

AGRICULTURAL ACADEMY

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**IMPLEMENTATION OF WASTE-FREE TECHNOLOGIES IN THE FOOD
INDUSTRY BY USING PLANT WASTE TO OBTAIN FUNCTIONAL BREAD
AND CONFECTIONERY PRODUCTS**

ABSTRACT

**of the dissertation work submitted for the scientific degree
"Doctor of Sciences"**

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substances (incl. enzymes, hormones, proteins)"**

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The dissertation comprises of 273 pages and includes 24 tables, 63 figures, and 14 equations. The bibliography contains 301 literary sources, with 7 in Cyrillic and 291 in Latin script.

The public defense of the dissertation will take place on 07.10.2024, starting at 13:00 hours in the conference hall of the Institute of Cryobiology and Food Technologies, in accordance with the Regulations on the conditions and procedure for obtaining scientific degrees and academic positions at the Agricultural Academy before a Scientific Jury composed of:

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Abbreviations used

APP – apple peels;
DPPH – 1,1-diphenyl-2-picrylhydrazyl;
EFSA – European Food Safety Authority;
FA – factor analysis;
FAO - Food and Agriculture Organization;
FN – fall number;
FNFC (Food with Nutrient Function Claims) – foods with nutrient function claims;
FOSHU (Food for Specified Health Use) – foods for specific health needs;
FRAP – a method for determining antioxidant activity using iron-reducing activity;
FUFOSE (The European Commission Concerted Action on Functional Food Science in Europe) – concerted actions of the European Commission regarding functional food science in Europe;
FUSIONS (Food Use for Social Innovation by Optimizing Waste Prevention Strategies) – use of food for social innovation by optimizing waste prevention strategies;
GPP – grape pressings;
HMF – hydroxymethyl furfural;
HPLC – high performance liquid chromatography;
MUFA – monounsaturated fatty acids;
PCA – principal component analysis;
PLS – partial least squares regression;
PUFA – polyunsaturated fatty acids;
RE – retinol equivalents;
RMSE – root mean square error;
SFA – saturated fatty acids;
SSE – sum of squared errors;
TPC – total phenols;
BiH – Bosnia and Herzegovina;
EU – European Union;
PB – wheat flour;
BG – Republic of Bulgaria;
RNM – R. N. Macedonia;
HR – Republic of Croatia;
TP – tomato presses;
HVP - food industry.

Introduction

Numerous calculations show that the generated food waste worldwide amounts to \$936 billion annually. Developed countries produce more waste across the food chain compared to developing countries. Additionally, approximately 20% of the food supplied for individual consumption is lost or wasted.

Utilization of food waste and by-products can help improve the economic, environmental, and social sustainability of the food chain during production. Currently, the solution involves transitioning to a circular bioeconomy model, which means moving towards sustainable, resource-efficient valorization of biomass in integrated, high-performance productions, while simultaneously utilizing residues and waste generated during production.

Circular bioeconomy is an economic system aimed at preserving the value of products, materials, and resources over an extended period. This is achieved by minimizing the use of untouched resources, realizing economic growth from natural resources, and reducing the amounts of generated waste.

The circular bioeconomy utilizes renewable biological resources, transforming them into value-added products such as human and animal foods, bio-based products, and bioenergy. The primary goal is to minimize the use of non-renewable resources. In this manner, the value of by-products will increase, leading to economic benefits and growth.

During the processing of fruits and vegetables to produce various products, the agri-food industry generates significant amounts of food waste (about 25%-60% of the mass of processed fruits and vegetables), most often in the form of pulp and/or seeds. They are a source of valuable macro- and micro-nutrients that can be considered functional ingredients. Therefore, it is advisable to utilize these food wastes in the production of various items (bread, bakery products, confectionery, etc.) to create functional foods and implement zero-waste technologies in the agri-food industry.

1 . Literature review

- ✚ From the conducted literature review, the following conclusions can be summarized:
- ✚ There are various approaches for valorizing by-products and reducing waste in the agri-food industry (AFI). These strategies contribute to improving the

economic and environmental sustainability of the food chain during production.

- ✚ By-products obtained during the processing of tomatoes, apples, and grapes are mostly used as animal feed. However, their management is labor-intensive and entails additional expenses.
- ✚ It has been proven that bakery and confectionery products can be most easily enriched with flour from plant by-products.
- ✚ The possibilities of incorporating flour from by-products of tomatoes, apples, and grapes into bakery and confectionery products is insufficiently researched. Drying is one of the simplest methods to grind plant by-products into flour and successfully using it when producing new foods.
- ✚ The utilization of by-products from tomatoes, apples, and grapes in bakery and confectionery products (such as crackers, biscuits, and cakes, respectively) requires the development of new production technologies.
- ✚ There is no consensus on the optimal ratio of added by-products from tomatoes, apples, and grapes to the mass of white wheat flour.
- ✚ There is a shortage of comprehensive scientific research data on the impact of added amounts of flour from tomato pressings, apple peels, and grape pressings on the nutritional value, antioxidant activity, and quality of the resulting crackers, biscuits, and cakes, respectively.
- ✚ New foods supplemented with by-products from tomatoes, apples, and grapes have elevated content of dietary fibers, fats, proteins, phenolic compounds, antioxidant activity, tocopherols, and carotenoids. These components have been demonstrated to positively affect one or more functions in the human body. Therefore, they can be considered as functional foods.
- ✚ There is a lack of data on consumer opinions from Bulgaria, Croatia, N. Macedonia, and Bosnia and Herzegovina regarding the management and utilization of waste from the agri-food industry.

2. Objectives and Tasks

The objective of this dissertation work is implementation of zero-waste technologies in the food industry, by using plant waste and adding flours enriched with

biologically active substances from them in the production of functional bakery and confectionery products.

To achieve this objective, the following tasks have been set:

Investigate consumer opinions from Bulgaria, Croatia, N. Macedonia, and Bosnia and Herzegovina regarding the management and utilization of waste from the AFI and the production of functional food products.

Study the possibilities of producing crackers with the addition of flour from tomato pressings.

2.1. Examine the properties of wheat flour and flour mixtures.

2.2. Determine the nutritional value and antioxidant activity of wheat flour, tomato pressings flour, and crackers.

2.3. Assess the quality of the obtained crackers.

2.4. Determine the optimal amount of tomato pressings flour added to crackers through mathematical analysis.

Investigate the possibilities of producing biscuits with the addition of flour from apple peels.

3.1. Examine the properties of wheat flour, apple peel flour, and flour mixtures.

3.2. Determine the nutritional value and antioxidant activity of the obtained biscuits.

3.3. Assess the quality of the obtained biscuits.

3.4. Determine the optimal amount of apple peel flour added to biscuits through mathematical analysis.

4. Investigate the possibilities of producing cakes with the addition of flour from grape pressings.

4.1. Examine the properties of wheat flour, grape pressings flour, and flour mixtures.

4.2. Determine the nutritional value and antioxidant activity of the obtained cakes.

4.3. Assess the quality of the obtained cakes.

4.4. Determine the optimal amount of grape pressings flour added to cakes through mathematical analysis.

3. Materials, Methods, and Equipment for Research

3.1 *Materials and Equipment for Research*

Experiments were conducted using commercially available three white wheat flour (Type 500) with acidity from 1.5 to 2.0 °H; wet gluten yield from 26 to 28 % and gluten relaxation from 6 to 9 mm, pressed yeast, cooking salt, granulated sugar, chicken eggs, sunflower oil, margarine, butter, full-fat cow's milk, baking soda, baking powder, glucose solution (freshly prepared), and drinking water. These ingredients were purchased from the commercial network in the Republic of Bulgaria.

To produce the final products (crackers, biscuits, and cakes) with the addition of by-products from the processing of tomatoes, apples, and grapes, flours were obtained from tomato pressings (TR), apple peels (APR), and grape pressings (GPP) respectively, under laboratory conditions.

In the experiments, flour mixtures were used, which were obtained by adding, based on the weight of the white wheat flour:

Tomato pressings flour in quantities of 4%, 6%, 8%, and 10%, or

Apple peel flour in quantities of 4%, 8%, 16%, 24%, and 32%, or

Grape pressings flour in quantities of 4%, 6%, 8%, and 10%.

The percentage variations were chosen based on information from a review of scientific literature, preliminary studies, and accumulated experience with flours from other by-products of the agri-food industry (AFI).

Control samples were prepared without the addition of tomato pressings flour, apple peel flour, or grape pressings flour.

3.2 Methods and Equipment for Research

3.2.1 Marketing Research on Consumer Opinion

The survey on users' opinions regarding the management and utilization of waste from WWT (wastewater treatment plants) was conducted in four countries through a questionnaire containing 15 questions. The questionnaire was available online through the Google Docs application in four languages (Bulgarian, Croatian, Macedonian, and Bosnian). Respondents were characterized in terms of their gender, age, and educational status.

