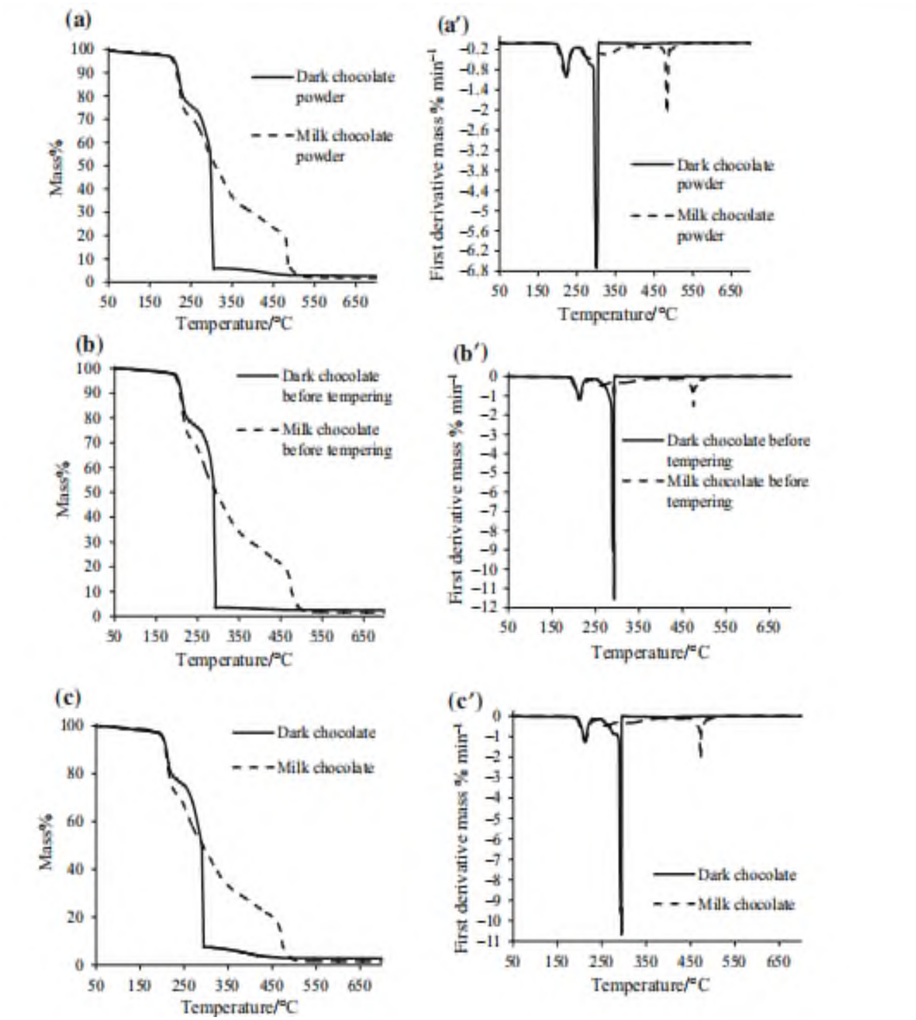


Figure 3. TG (a–c) and DTG (a` – c`) curves of dark and milk chocolates of different processing stages in oxygen

In the second step in TG curves of all production stages, the differences between milk and dark chocolates were observed (Figures 2a–c). This phenomena indicated that amount of cocoa liquor in dark chocolate (powder, before tempering and chocolate bar) was higher. The dark chocolate powder TG curve showed higher rate of mass loss at third step than others TG curves. There were no differences in TG curves courses for different stages of dark/milk chocolates production, except of the TG course of dark chocolate powder. The first derivatives designated for fats and chocolates allowed identification of chocolate ingredients (Figures 2a` –c`). In the case of the first peaks on DTG curves, for all samples, a temperature ranged from about 211–214 °C.

The first peak proved sugar melting. The first peaks were more distinct for samples of milk chocolate at every production stage than for dark chocolate samples. Milk chocolate was characterized by higher amount of sugar in composition. In dark chocolate (for all stages of production) at a temperature ranged from 241 to 348 °C, the first derivative exhibits the presence of cocoa liquor, so no distinct peaks are observed for milk chocolate in this temperature region (Figures 2a` –c`).

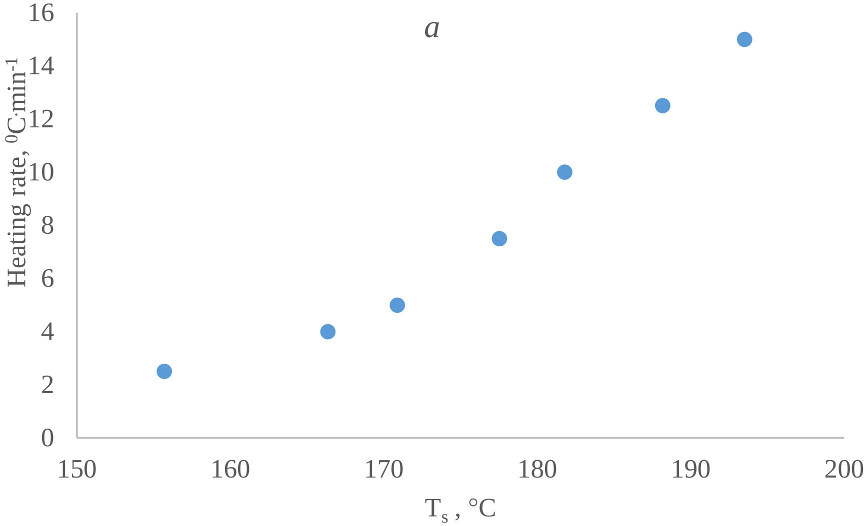
The third peaks on DTG curves for all samples can be observed at temperature ranged from about 387–391 °C. The intensity of those peaks was more distinct for dark chocolates at all of production stages, because the content of cocoa butter was much higher than in milk chocolate. Peaks characterizing fat in milk chocolate do not have such a clear course. By changing the atmosphere to oxygen, a final decomposition is obtained. There were differences in the TG curves and first derivatives for the chocolate powders, chocolate before tempering, and the finished dark and milk chocolate, in oxygen. The results of the samples analysis in oxygen for the three stages of dark and milk chocolates production are presented in Figure 3. The shapes of TG curves showed three stages for dark and milk chocolates of different processing stages.

The first transition was observed in the range of 50–230 °C (dark and milk chocolates), the second—230–300 °C (dark chocolate) and 230–500 °C (milk chocolate), and the third one—300–700 °C (dark chocolate), 500–700 °C (milk chocolate). The mass loss occurred with high rate for dark chocolate products than for milk chocolate products (Figure 3a–c). The first peaks maximum temperature range corresponds to the thermal decomposition of sugar on all of DTG curves (Figures 3a` –c`). The second transition was observed only for dark chocolates products. The peaks course indicated that the cocoa butter was oxidized. The DTG curves in oxygen for all dark chocolate products showed peak at maximum temperature range from 291 to 294 °C. Peaks characterizing fat in milk chocolate were characterized by less intensity.

The third melting transition was observed on DTG curves of milk chocolate products. The last peaks represent the decomposition of sugar, like in Figure 1d`. The maximum temperatures were observed at 493 (milk chocolate powder), 500 (milk chocolate before tempering), and 473 °C (milk chocolate).