3.2.2 Recipe and Technology for Making Crackers, Biscuits, and Cake

The finished products (crackers, biscuits, and cake) with the addition of flour from tomato pomace, apple peels, or grape pomace (depending on the type of product) are obtained as follows:

- Obtaining crackers with adding tomato pomace flour – based on the method presented by Nakov and Ivanova (2020), with slight modifications;
- Obtaining biscuits with adding apple peels flour – based on the AACC 10-50D (2000) method, with slight modifications;
- Obtaining cake with adding grape pomace flour - following the method of Velioğlu et al. (2017), with slight modifications.
- 3.2.3 Determination of Flour and Flour Mix Properties
- Amylographic indices – A Micro-visco amylograph (Brabender OHG, Duisburg, Germany) was used;
- "Falling number" α -amylase activity – according to the AACC 56-81B (2000) method.

3.2.4 Determination of Nutritional Value and Antioxidant Activity of Flour, Flour Mixtures, and the Obtained Finished Products

- Preparation of samples from finished products – AACC 62-20A (2000);
- Moisture content - ISO 6540:1980 (1980);
- Minerals - ISO 5984:2002 (2002);
- Fats - ISO 136:2016 (2016);
- Proteins - Mæhre et al. (2018);
- Dietary fibers (soluble, insoluble, and total) - AACC 32-07.01 (2000);
- Total carbohydrates - Nakov et al. (2022);
- Energy value, kcal/100g - Stamatovska et al. (2019);
- pH - AACC 02-52.01 (2000);
- Carbohydrate fractions - the content of the various free sugars in the samples was investigated using a liquid chromatograph - Nexera-i LC2040C Plus ultra system (Shimadzu Corporation, Kyoto, Japan), equipped with a Zorbax Carbohydrate column (4.6×150 mm, 5 μ m, Santa Clara, CA, USA) and a Zorbax Reliance Cartridge (Santa Clara, CA, USA), as well as a refractometric detector RID-20A.
- Total phenolic content, antioxidant activity, phenolic fractions, and total carotenoids:
- For crackers – according to the method presented by Brandolini et al. (2022);
- For biscuits – according to the method presented by Slinkard and Singleton (1977);
- For cakes – according to the method presented by Nakov et al. (2018a);

- Tocopherols and carotenoid fractions - by HPLC, according to the method of Hidalgo and Brandolini (2010);
- Fatty acids - by gas chromatograph Shimadzu-2010 (Kyoto, Japan);
- Anthocyanins – by the spectrophotometric method presented by Abdel-Aal and Hucl (1999).

3.2.5 Qualitative Characteristics of the Obtained Finished Products

❖ Physical indicators

Thickness, diameter, and expansion factor of the obtained products were determined according to the method presented by Jukić et al., 2019.

The volume of the products was determined using the Volscan Profiler (Stable Micro Systems Ltd., Godalming, UK).

Textural Indicators: Measured using a TA-XT2 Plus texture analyzer.

Color: Determined using the CIE L*, a*, b* system.

Sensory Analysis: Conducted in accordance with the guidelines for the study of ethics and foods established by the European Union.

3.2.6 Determining the Optimal Amount of Flour from By-products in Crackers, Biscuits, and Cakes Through Mathematical Analysis

Crackers: Used a linear programming algorithm (Yang and Yamashita, 2021).

Biscuits: Determined based on mathematical relationships presented by Wyman et al. (2013).

Cakes: Through the Matlab software system.

3.2.7. Statistical Analysis

The experimental data were analyzed using one-way analysis of variance (ANOVA). Upon detecting significant differences ($p \leq 0.05$), the least significant difference (LSD) was calculated at $p \leq 0.05$. The analyses were conducted using the statistical software XLSTAT. The mean and standard deviation values were calculated using the Office Excel program (Microsoft Corporation, Redmond, WA, USA).

4. Results and Discussion

4.1 Researching the opinion of users from the Republic of Bulgaria, the Republic of Croatia, the Republic of N. Macedonia and Bosnia and Herzegovina, regarding the management and utilization of waste from HVP

The opinion of users from the four countries (RB, RK, RNM and BH) regarding the management and utilization of this waste is evident from the answers in Table 1 and fig. 1 – 8.

Table 1. "Which branch of the food industry produces the most waste?"

	<i>BG</i>	<i>HR</i>	<i>RNM</i>	<i>BiH</i>
<i>Milk processing and production of dairy products</i>	4.70	6.90	4.90	7,8
<i>Meat processing and production of meat products</i>	36,40	24.10	38.80	59.40
<i>Milling, baking and confectionery</i>	4.70	6.90	1.00	1.60
<i>Fishing industry and production of fish and marine products</i>	14.00	10.30	7.80	3.10
<i>Canning industry and production of dried and preserved fruits, vegetables and seeds</i>	19.60	15.50	22.30	3.10
<i>Production of beverages (non-alcoholic and alcoholic)</i>	17.80	22.40	6.80	15.60
<i>Production of sugar and sugar products</i>	2.80	13.80	18.40	9.40

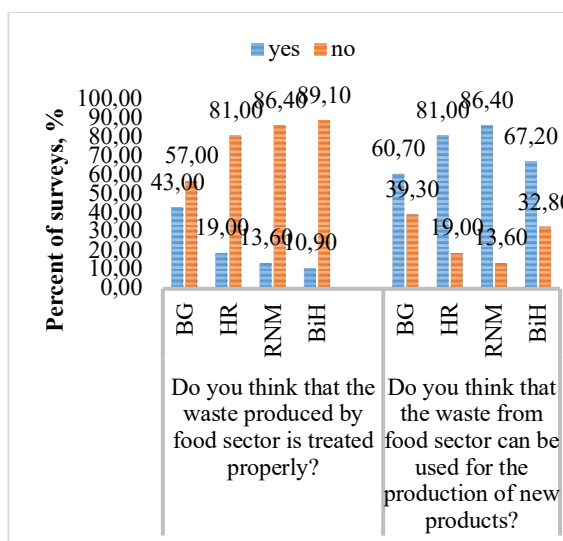


Figure 1. Answers to the questions: "Do you think that the waste produced by the food sector is treated properly?" and "Do you think that the waste from the food

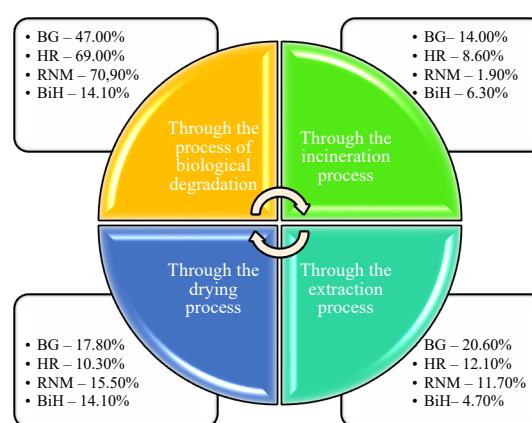


Figure 2. Answers to the question: "By what process could the waste obtained from the food sector be processed?"

sector can be used for the production of new products?"

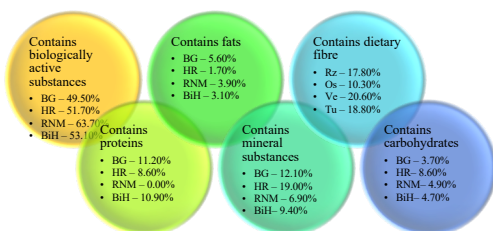


Figure 3. Answers to the question: "Why do you think that the waste from the food sector could be reused?"

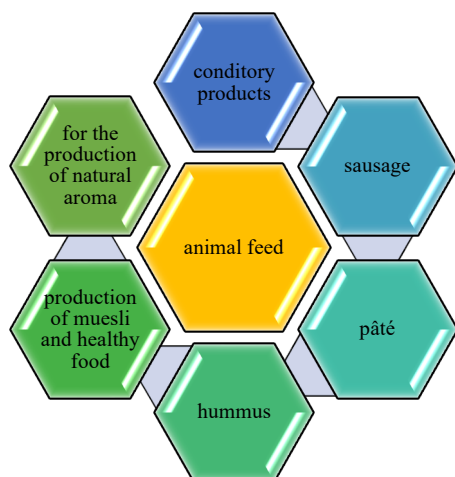


Figure 5. Products containing HVP waste, according to respondents

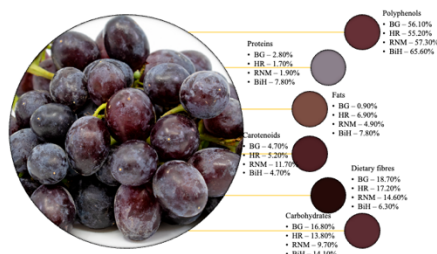


Figure 7. Answers to the question: "Which of the listed components do you think are most present in the waste from the production of tomato juice?"

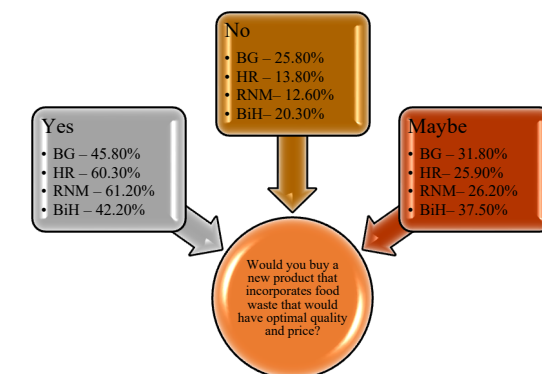


Figure 4. Answers to the question: "Would you buy a new food product that contains food sector waste and is of optimal quality and price?"

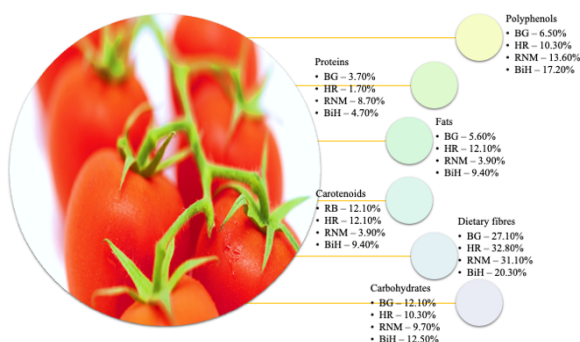


Figure 6. Answers to the question: "Which of the listed components do you think are most present in the waste from the production of tomato juice?"

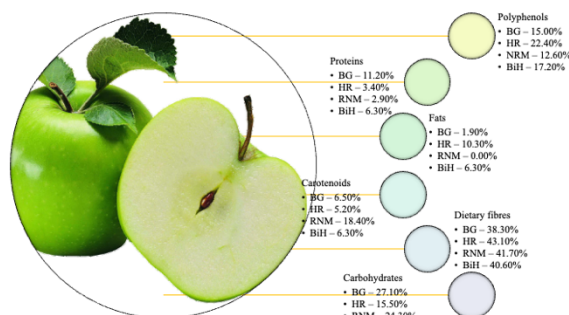


Figure 8. "Which of the components do you think are most present in the waste from the production of apple juice?"

think are most present in winemaking waste?"

the production of apple juice and other apple products?"

More than 50% of all those surveyed believe that the management of waste from HRP is not correct and most often this waste is processed through biological decomposition.

More than 70% of the respondents have not found food products containing HVP waste, but if such a product were available on the market, they would buy it.

HVP waste contains the most biologically active substances, as well as dietary fibers. For the waste that is obtained during the production of wine, more than half of the respondents believe that it contains the most polyphenols; for those obtained during the processing of apples, that they contain the most dietary fiber; and for those obtained during the processing of tomatoes, that they contain the most carotenoids.

Due to the lack of products on the market that contain HVP waste on the one hand, and the desire of consumers to consume this type of product on the other hand, technologies have been developed to obtain three types of functional food products (crackers, biscuits and cake), enriched with flour obtained from plant wastes from HVP – flour from tomato pomace, flour from apple peels and flour from grape pomace, respectively.

4.2 Investigation of the possibilities of obtaining crackers with the addition of flour from tomato presses

4.2.1 Investigation of the properties of wheat flour and flour mixtures

4.2.1.1 Amylographic characteristics of wheat flour and flour mixtures

Table 2 presents the results for maximum viscosity, viscosity reduction, viscosity recovery, final viscosity and gelatinization temperature of mixtures enriched with wheat flour and TP flour.

Table 2. Amylographic indicators of wheat flour and flour mixtures with the addition of TP flour. (0% TP – control (100% white wheat flour); mixtures with the addition of 4%, 6%, 8%, and 10% TP flour)

Addition of TP, [%]	Maximum viscosity, [BU]	Viscosity reduction, [BU]	Viscosity Recovery, [BU]	Final viscosity, [BU]	Gelatinization temperature, [°C]
0 (K)	895.0 ^d ±12.7	297.0 ^d ±4.2	444.5 ^c ±6.4	1042.5 ^a ±14.9	60.7 ^b ±0.6
4	898.5 ^d ±2.1	308.0 ^d ±2.8	457.0 ^c ±14.1	1047.5 ^{bc} ±14.9	61.3 ^{ab} ±0.3
6	946.0 ^c ±5.7	345.0 ^c ±2.8	457.0 ^c ±1.4	1058.0 ^{bc} ±4.2	61.3 ^{ab} ±0.1
8	971.0 ^b ±5.7	390.0 ^b ±14.1	487.0 ^b ±11.3	1068.0 ^b ±2.8	61.5 ^{ab} ±0.5
10	1024.0 ^a ±5.7	422.5 ^a ±10.6 ^a	545.5 ^a ±16.3	1147.0 ^a ±10.0	61.8 ^a ±0.2

Mean values were calculated from three replicates. Values in the same column, with different exponents, are statistically different ($p < 0.05$) based on Fisher's LSD test.

4.2.1.2 "Falling number" of wheat flour and flour mixtures

The falling number (FN) method was developed as a simple viscometric method for the estimation of α -amylase activity (EC 3.2.1.1) in wheat flour (*Triticum* spp.).

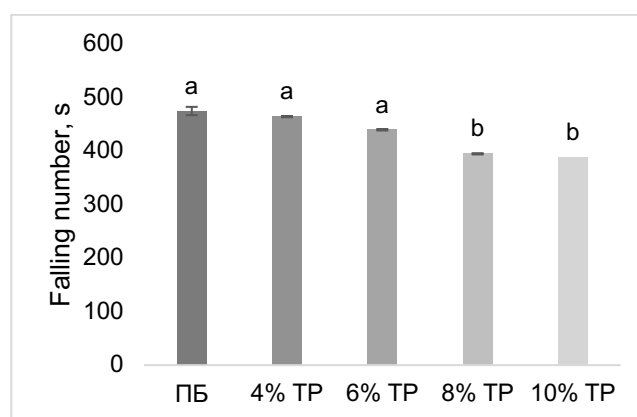


Figure 9. "Falling number" of wheat flour (WH) and flour mixtures with addition of TP flour. Bars show standard deviations. Different letters indicate significant differences ($p \leq 0.05$) between samples.

From fig. 9, it is evident that the mixture of wheat flour and water has the highest FN value (475 ± 7.07 s), while the mixture containing 10% flour from TP has the lowest FN (389 ± 1.19 s). The figure also illustrates that by increasing the amount of TR flour in the mixture, FN decreases.

The addition of TP flour to white wheat flour results in an increase in both the maximum and final viscosity of the investigated suspension, and a slight decrease in the falling number, while the α -amylase activity remains low.

4.2.2 Nutritional value and antioxidant activity of wheat flour, tomato press flour and crackers

4.2.2.1 Chemical characteristics of wheat flour, tomato press flour and crackers

Fig. 10 shows the main chemical parameters of white wheat flour and waste flour, after processing tomatoes into tomato juice, as well as crackers without and with the addition of TP flour.