2. Differential scanning calorimetry (DSC) analyses

A computer-coupled apparatus examined the DSC curves of each sample that was analyzed. The obtained T_s, T_{on}, and T_p values for milk fat samples, which were measured for seven heating rates, are presented in Figure 4. In the thermal DSC analysis, the influence of heating rate of the samples on the T_s, T_{on}, and T_p values were observed. All the values of oxidation increased with increasing heating rate, only in the T_{end} values were changeable among all heating rates.


a
Heating rate, 0C·min-1
16
14
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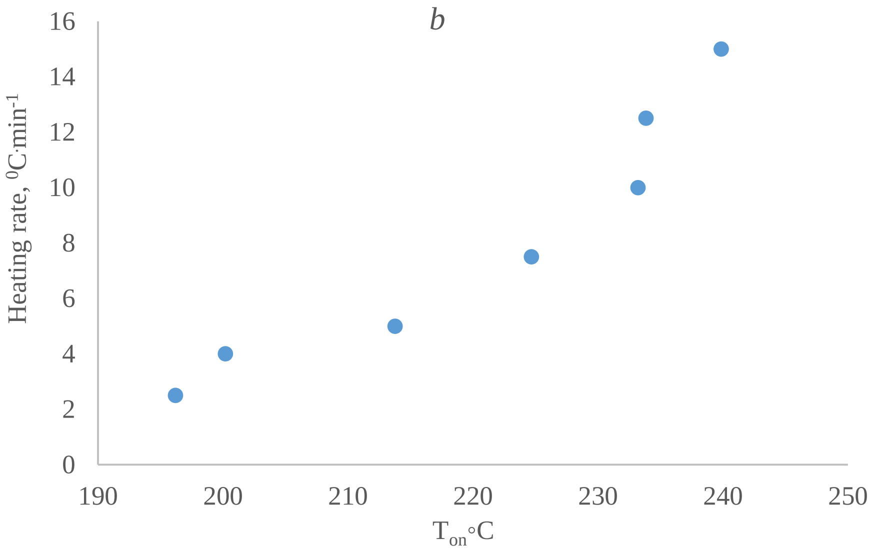
190
200
Ts , °C


b
Heating rate, 0C·min-1
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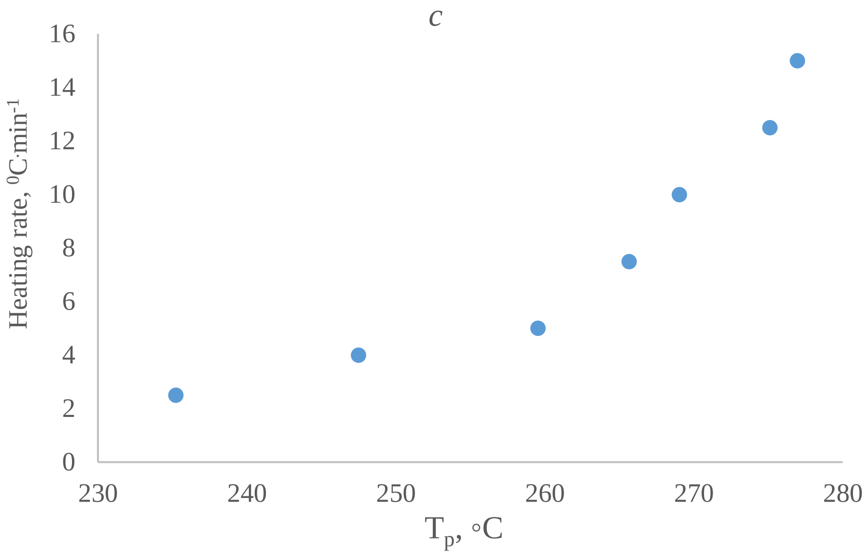


Figure 4 . The dependence of temperature values of DSC curves of milk fat samples from the heating rates of 2.5, 4, 5, 7.5, 10, 12.5 and 15 °C· min^{-1}: a – T_s; b – T_{on}; c – T_p

In general, the T_s was determined between ~155–193 °C, the T_{on} was considered between ~196–239 °C, the T_p was mentioned ~235–246 °C at 2.5, 4, 5, 7.5, 10, 12.5 and 15 °C· min^{-1}, respectively. Thus, as proper heating rates increased, T_s, T_{on}, and T_p of oxidation were rising gradually.

The dependence of heating rate to time was directly proportional in all values (Figure 5).

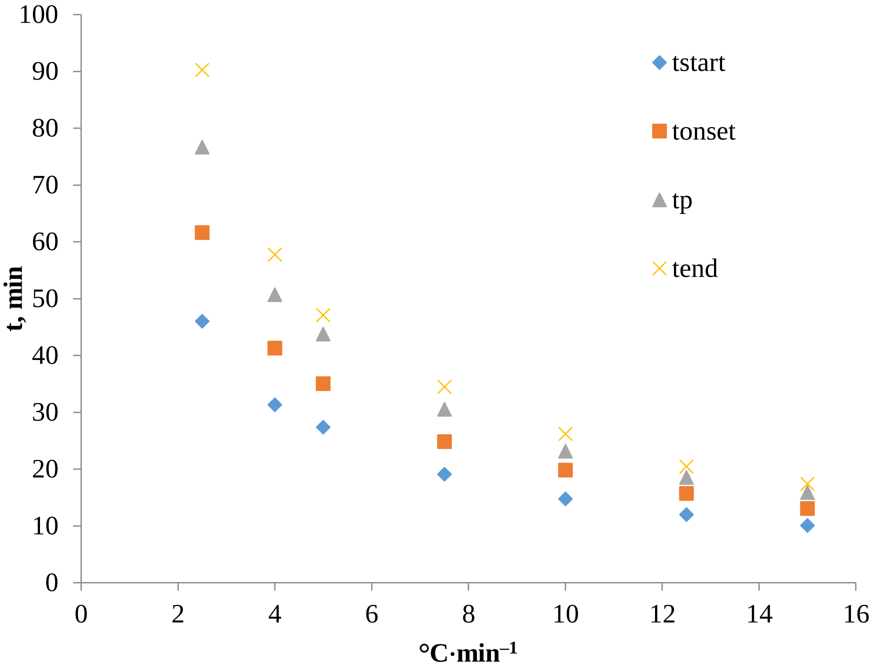


Figure 5. The dependence of heating rate to t_{start}, t_{onset}, t_{peak}, t_{end} oxidation time of DSC curves of milk fat samples in 2.5, 4, 5, 7.5, 10, 12.5 and 15 °C· min^{-1}

The curves explain the dependence on the start/onset/peak/end of oxidation time and duration of oxidation to the heat flow, which oxidation begins and ends quickly at high heat rate. Thus, on the low value of heating rate, the start oxidation time was observed at 46th minute, the onset oxidation time was accepted at 61th minute, the peak oxidation time was culminated at 76th minute, and the end oxidation time was considered at 90th minute. However, on the high value of heating rate, the start/onset/peak/end of oxidation time determined at 10th, 13th, 15th, 17th minutes, respectively. These regularities were observed for the rest heating rates.

Although oxidation temperature is an intensive property, the melting point considers the important indicator to explain the purity of samples.