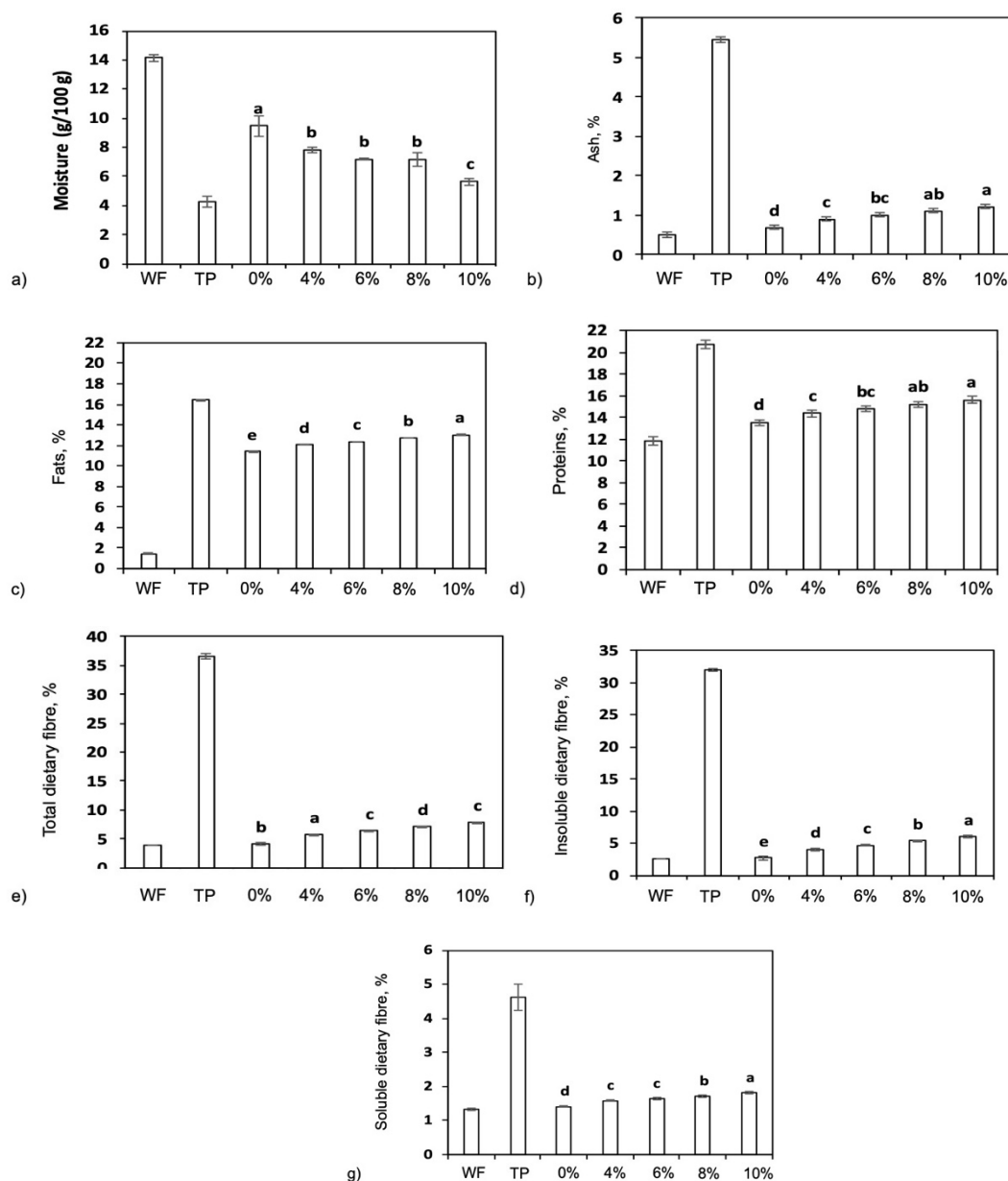


Figure 10. Chemical composition of wheat flour, TP flour and crackers with the addition of TP flour. Bars show standard deviations. Different letters indicate significant differences ($p < 0.05$) between samples.

Flour from TP has significantly better nutritional value and antioxidant activity, compared to wheat flour, with values of all investigated indicators being several times higher in TP flour.

The addition of TP flour to the recipe composition of crackers significantly improves their nutritional value as:

- The content of mineral substances increases to 1.22% compared to the control crackers.
- The amount of fat increases slightly (by 1.65% for crackers with 10% addition of TP flour) compared to the control sample;
- The protein content is 15% higher than in the control sample.
- The content of dietary fibers (total, soluble, and insoluble) significantly increases compared to the control crackers: total, soluble and insoluble fibers increase by 91%, by 28%, and by 128%.

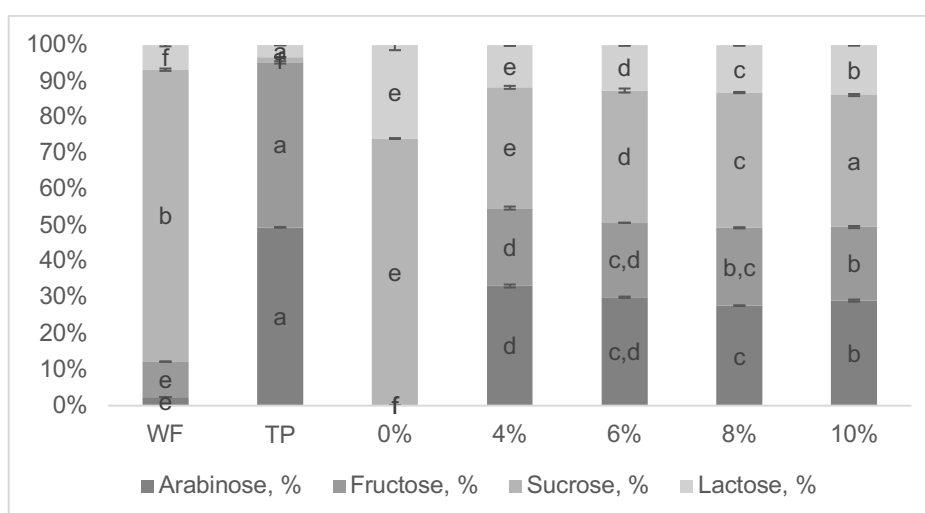


Figure 11. Carbohydrate fractions in wheat flour, TP flour and crackers with the addition of TP flour. Bars show standard deviations. Different letters indicate significant differences ($p < 0.05$) between samples.

The content of the carbohydrate fractions (fig. 11), including arabinose, fructose, sucrose, and lactose progressively increases with the rise in the amount of TP flour in the crackers.

4.2.2.2 Energy value of crackers

Fig. 12 shows the energy value of crackers both without and with the addition of tomato pulp flour. It can be seen that as the amount of TP flour in the composition

of the crackers increases, their energy value also rises slightly (from 454.19 kcal in crackers with 0% TP flour to 460.32 kcal in crackers with 10% TP flour).

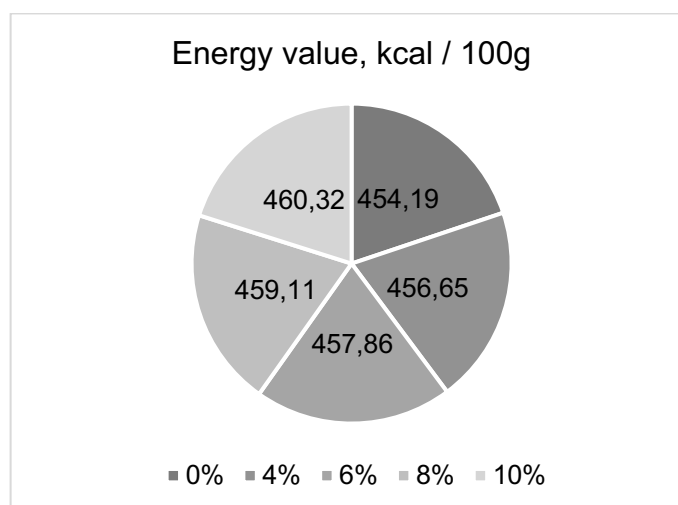


Figure 12. Energy value of crackers with the addition of TP flour

4.2.2.3 Carotenoid fractions and tocols in wheat flour, tomato press flour and crackers

The analyzes conducted through HPLC revealed the presence of lutein (1.26 mg/kg bw) and zeaxanthin (0.06 mg/kg bw) in wheat flour and lutein (4.14 mg/kg bw), zeaxanthin (0.36 mg /kg bw), 15-cis-neurosporene (20.59 mg/kg bw), δ -carotene-isomer (10.00 mg/kg bw) and trans-lycopene (11.89 mg/kg bw) in tomato press flour (Table 3). The total carotenoid content of TP flour (Fig. 13a) was 35 times greater than that of wheat flour (1.32 mg/kg bw and 46.89 mg/kg bw, respectively).

Table 3. Carotenoid fractions and tocols (mg/kg BW; mean $\pm$ standard deviation) of wheat flour, TP flour and crackers with the addition of TP flour

Indicators	PB	TP	0% (K)	4%	6%	8%	10%
<u>Carotenoid fractions</u>							
Lutein	1.26 $\pm$ 0.06	4.14 $\pm$ 0.24	0.53 $\pm$ 0.03	0.64 $\pm$ 0.07	0.59 $\pm$ 0.05	0.57 $\pm$ 0.02	0.59 $\pm$ 0.01
Zeaxanthin	0.06 $\pm$ 0.00	0.36 $\pm$ 0.03	0.02 ^c $\pm$ 0.00	0.04 ^b $\pm$ 0.01	0.04 ^b $\pm$ 0.01	0.04 ^{ab} $\pm$ 0.00	0.05 ^a $\pm$ 0.00
15- cis - neurosporen	n.d	20.59 $\pm$ 1.43	nd ^d	2.24 ^c $\pm$ 0.22	2.46 ^{bc} $\pm$ 0.19	2.77 ^b $\pm$ 0.11	3.47 ^a $\pm$ 0.19
δ -carotene isomer	n.d	10.00 $\pm$ 1.04	n d	1.56 $\pm$ 0.03	1.61 $\pm$ 0.02	1.63 $\pm$ 0.07	1.69 $\pm$ 0.02

<i>trans</i> - lycopene	n.d	11.89±0.75	nd ^c	2.35 ^b ±0.09	2.49 ^b ±0.04	2.53 ^b ±0.09	2.76 ^a ±0.00
<u><i>Tokoli</i></u>							
α -tocopherol	n.d		18.52 ^c	21.40 ^b	23.65 ^a	24.10 ^a	25.46 ^a
		55.30±5.19	±0.45	±1.27	±0.92	±0.28	±0.17
α -tocotrienol	n.d	n.d	7.76±0.62	9.10±0.71	8.83±0.91	8.64±0.91	8.81±0.04
β -tocopherol	n.d	3.24±0.38	2.53±0.05	2.05±0.34	3.03±0.90	2.25±0.81	2.24±0.18
β -tocotrienol	13.00±0.8 5	n.d	13.21 ±0.29				
				14.51±1.24	14.15±1.43	14.47±0.92	14.36±0.11
γ-tocopherol	n.d	116.65±4.0 3	nd ^d				
				2.17 ^c ±0.37	2.80 ^b ±0.25	3.94 ^a ±0.03	4.55 ^a ±0.01
δ-tocopherol	n.d	n.d	15.57±0.24	16.09±0.41	15.43±1.30	15.20±1.18	15.02±0.14
δ-tocotrienol	n.d	3.47±0.14	n.d	0.90±0.09	1.55±0.32	1.60±0.10	1.19±0.30

4.2.2.4 Phenolic compounds in wheat flour, tomato press flour and crackers

While refined wheat flour contains no free phenolic compounds, it does contain three insoluble bound phenolic acids (coumaric, ferulic, and ferulic derivative). TP flour, on the other hand, contains several free and bound phenolic acids and flavonoids (Table 4).

Table 4. Phenolic content (mean $\pm$ standard deviation mg/kg BW) of wheat flour, TP flour and crackers with the addition of TP flour

Indicators	PB	TP	0% (K)	4%	6%	8%	10%
Free soluble							
<u>Phenolic acids</u>							
4OH-benzoic acid der.			87.60 $\pm$ 4.23	94.78 $\pm$ 8.48	92.90 $\pm$ 9.21	91.06 $\pm$ 3.40	92.21 $\pm$ 8.44
Coumaric acid		6.84 $\pm$ 0.10		0.40 ^d $\pm$ 0.02	0.57 ^c $\pm$ 0.01	0.74 ^b $\pm$ 0.02	0.92 ^{and} $\pm$ 0.01
Coumaric acid der.		49.97 $\pm$ 2.15		3.09 ^d $\pm$ 0.11	4.27 ^c $\pm$ 0.08	5.52 ^b $\pm$ 0.10	6.35 ^a $\pm$ 0.01
Ferulic acid		28.22 $\pm$ 1.13	2.55 ^c $\pm$ 0.03	4.30 ^b $\pm$ 0.04	4.28 ^b $\pm$ 0.00	4.44 ^b $\pm$ 0.12	5.13 ^a $\pm$ 0.08
Gallic acid		81.98 $\pm$ 2.98	9.93 ^d $\pm$ 0.17	70.99 ^c $\pm$ 2.80	124.81 ^b $\pm$ 7.23	160.65 ^a $\pm$ 4.49	173.12 ^a $\pm$ 10.93
Syrenic acid		42.53 $\pm$ 0.80					
<u>Flavonoids</u>							
Naringenin		39.02 $\pm$ 0.14		2.96 ^c $\pm$ 0.24	5.20 ^b $\pm$ 0.10	6.98 ^a $\pm$ 0.31	7.69 ^a $\pm$ 0.35
Naringenin der.		33.78 $\pm$ 0.27		0.73 ^d $\pm$ 0.01	1.28 ^c $\pm$ 0.04	1.84 ^b $\pm$ 0.13	2.39 ^a $\pm$ 0.01
Quercetin der.		56.74 $\pm$ 0.24		1.86 ^d $\pm$ 0.02	3.23 ^c $\pm$ 0.11	4.15 ^b $\pm$ 0.04	5.00 ^a $\pm$ 0.20
Routine		489.26 $\pm$ 6.50		9.81 ^d $\pm$ 0.03	17.26 ^c $\pm$ 0.18	23.76 ^b $\pm$ 0.55	30.20 ^a $\pm$ 1.17
Insoluble bound							
<u>Phenolic acids</u>							
Caffeic acid		29.75 $\pm$ 0.18					
Coumaric acid	0.16 $\pm$ 0.01	5.54 $\pm$ 0.65	0.16 ^c $\pm$ 0.01	0.36 ^b $\pm$ 0.03	0.44 ^b $\pm$ 0.04	0.53 ^a $\pm$ 0.03	0.58 ^a $\pm$ 0.05
Coumaric acid der.		0.26 $\pm$ 0.01					
Ferulic acid	67.28 $\pm$ 4.21	11.47 $\pm$ 0.92	67.35 $\pm$ 0.44	63.93 $\pm$ 4.79	67.65 $\pm$ 3.09	65.33 $\pm$ 2.86	64.25 $\pm$ 0.51
Ferulic acid der.	5.79 $\pm$ 0.38		6.16 $\pm$ 0.02	5.88 $\pm$ 0.22	6.09 $\pm$ 0.03	5.91 $\pm$ 0.03	5.83 $\pm$ 0.41
<u>Flavonoids</u>							
Naringenin		172.46 $\pm$ 11.81		3.92 ^c $\pm$ 0.31	6.05 ^b $\pm$ 0.50	6.86 ^{ab} $\pm$ 0.67	8.10 ^a $\pm$ 0.41
Naringenin der.		65.47 $\pm$ 2.29		4.23 ^b $\pm$ 0.07	5.50 ^a $\pm$ 0.53	5.47 ^a $\pm$ 0.06	6.37 ^a $\pm$ 0.40
Quercetin der		98.14 $\pm$ 6.23		5.77 ^c $\pm$ 0.57	7.46 ^c $\pm$ 0.59	10.28 ^b $\pm$ 1.07	13.24 ^a $\pm$ 0.59

nd: not found i.e. below the detection limit. Cracker values in the same order, with different exponents, are statistically different ($p < 0.05$) based on Fisher's LSD test.

The content of free soluble phenolic acids (coumaric acid, ferulic acid, gallic acid), free soluble flavonoids (naringenin, quercetin, and rutin) as well as

insoluble bound phenolic acids (coumaric acid, ferulic acid) and insoluble bound flavonoids progressively increases with the amount of TP flour in the crackers.

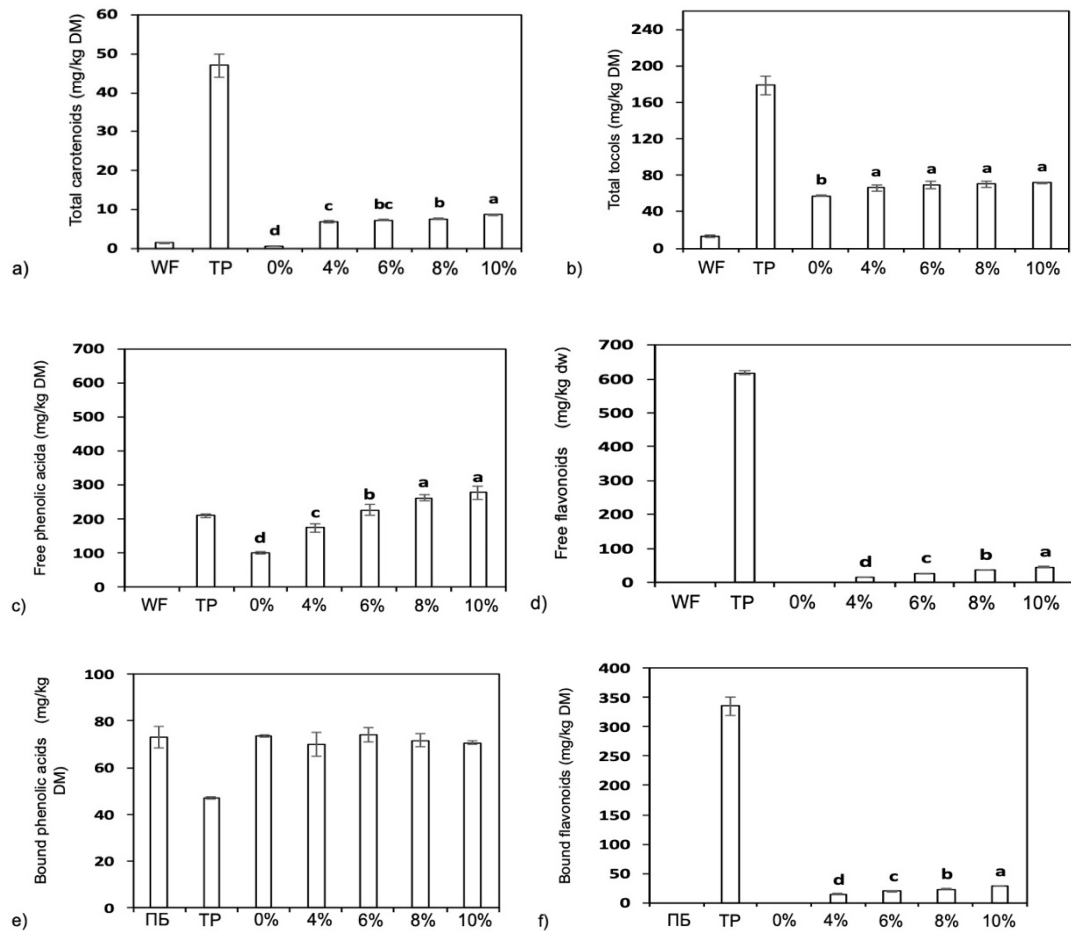


Figure 13. Total carotenoids, total tocopherols, free phenolic acids and flavonoids, bound phenolic acids and flavonoids in wheat flour, TP flour and TP flour-supplemented crackers. Bars show standard deviations. Different letters indicate significant differences ($p < 0.05$) between samples.

Increasing the amount of TP flour in fortified crackers leads to a progressive increase in several soluble free phenolic acids (p-coumaric, p-coumaric der, ferulic, gallic) and flavonoids (naringenin, naringenin der, quercetin der. rutin), as well as some insoluble bound phenolic acids (caffeine) and flavonoids (naringenin, naringenin der, quercetin der.). The addition of 10% TP flour increased the content of free phenolics and bound phenolics by 322% and 133%, respectively, leading to a significant improvement in the nutritional characteristics of the crackers.