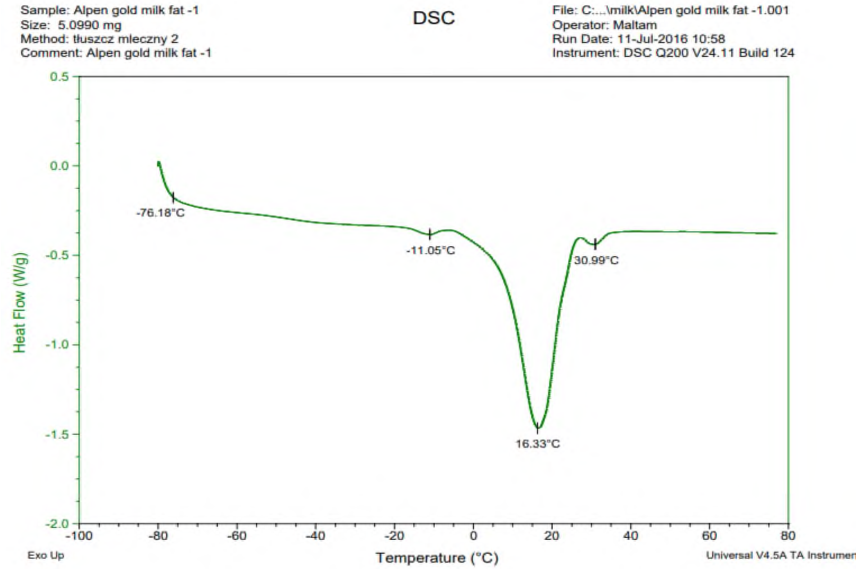


Figure 6. DSC analysis of oil extracted from milk chocolate

Melting curves of extracted milk fat samples on DSC were characterized by endothermic behavior. The first, mild peak was observed at temperature nearly – 11.66 °C, due to the low-melting triacylglycerols (with high unsaturated fatty acids content), the second distinct peak was observed at temperature ~16.5 °C, related to the presence of the low-melting triacylglycerols content of milk fat, which has a lower melting point than cocoa butter and the third at ~30.99 °C, expected of high-melting fats, which present in milk fat (Figure 6).

The observation of two or more peaks is associated with the presence of different crystal structures in the product, which indicates the polymorphism of the fat structures, and the presence of two or more peaks in the melting curves is a common result in the study of the polymorphous structures of chocolate.

Differential scanning calorimetry (DSC) is an important technique used in providing information about processing methods, such as tempering and cooling of the product, as well as the interpretation of the DSC curve on melting characteristic which is the most complex and complicated for evaluation of "quality" in chocolate.

Figure 7 illustrated DSC bar charts of melting fats extracted from dark chocolate samples based on their DSC curves (D1 – D36). Samples and temperature are illustrated on abscissa and ordinate, respectively (Figure 8) .

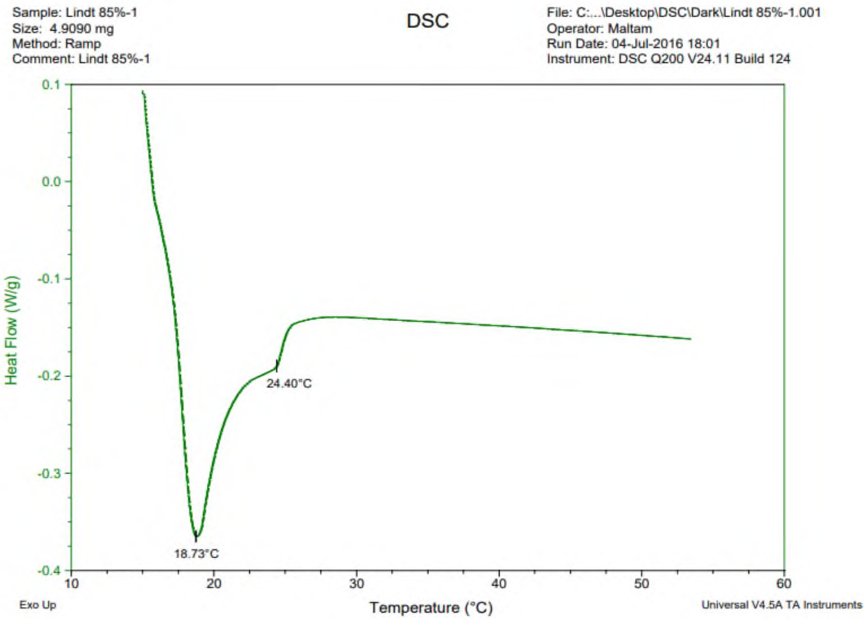


Figure 7. DSK curve of sample D8

In the case of fat extracted from D1 – D36, the maximum temperature of first endothermic peaks were observed at temperature from 18.49°C to 19.63°C and eventually the second distinct, endothermic peaks from 23.40°C to 25.38°C, except D13, D34-D36 samples. The first and second columns may indicate the melting of the crystalline form I of cocoa butter (melting range is 16–18°C) those are illustrated by blue and orange, and the third columns present melting of crystalline form II (melting range 22–24°C) those are on gray. There were differences in the course of four samples. .

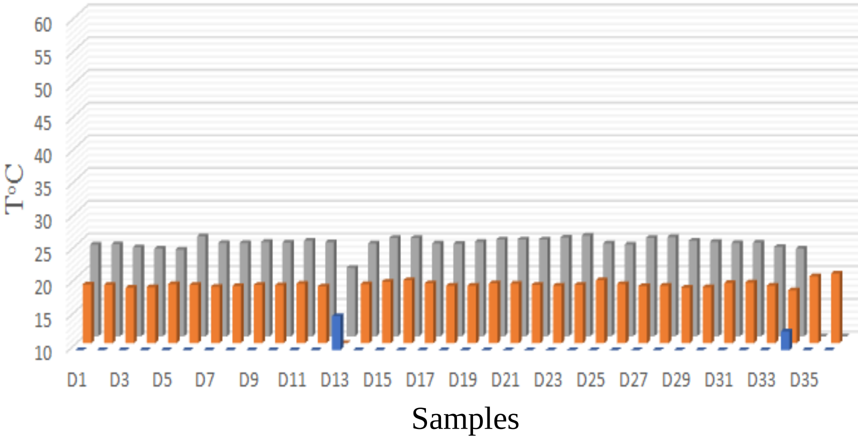


Figure 8. DSC bar charts of melting profiles of fats extracted from dark chocolate samples (D1 – D36)

The appearances of a peak on the curve of fat extracted from dark chocolate D13 were at 15.17 and 20.47°C, D34 were at 12.88, 18.10 and 23.40°C, D35-D36 were at 20.26 and 20.64°C respectively, which conclude that in these cases probably melting of a single crystalline form of fat was observed.

As is known, the main fat phase of milk chocolate contains cocoa butter and milk fat. The DSC bar charts on melting profiles of fats extracted from milk chocolate samples are shown in Figure 9 according to their DSC curves. Samples and temperature are illustrated on abscissa and ordinate, respectively Figure 10.