4.2.2.5 Antioxidant activity of wheat flour, tomato press flour and crackers

The antioxidant activity of the lipophilic and hydrophilic extracts is presented in Fig. 14.

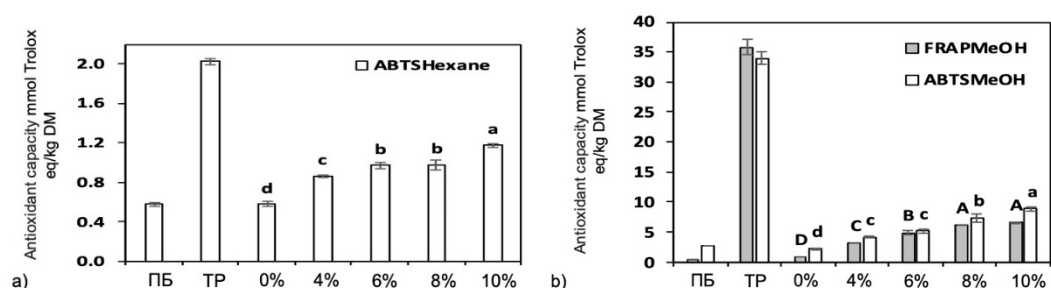


Figure 14. Antioxidant activity of: a) lipophilic extracts (in hexane); b) hydrophilic extracts (in 80% methanol) of wheat flour, TP flour and crackers with addition of TP flour. Bars show standard deviations. Different letters indicate significant differences ($p < 0.05$) between samples.

The antioxidant activity of both the lipophilic and hydrophilic extracts increased by an average of about 120 times compared to the control samples.

4.2.2.6 Fatty acid composition of crackers

The fatty acids determined in the crackers with different flour content from TP are shown in Table. 5.

Table 5. Fatty acids in crackers with the addition of TP flour

Fatty acid, %	0% TP	4% TP	6% TP	8% TP	10% TP
Palmitic (C16:0)	20.28 ^d ± 0.01	20.54 ^c ± 0.01	20.58 ^c ± 0.07	20.88 ^b ± 0.01	21.35 ^a ± 0.01
Stearic (C18:0)	4.16 ^{is} ± 0.00	4.18 ^d ± 0.00	4.54 ^c ± 0.01	4.77 ^b ± 0.00	4.92 ^a ± 0.02
Oleic(C18:1)	31.09 ^d ± 0.01	32.04 ^c ± 0.01	32.06 ^c ± 0.11	32.19 ^b ± 0.01	33.10 ^a ± 0.01
Linoleic (C18:2)	38.60 ^d ± 0.14	39.24 ^c ± 0.02	39.31 ^c ± 0.01	40.66 ^b ± 0.01	41.74 ^a ± 0.01
MUFA	33.52 ^{is} ± 0.01	33.99 ^d ± 0.01	34.28 ^c ± 0.02	33.92 ^b ± 0.11	33.75 ^a ± 0.01
PUFA	40.64 ^d ± 0.16	40.41 ^c ± 0.01	40.21 ^c ± 0.01	40.78 ^b ± 0.02	40.94 ^a ± 0.02
SFA	25.83 ^d ± 0.01	25.62 ^c ± 0.01	25.53 ^b ± 0.01	25.52 ^a ± 0.09	25.35 ^a ± 0.01

Cracker values in the same order, with different exponents, were statistically different ($p < 0.05$) based Fisher's LSD test.

The amount of palmitic, oleic and linoleic acids increases on average by about 5%-7%, with an increase in the amount of added TP flour.

4.2.3 Quality of the resulting crackers

4.2.3.1 Physical, textural characteristics and color of crackers

The physical characteristics of the crackers with different contents of TP flour are shown in Table 6.

Table 6. Physical indicators of crackers with the addition of TP flour

Indicators	0% TP	4% TP	6% TP	8% TP	10% TP
Diameter, (mm)	35.8±0.0 ^a	35.1±3.0 ^a	34.9±2.0 ^a	34.3±0.7 ^a	34.5±1.8 ^a
Thickness, (mm)	8.4±0.9 ^a	7.8±0.0 ^{ab}	7.6±0.4 ^{ab}	6.7±0.2 ^{bc}	6.1±0.1 ^c
expansion factor,	4.3±0.5 ^b	4.5±0.4 ^b	4.6±0.5 ^b	5.2±0.3 ^{ab}	5.7±0.2 ^a
Volume, (cm ³)	7.1±0.1 ^a	4.9±0.1 ^b	4.6±0.3 ^b	3.7±0.1 ^c	3.5±0.0 ^c
Specific volume, (cm ³ /g)	1.8±0.1 ^a	1.7±0.0 ^{ab}	1.5±0.01 ^{bc}	1.5±0.1 ^c	1.4±0.1 ^c

Mean values were calculated from three replicates. Values in the same column, with different exponents, are statistically different ($p<0.05$) based on Fisher's LSD test.

The addition of TP flour significantly reduced the hardness of the crackers from 65.42 N (control) to 26.28 N (crackers with the addition of 10% TP), and increased their chewiness as the content of TP flour increased (Table 7).

Table 7. Textural indicators of crackers with the addition of TP flour

Indicators	0% TP	4% TP	6% TP	8% TP	10% TP
Hardness, (N)	65.4 ^a ±9.5	42.7 ^b ±5.0	36.4 ^{bc} ±3.5	30.0 ^{cd} ± 2.7	26.3 ^d ±4.4
Chewability, (N)	4.8 ^d ±2.6	8.0 ^c ±1.9	10.4 ^{bc} ±1.7	12.0 ^{ab} ±1.9	13.8 ^a ±3.0

Mean values were calculated from three replicates. Values in the same column, with different exponents, are statistically different ($p<0.05$) based on Fisher's LSD test.

The data presented in Table 8 illustrate the color of the dough and the finished crackers.

Table 8. Color of dough and crackers with the addition of TR flour

Parameter	0% TP	4% TP	6% TP	8% TP	10% TP
<i>Dough</i>					
L^*	68.5 ^a ± 2.5	68.1 ^a ± 2.5	65.6 ^b ± 2.2	62.8 ^{ab} ± 2.8	58.1 ^c ± 1.3
a^*	-0.4 ^e ± 0.04	5.4 ^d ± 0.9	8.1 ^c ± 0.3	9.7 ^b ± 0.8	10.9 ^a ± 0.9
b^*	19.7 ^d ± 0.3	25.7 ^c ± 0.4	27.8 ^b ± 0.4	28.3 ^{ab} ± 0.1	28.4 ^a ± 0.5
<i>Crackers</i>					
L^*	69.7 ^a ± 0.8	66.1 ^b ± 1.2	61.9 ^c ± 0.7	61.0 ^c ± 1.6	58.4 ^d ± 2.3
a^*	-0.7 ^{and} ± 0.03	3.8 ^a ± 0.7	6.8 ^a ± 1.2	7.3 ^b ± 0.3	7.6 ^c ± 1.6
b^*	16.9 ^a ± 0.2	23.9 ^{ab} ± 0.6	25.3 ^{bc} ± 2.3	26.9 ^c ± 1.1	27.5 ^d ± 1.2

Mean values were calculated from three replicates. Values in the same column, with different exponents, are statistically different ($p < 0.05$) based on Fisher's LSD test.

The color of the dough, and subsequently the ready-made crackers, becomes darker as the amount of TP flour increases.

4.2.3.2 Sensory characteristics of crackers

Sensory analysis of the crackers (fig. 15) showed that all those with the addition of TP flour had good acceptability.

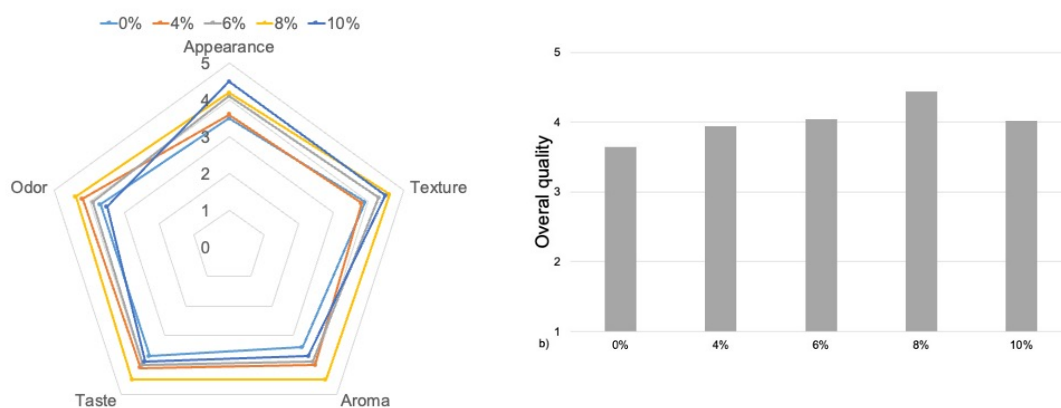


Figure 15. Sensory profile (a) and overall acceptability (b) of crackers with the addition of TP flour

Crackers with the addition of 8% TP flour have the best overall acceptability, texture, aroma, taste and smell.