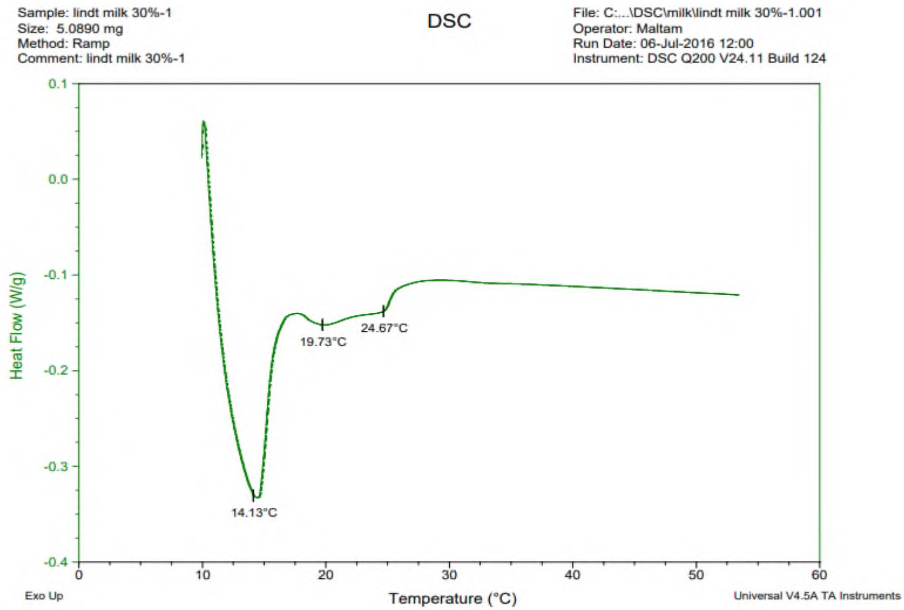


Figure 9. DSC curve of sample M9

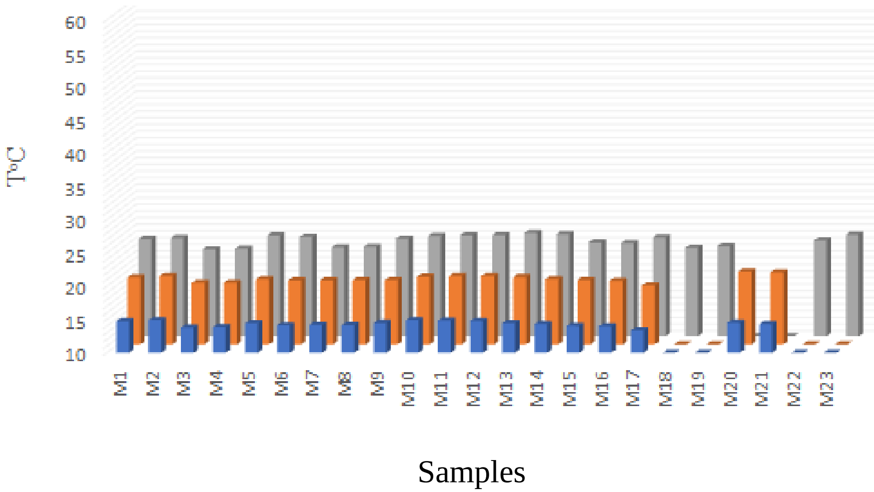


Figure 10. DSC bar charts of melting profiles of fats extracted from milk chocolate samples (M1-M23)

The DSC diagrams of melting of fats extracted from milk chocolates were characterized by endothermic peaks too. Thus, the maximum temperature of the first endothermic peaks was observed at temperature ranges from 13.36°C to 14.91°C, the second distinct, endothermic peaks from 18.90°C to 20.97°C and eventually, the third mild endothermic peaks from 23.06°C to 25.53 °C, except M18-M23 samples. The first columns could be related to milk fat which consist of low-melting triacylglycerols content. The result of M18, M19, M22 and M23 shows themselves at 23.30, 23.56, 24.38 and 24.27°C, in accordance with the results of overlapping the peaks of endothermic curves of milk fat and cocoa butter.

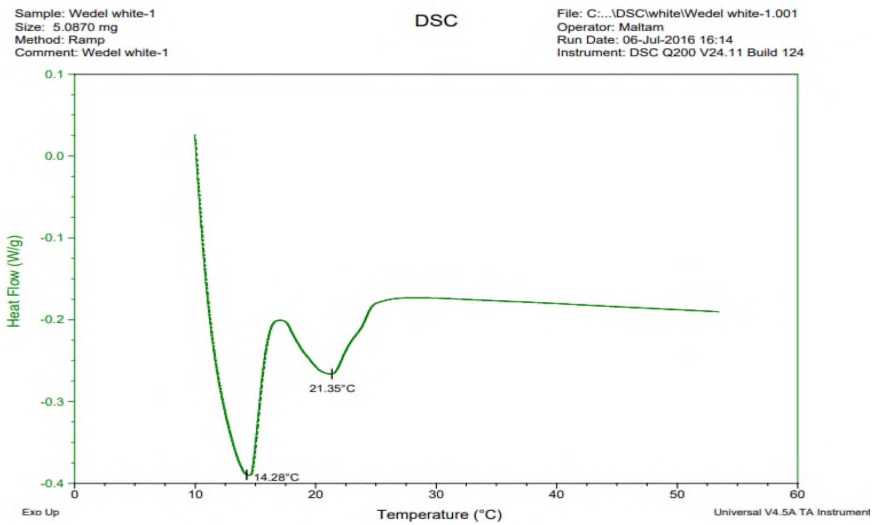
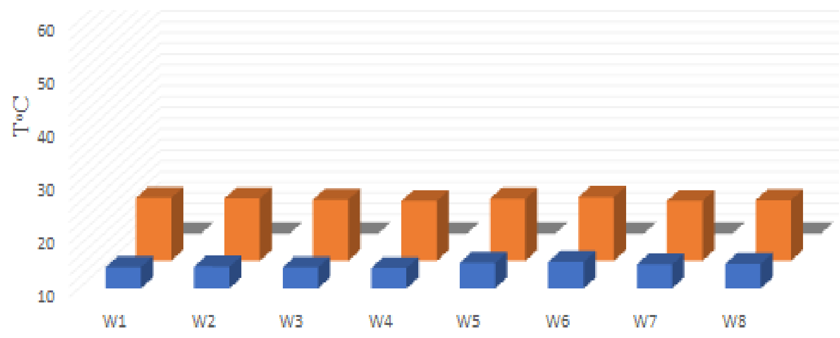


Figure 11. DSC curve of sample W7

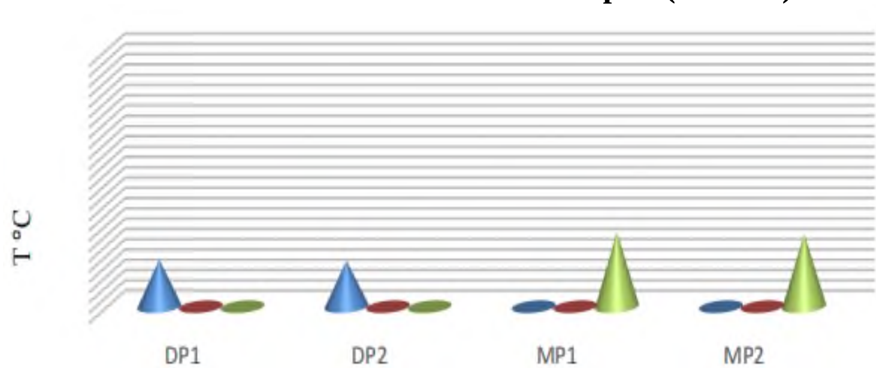
However, M20 and M21 show different melting profiles and temperature range of first distinct was observed at 14.52 and 14.29°C, the second peaks of endothermic curves were determined at 20.97 and 20.84°C which due to the milk and cocoa butter separately.

Figure 11 illustrated DSC bar chart of melting profiles of fats extracted from white (W1-W8) chocolates samples according to their DSC curves. Samples and temperature are illustrated on abscissa and ordinate, respectively (Figure 12).



Samples

Figure 12. DSC bar charts of melting profiles of fats extracted from white chocolates samples (W1-W8)



Samples

Figure 13. DSC bar charts of melting profiles of fats extracted from chocolate powder samples (DP1-DP2, MP1-MP2)

As usual the DSC melting curves of fat extracted from white chocolate samples (W1 – W8) were characterized by endothermic peaks. Based on DSC curves, the first mild, endothermic peaks were ranged at temperature ranges from 13.81 to 14.93°C, the second distinct, endothermic peaks from 21.21 to 21.94 °C, respectively. There were not observed other endothermic peaks. By comparing these results, it can be explained that due to using milk fat in the production of white chocolate, the melting profiles of white chocolate samples were characterized with low-melting triacylglycerols. Thus, the endothermic peaks may relate to the content of 1st polymorphic form of milk fat and 2nd , also 3rd polymorphic form of cocoa butter. The DSC bar chart of melting profiles of fats extracted from dark chocolates powder samples (DP1-DP2) and milk chocolate powder samples (MP1-MP2) were described on Figure 13 according to their DSC curves. Samples and temperature are illustrated on abscissa and ordinate, respectively.

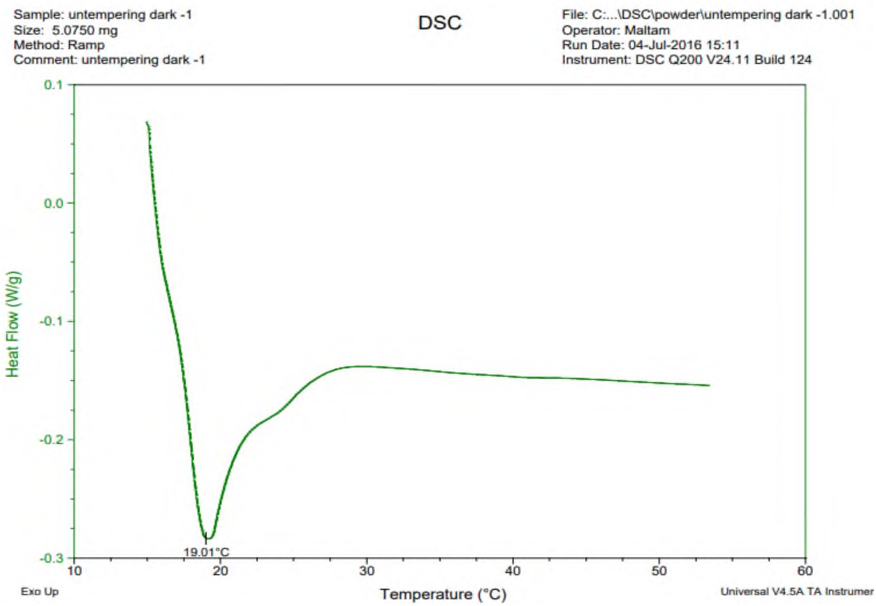


Figure 14. DSC curve of sample DP1

As per the DSC bar charts of melting profiles of fats extracted from chocolate powder based on DSC curves of samples were described in the current experiments. Each sample was characterized by a mild endothermic peak. Thus, the peak of dark chocolate powder samples (DP1-DP2) was at 19.21 and 18.96°C which could be respectively related to the polymorphic forms of cocoa butter (Figure 14). The peak of milk chocolate powder samples (MP1-MP2) following milk fat polymorphic form was at 24.54 and 24.21°C

(Figure 15). Although there is not a unique formation to temper chocolate, it confirms that milk chocolate needs lower tempering temperature than dark chocolate.

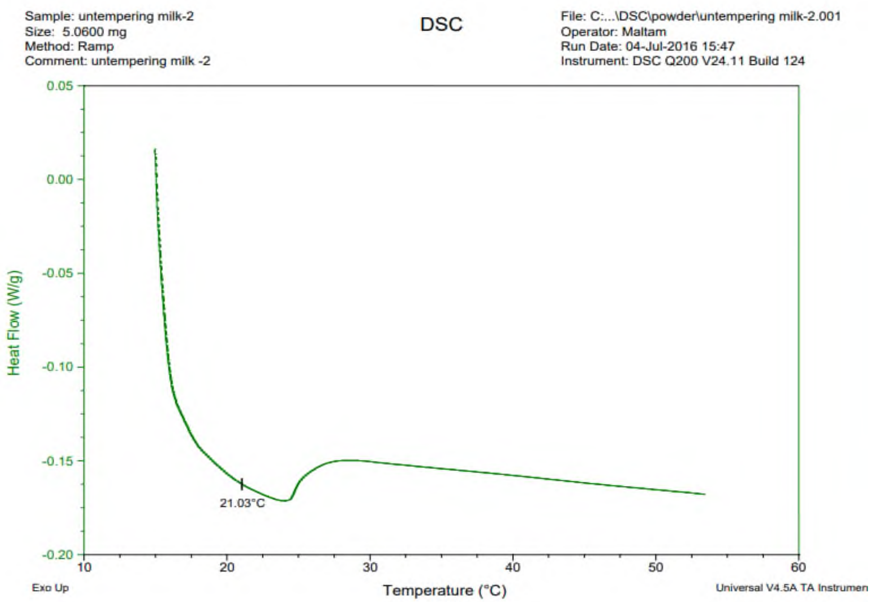


Figure 15. DSC curve of sample MP2

3. Inductively coupled plasma - optical emission spectrometry (ICP-OES) analyzes and environmental aspects of confectionery production

The composition of 44 chocolate varieties was determined according to 19 elements. The results were expressed in mg/kg and shown in Table 1. The obtained results are grouped according to groups I-IV.

The results obtained for Se element are more detailed than the results of the previous study conducted on all samples. The content of Mo element was constant in all samples. The amount of Pb was the same in samples I, III and IV.

Table 1

Inductively coupled plasma-optical emission spectrometer analysis of chocolate samples

Elements	Wave-length (nm)	Plasma View mode	Samples							
			I		II		III		IV	
			Mean mg/kg	RSD %	Mean mg/kg	RSD %	Mean mg/kg	RSD %	Mean mg/kg	RSD %
As	193.696	axial	-	8.02	-	8.28	-	19.19	-	21.01
Se	196.026	axial	1.64609	14.73	1.4403	24.13	2.26337	6.30	1.4403	5.14
Mo	202.031	axial	0.20576	13.20	2.0576	5.47	-	48.32	2.0576	6.15
Zn	202.548	axial	30.4526	0.29	47.325	0.68	59.2593	0.14	75.7202	0.42
Sb	206.836	axial	-	7.63	-	14.45	-	22.64	-	23.66
Pb	220.353	axial	1.0288	2.25	1.2345	6.15	1.02881	6.41	1.0288	7.76
Co	228.616	axial	0.82305	3.28	1.0288	2.03	0.823	3.91	0.823	3.80
Cd	228.802	axial	0.20576	4.29	0.20576	5.19	0.20576	4.29	0.20576	5.19
Ni	231.604	axial	-	2.23	-	2.61	27.1605	0.22	27.572	0.28
Ba	233.527	axial	46.5021	0.71	48.148	1.69	19.023	0.71	9.05349	1.60
Fe	238.204	axial	129.01	0.43	160.9	1.65	129.012	0.43	161.11	0.52
Mn	259.372	axial	12.7572	0.45	13.1687	1.89	42.18	0.15	42.3868	0.92
Cr	267.716	axial	0.20576	0.75	1.0288	1.11	0.20576	1.01	1.0288	1.10
Mg	285.213	radial	2382.7	2.01	2662.55	1.09	2456.79	2.02	2748.97	0.94
Be	313.107	axial	-	30.49	-	6.85	-	5.73	-	6.85
Ca	317.933	radial	6246.9	1.72	1282.3	2.58	6246.9	1.72	1282.1	2.58
Cu	327.393	axial	24.074	2.41	28.189	0.37	24.07	2.41	28.6008	0.42
Li	610.362	axial	-	2.00	-	2.76	21.811	0.72	24.2798	0.62
K	766.490	radial	815.637	0.54	953.7	0.17	8205.76	0.54	9594.65	0.17