4.2.4 Determination of the optimal amount of flour from tomato paste in crackers, by mathematical analysis

Fig. 16 shows the resulting model in graphical form. The optimal percentage of the addition of tomato pulp flour in crackers was applied.

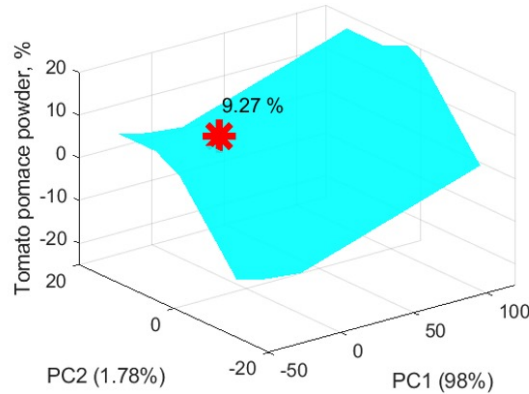


Figure 16. Determination of the optimal amount of TP flour in crackers

The optimal added amount of TP flour in crackers, as determined by mathematical analysis, is 9.27%, which confirms the conclusions drawn from the sensory analysis.

4.2.5 Example diagram of the technological operations for the utilization of tomato presses and obtaining crackers

The research conducted in this dissertation has led to the proposal of a scheme outlining the technological operations for the utilization of tomato presses and the production of crackers (Fig. 17).

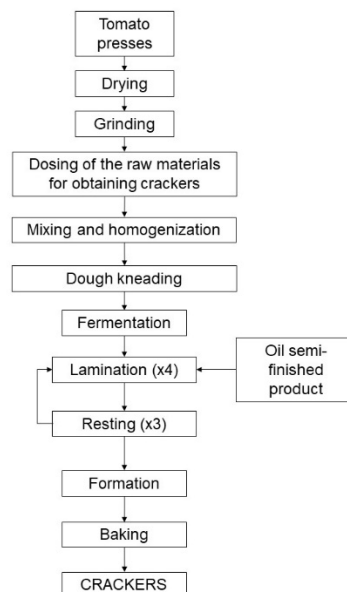


Figure 17. Example scheme of technological operations for the utilization of tomato presses and obtaining crackers

4.3 Researching the possibilities of obtaining biscuits with the addition of apple peel flour

4.3.1 Investigation of the properties of wheat flour, apple peel flour and flour mixtures

4.3.1.1 Chemical characterization and antioxidant activity of wheat flour and apple peel flour

The chemical composition and antioxidant activity of the white wheat flour and APP flour used in the preparation of the biscuits are presented in Table 9.

Table 9. Chemical composition and antioxidant activity (DPPH and FRAP methods) of wheat flour and apple peel flour

Indicators , %	Wheat flour	Apple flour crusts
Moisture content	12.01±0.07	3.23±0.09
Mineral substances	0.50±0.07	4.78±0.01
Fats	1.38±0.14	10.15±0.24
Proteins	13.21±0.60	3.20±0.98
Soluble fiber	4.71±0.10	32.03±1.44
Insoluble fiber	2.50±0.09	11.86±0.31
Total dietary fiber	7.21±0.54	43.89±1.85
Total carbohydrates	84.91±1 , 25	81 , 87±1 , 19
arabinose	0.20±0.01	-
fructose	-	3.52±0.01
mannose	0.32±0.01	2.23±0.01
galactose	0.11±0.00	-
sucrose	0.04±0.00	1.58±0.00
lactose	1.53±0.01	-
Total phenols, (µg GAE/100 g CB)	101.4±18.22	1086.7±15.50
DPPH, (µg TE/g CB)	96.6±0.50	228.1±1.42
FRAP, (µg TE/g CB)	378.0±11.3	7142.3±218.6

Mean values were calculated from three replicates.

APP flour has a significantly higher content of minerals, fat, dietary fiber (soluble, insoluble and total), total phenolics and antioxidant activity compared to white wheat flour.

4.3.1.2 Amylographic characteristics of wheat flour and flour mixtures

Table 10 presents the amylographic parameters of wheat flour and mixtures with increasing concentrations of APP flour determined using a micro-visco amylograph (maximum viscosity, viscosity decrease, viscosity recovery, final viscosity and gelatinization temperature).

Table 10. Amylographic indicators of wheat flour and flour mixtures with the addition of APP flour. 0% APP – control (100% white wheat flour); mixtures with the addition of 4%, 8%, 16%, 24%, 32% APP flour

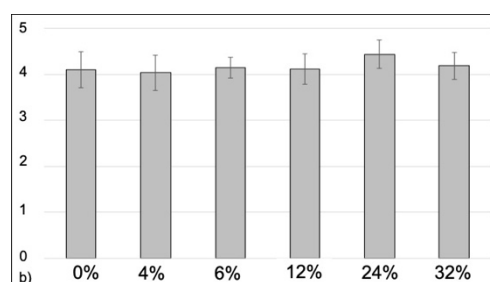
Addition of APP, [%]	Maximum viscosity, [BU]	Viscosity reduction, [BU]	Viscosity recovery, [BU]	Final viscosity, [BU]	Gelatinization temperature, [°C]
0 (K)	320.0 ^a ±4.04	208.0 ^a ±2.63	167.0 ^a ±5.66	279.0 ^a ±7.07	61.1 ^d ±0.71
4	291.5 ^b ±7.78	182.0 ^{ab} ±2.79	162.0 ^{ab} ±0.00	271.5 ^{ab} ±4.95	61.2 ^d ±0.35
8	275.5 ^{bc} ±0.71	161.0 ^{bc} ±4.24	154.0 ^{ab} ±1.31	268.5 ^{abc} ±6.36	62.1 ^c ±0.00
16	261.0 ^c ±1.41	151.5 ^c ±4.95	158.5 ^b ±0.71	268.0 ^{abc} ±4.24	62.4 ^{bc} ±0.07
24	260.0 ^c ±1.52	142.5 ^c ±2.12	140.0 ^c ±2.83	260.0 ^{bc} ±0.00	63.1 ^{ab} ±0.07
32	259.0 ^c ±1.40	138.0 ^c ±1.41	137.5 ^c ±0.71	258.5 ^c ±0.71	63.8 ^a ±0.42

Mean values were calculated from three replicates. Values in the same column with different exponents are statistically different ($p < 0.05$) based on Fisher's LSD test.

An increase in the amount of APP flour in flour mixtures results in a decrease in the maximum and final viscosity of the suspension and an increase in the starch gelatinization temperature.

4.3.1.3. "Falling number" of wheat flour and flour mixtures

Fig. 18 illustrates that the mixture of wheat flour and water has the highest



FN value, i.e., the control (463 ± 3.54 s), and the lowest value is observed in the mixture containing 32% APP flour (350 ± 0.00 s).

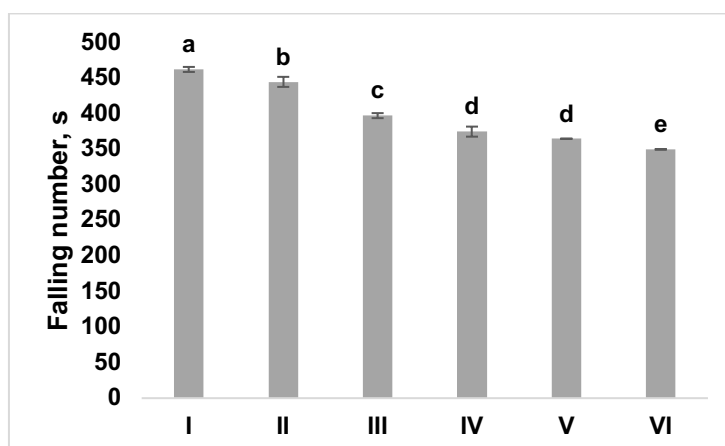


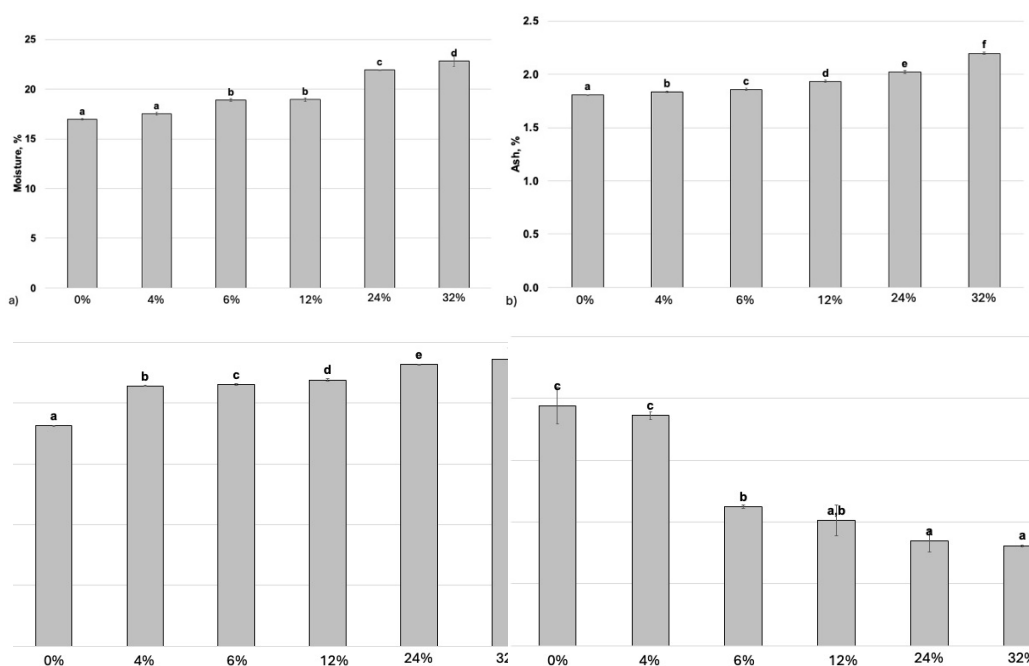
Figure 18. "Falling number" of wheat flour and flour mixtures with the addition of APP flour

With an increase in the amount of APP flour in the flour mixtures there is a slight decrease in Falling number. All flour mixtures have relatively high falling number values (low α -amylase activity), which is desirable in biscuit production.