(macroelements/conditionally essential nutrients/potentially toxic nutrients/vital nutrients/unspecified)

The amount of Co was almost the same. The composition of Cd element was the same in all samples. The content of Cr in group I, III samples and group II, IV samples was the same. The content of Mg was in high and close ranges in all samples. The amount of Ca was the same in group I, III samples and II, IV samples. The content of Cu in all samples was almost close to each other.

The obtained results are consistent with the results of the research conducted in this direction.

Depending on the soil where the raw material, especially the cocoa, is grown, the main metal-element content of chocolate products varies.

As you know, milk is a source of calcium. Considering that cocoa seed is richer in Fe, Cu, Mg elements, group I and III samples correspond to milk chocolate, and group II and IV samples correspond to dark chocolate.

That is why cocoa powder and milk determine the mineral composition of chocolate in the finished product. Environmental pollutants shape the origin of raw materials. In the studied samples, Cd as a heavy metal is present in low concentrations and is taken up from the soil by plants. Thus, soils of volcanic origin are known for their high Cd content. Based on the Cd content of the samples in the current study, cacao beans correspond to crops grown in soils of volcanic origin in Venezuela and Ecuador with heavy metal content of 0.18–1.5 mg/kg.

The element Pb is present in the environment due to natural and anthropogenic effects. As a rule, raw materials can be contaminated with the element Pb during cultivation, cultivation, storage or production. If the source of Pb in chocolate is the cocoa liquor (liquid), then the Pb content of dark chocolate will be higher than the Pb content of milk chocolate.

The greatest food safety risks are taken into account during the production and consumption of cocoa and confectionery products. According to ISO22000:2005 standards, food contains biological, chemical and physical agents that can adversely affect health. Biological hazard is mainly due to the introduction of raw materials and improper processing; hard to physical hazards - mechanical foreign objects; chemical hazards include 2 types of contamination 1) raw material contamination during input and 2) contamination that may occur during production. If there is a high dose of metal in confectionery products, it can lead to consumer poisoning.

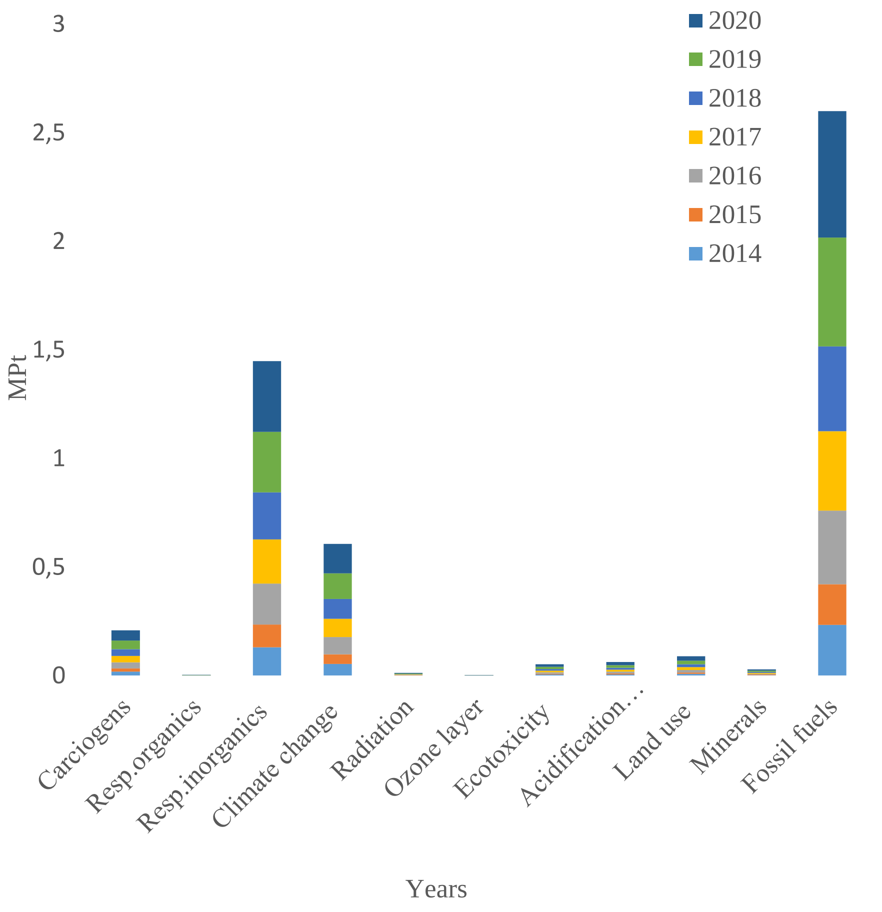


Figure 16. Evaluation of the midpoints of cocoa, chocolate, and confectioneries production in Azerbaijan between 2014-2020 years

Life cycle assessment and risk analysis and critical control points (HACCP) interact with metal content of chocolate samples. This interaction manifests itself in hot spots of production and consumption. Thus, metal content and risk analysis and critical control points (HACCP) are important in evaluating the environmental aspects related to the production and consumption of chocolate.

In the inventory analysis, data about cocoa, chocolate, and sugar confectioneries products are collected according to the statistical results of "Food Balance of Azerbaijan" in production, consumption as food products, and total utilization for 2014-2020 and are modeled through SimaPro 9.3.0.2 Analyst Demo software capabilities based on the gate-to-gate.

As shown in Figure 1, all midpoints of cocoa, chocolate, and confectioneries produced were reached their lowest level in 2015 and their highest level in 2020.

Generally, according to quantitative indicators of all midpoints have increased in the direction of 2015 < 2014 < 2016 < 2017 < 2018 < 2019 < 2020. Moreover, the noticeable values of all midpoints increase in sequence carcinogens, followed by climate change, respiratory inorganics, and fossil fuels (Figure 17).

LCIA is an important tool in any LCA study and there are several methods available to express quantitatively different life cycle impact indicators. To the point of Single Score Analysis, Eco-Indicator’99 is widely used to an environmental load of a product/process/service. Due to the damages in environmental load, endpoints are categorized as human health, ecosystem quality, and resources. The following impact indicators refer to one of the endpoints described earlier and the impact categories of the eco-indicator’99 methodology are collected within 11 midpoints: carcinogens, respiratory organics, respiratory inorganics, climate change, radiation, ozone layer depletion, ecotoxicity, acidification/eutrophication, land use, minerals, fossil fuels.

The value of midpoints and endpoints are calculated and compared through the eco-indicator unit by MPt.

All LCA midpoints of cocoa, chocolate and confectionery production reached their lowest level in 2015 and their highest level in 2020. In general, the quantitative indicators of all midpoints increased in the direction 2015 < 2014 < 2016 < 2017 < 2018 < 2019 < 2020 (Figure 16).

The regularity obtained in the quantitative assessment of the midpoints for the production of cocoa, chocolate and confectionery in Figure 16 was not observed in the assessment of consumption and general use as food products.

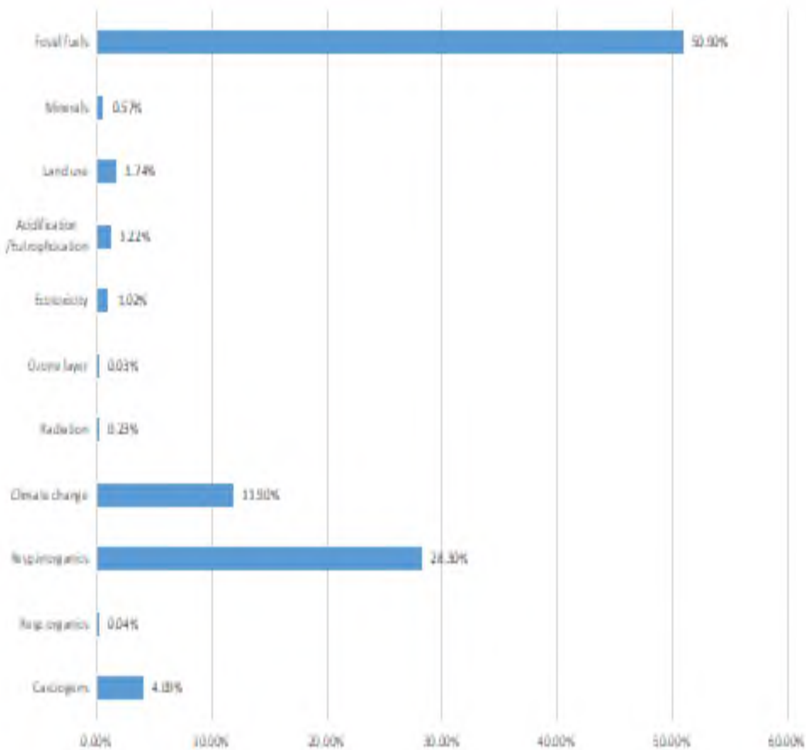
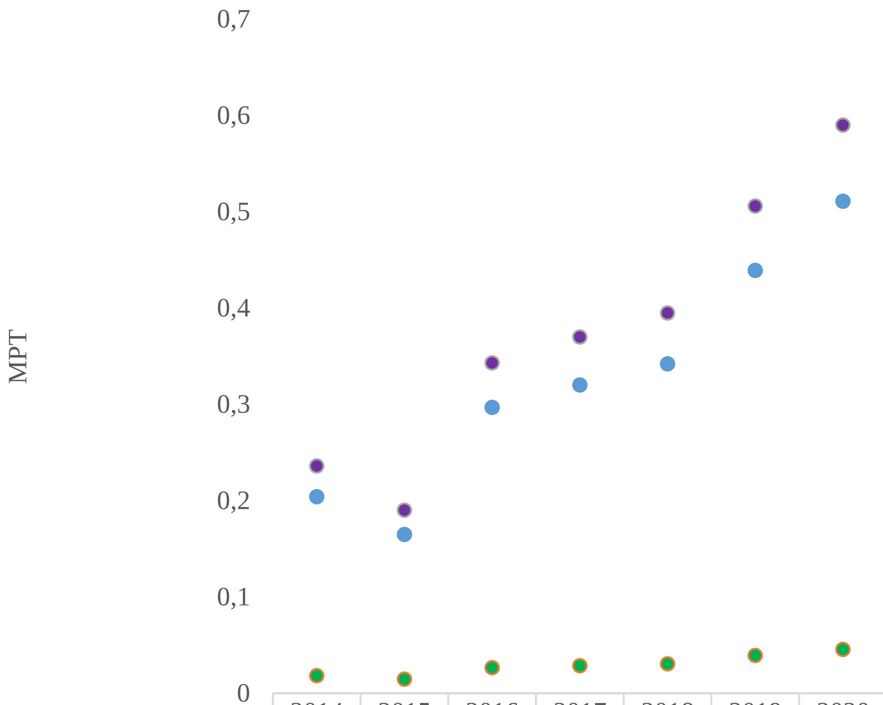


Figure 17. Evaluation by percent of the midpoints of production, consumption as food products, and total utilization of the cocoa, chocolate, and confectioneries in Azerbaijan between 2014-2020 years

The relationship between midpoints of the total utilization is the same as the production and consumption as food products in cocoa, chocolate, and confectioneries (Figure 17). In addition, a comparison of all midpoints eco-indicator units in the produced and consumed as food product of cocoa, chocolate, and confectioneries indicates that the noticeable values of all midpoints are the same as in production and increases carcinogens, climate change, respiratory inorganics, and fossil fuels in sequence (Figure 17).



	2014	2015	2016	2017	2018	2019	2020
Human health	0,204	0,165	0,297	0,32	0,342	0,439	0,511
Ecosystem Quality	0,0182	0,0147	0,0265	0,0285	0,0305	0,0391	0,0455
Resourcdes	0,236	0,19	0,343	0,37	0,395	0,506	0,59

Figure 18. Evaluation of the endpoint of cocoa, chocolate, and confectioneries production in Azerbaijan between 2014-2020 years

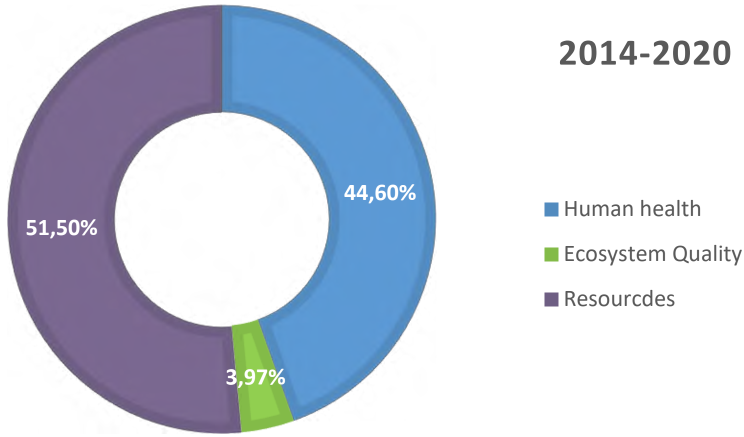


Figure 19. Evaluation by percent of the endpoints of production, consumption as food products, and total utilization of the cocoa, chocolate, and confectioneries in Azerbaijan between 2014-2020 years

As mentioned in Figure 18, the endpoints of produced cocoa, chocolate, and confectioneries between the 2014-2020 years were described. A relative increase was observed in the linear dependence of resources (Figure 18).

Human health and ecosystem quality of produced cocoa, chocolate, and confectioneries were at their lowest value in 2015, which explains the quantitative indicators of related midpoints in the mentioned year (Figure 16).

According to both endpoints, their gradual dependence on quantitative indicators of them increased over the years (Figure 18).

According to the percentage description of endpoints, ecosystem quality was in its 3.97 % value, followed by human health with 44.60% and resources with 51.50 %, respectively (Figure 19).

RESULTS

1. Environmental modeling of life cycle assessment of cocoa, chocolate and confectionery in Azerbaijan in 2014-2020 has been observed with the increase of the quantitative indicators of eco-indicators (carcinogens, organic and inorganic substances affecting the respiratory tract, climate change, radiation, depletion of the ozone layer, land use, acidification/eutrophication, ecotoxicity, etc.) that adversely affecting human health and ecosystem quality [12, 13, 14].

2. By applying inductively coupled plasma-optical emission spectrometry method (ICP-OES) toxic elements were detected in various chocolate samples according to their amounts ~815÷9594 mg/kg K (Potassium), ~1282÷6246 mg/kg Ca (Calcium), ~2382÷2748 mg /kg Mg (Magnesium) macroelements; ~129÷161 mg/kg Fe (Iron), ~30÷75 mg/kg Zn (Zinc), ~1.44÷2.26 mg/kg Se (Selenium), ~24÷28 mg/kg Cu (Copper), ~0.2 ÷2 mg/kg Mo (Molybdenum), ~0.2÷1 mg/kg Cr (Chromium), ~12÷42 mg/kg Mn (Manganese), ~27 mg/kg Ni (Nickel), ~0.8÷1 mg/kg Co (Cobalt) trace elements; ~1 mg/kg Pb (Lead), ~0.2 mg/kg Cd (Cadmium). Inductively coupled plasma-optical emission spectrometry (ICP-OES) method has proven to be useful in determining the origin of ingredients used in the preparation of a variety of chocolate samples and the range of chocolate products [7].

3. According to the Cd level of the chocolate samples, it was established that the cocoa beans used as raw materials correspond to products grown on the volcanic soils of Venezuela and Ecuador [7].

4. The opportunities of application of thermogravimetry (TG) and differential thermogravimetry (DTG) have been proven in the detection and study of cocoa liquor, sugar and fats in chocolate products that are at various stages of processing. Therefore, the role of thermal methods in determining the compliance of the composition of chocolate products with standards has been identified [1, 4, 5, 6, 12] .

5. In accordance with the differential scanning calorimetry (DSC) results, fats extracted from dark and white chocolate samples have two endothermic melting points, and fats extracted from milk

chocolate samples have three endothermic melting points; However, milk and white chocolate products have been shown to contain more short chain fatty acids than dark chocolate samples [9, 10, 12, 15].

6. According to the melting properties of fats extracted from chocolate powder samples on differential scanning calorimetry (DSC), the melting point of fats extracted from dark chocolate powder samples corresponds to lower temperatures than the melting point of fats extracted from milk chocolate powder samples. This pattern proved the role of the tempering stage in the formation of modified forms of fats with different melting points [9, 10, 12, 15].

7. Quantities of the starting temperature (T_{log}), decomposition temperature ($T_{preliminary}$), temperature at the maximum value of heat flow (T_{max}) and oxidation temperature (T_{final}) of the DSC curve of milk fat samples at different heating rates correspond to temperature ranges of ~155–193 °C, ~196–239 °C, ~235–246 °C, respectively. Thus, it was established that the quantities of oxidation $t_{log}/t_{prelim}/t_{max}/t_{final}$ at a low heating rate correspond to the 46th, 61st, 76th, 90th minutes of melting and at a high heating rate to the 10th, 13th, 15th, and 17th minutes. Triacylglycerol of these samples proved to contain both short- and long-chain carboxylic acids [2, 3, 4, 11].

8. The study of the impact of different processing stages on the thermal properties of chocolate samples determines the thermal properties of the composition of the product, the interaction between non-organic composition of the product and hazard analysis and critical control points (HACCPs) and life cycle assessment evaluates the environmental aspects of the production and consumption of chocolate products [1-15].

The main content of the dissertation was published in the following scientific works:

1. Ostrowska-Ligęza, E., Wirkowska-Wojdyła, M., Górska, A., Bryś, J., Rejch, A., Shamilowa, M. Thermokinetic analysis of cocoa butter by differential scanning calorimetry // 33rd Scientific Conference Oilseed Crops – Advances in genetics, breeding,

technology and analytics of lipids. Poznań, Poland, - 5-6 April, - 2016, - p. 40.

2. Ratusz, K., Popis, E., Shamilova, M. The influence of storage conditions on the quality and oxidative stability of camelina sativa cold-pressed oil // 33rd Scientific Conference Oilseed Crops – Advances in genetics, breeding, technology and analytics of lipids. Poznań, Poland, - 5 - 6 April,- 2016 - p. 106.

3. Ratusz K., Ciemniewska-Żytkiewicz H., Wroniak M., Shamilova M. Physicochemical quality and oxidative stability of cold-pressed camelina (camelina sativa) oils // Bioeconomy in Agriculture, International Conference. Puławy, Poland, - 21 - 22 June, - 2016,- p.89-90.

4. Ostrowska-Ligęza, E., Shamilowa, M., Górska, A., Wirkowska-Wojdyła, M., Bryś, J. Melting characteristics of dark and milk chocolates in various stages of production by using differential scanning // 11th International Seminar on Thermal Analysis and Calorimetry to the memory of Prof. St. Bretsznajde, - Płock, Poland, - 26 - 29 September, - 2016, - p.86.

5. Ostrowska-Ligęza, E. Thermogravimetric characterization of dark and milk chocolates at different processing stages / E. Ostrowska-Ligęza, A. Górska, M. Wirkowska-Wojdyła, J. Bryś, K. Dolatowska-Żebrowska, M. Shamilowa, K. Ratusz // Journal of Thermal Analysis and Calorimetry, - Budapest: - 26 February, - 2018. 134, - p. 623-631.

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9. Shamilowa, M., Hajiyeva, S., Ostrowska–Ligęza, E. Possibilities of differential scanning calorimetry (DSC) method for studying thermal properties of fats extracted from milk, white, dark chocolates and chocolate powder // V International Scientific Conference of Young Researchers. Baku, Azerbaijan, - 29 - 30, April, - 2021, - p.1034-1036.

10. Hajiyeva, S. Characterization of thermal properties of fats extracted from milk, white, dark chocolates and chocolate powder by differential scanning calorimetry (DSC) technique / S. Hajiyeva, M.Shamilova // New Materials, Compounds and Applications, - Baku: - 7 August, - 2021. 5 (2), – p. 102-109.

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13. Hajiyeva, S. The Ecological Profile of Cocoa, Chocolate, And Sugar Confectioneries in Azerbaijan / S.Hajiyeva, M.Shamilova-Jalilova // Advances in Biology & Earth Sciences, – Baku: - 18 April, - 2022. 7(1) – p. 29-39.

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15. Ostrowska-Ligęza, E., Shamilova-Jalilova, M.

Thermal properties of fats extracted from milk, white, dark chocolates and chocolate powder by differential scanning calorimetry (DSC) technique // Modern problems of theoretical and experimental chemistry International Conference devoted to the 90th anniversary of academician Rafiga Aliyeva. Baku State University, Baku, Azerbaijan, - 29 - 30 September, -2022, - p.116-117.

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