4.3.2 Nutritional value and antioxidant activity of the obtained biscuits

4.3.2.1 Chemical characteristics of biscuits

Fig. 19 illustrates the chemical parameters of various samples.



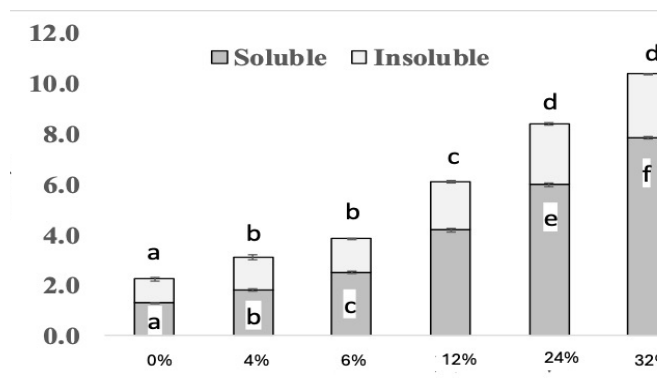


Figure 19. Chemical composition of biscuits with the addition of APP flour

The addition of APP flour in the recipe leads to a slight increase in moisture content, mineral substances and fats in the biscuits, while significantly elevating the dietary fiber content. Fig. 20 illustrates the content of the main carbohydrate fractions in the biscuits without and with the addition of ARP flour.

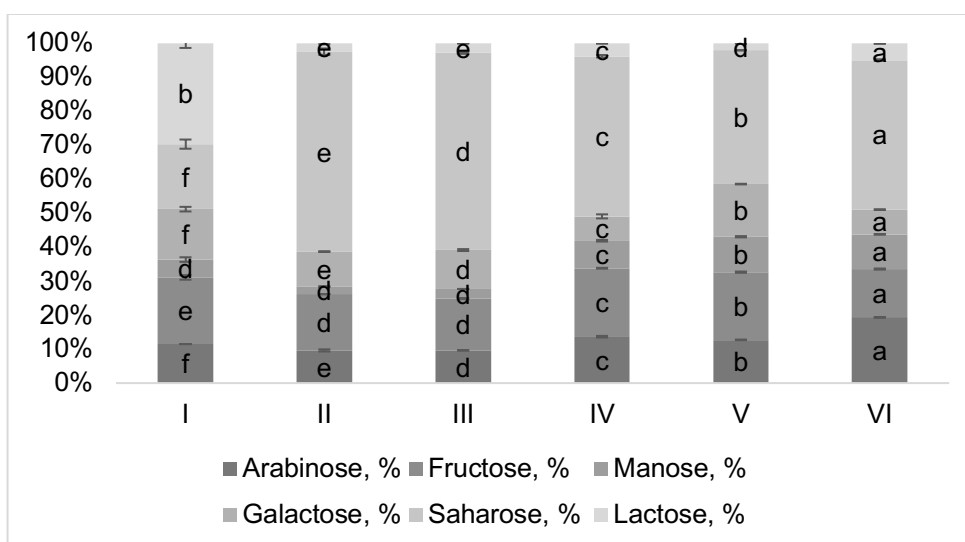


Figure 20. Carbohydrate fractions in biscuits with the addition of APP flour

In biscuits with the highest content of APP flour (32%), the amount of the carbohydrate fractions arabinose, fructose, mannose, galactose, sucrose and lactose was found to be as follows: 1.69%; 1.24%; 0.89%; 0.64%; 3.84% and 0.43%, respectively.

4.3.2.2 Energy value of biscuits

The energy value of biscuits with different content of APP flour is presented in Fig. 21.

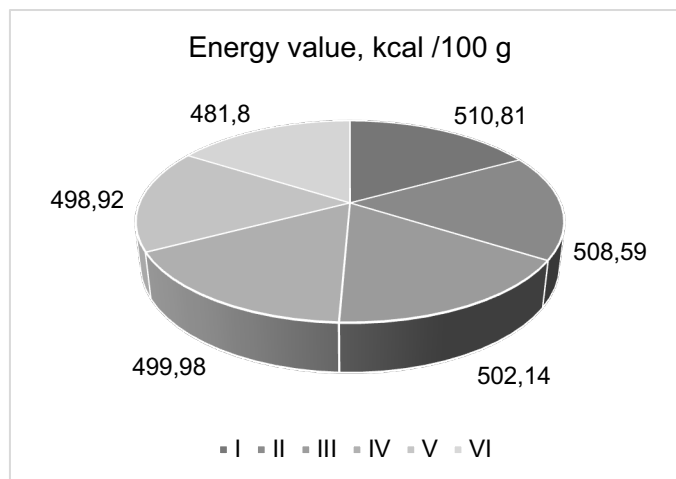


Figure 21. Energy value of biscuits with the addition of APP flour

The figure shows that as the amount of APP flour in the biscuits increases, their energy value decreases, and the difference between the control and biscuits with 32% APP flour is 29.01 kcal/100g.

4.3.2.3 Total phenolic content and antioxidant activity of biscuits

The total phenolic content and antioxidant activity of biscuits with different APP flour content is illustrated in Fig. 22.

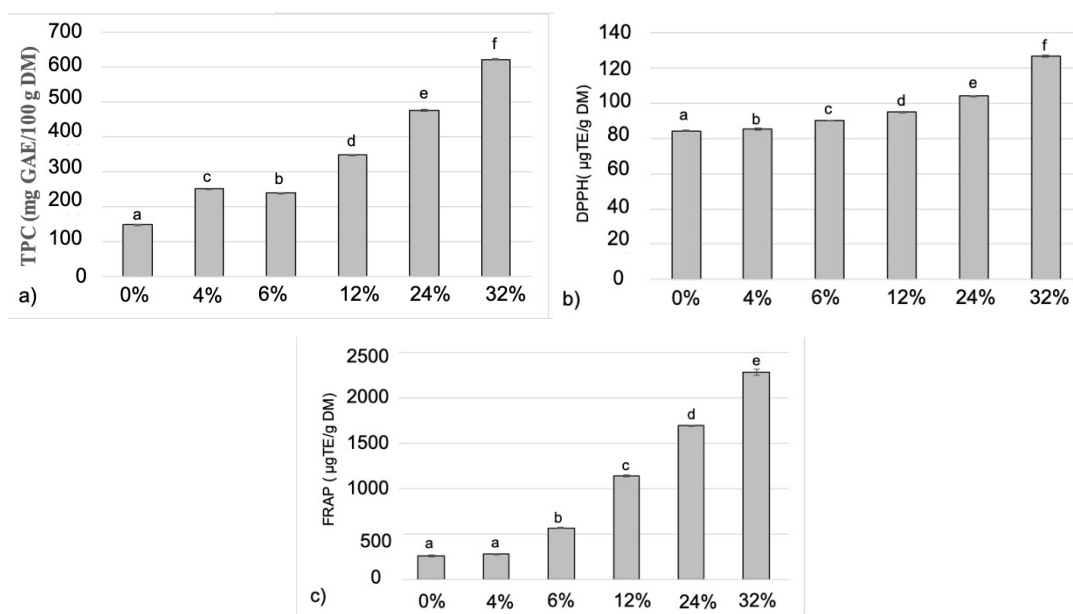


Figure 22. a) Total phenol content (TPC) and antioxidant activity (b – DPPH method, c – FRAP method) in biscuits with the addition of APP flour

ANOVA revealed significant differences between different types of biscuits. The total phenolic content of the control (Fig. 41a) was 146.15 mg GAE/g and even the addition of the smallest amount of APP flour in the biscuits (4%) resulted in a significant increase in the TPC content (250.6 mg GAE/g). Biscuits supplemented with 32% APP flour reached a TPC content of 622.12 mg GAE/g.

4.3.3 Quality of the resulting biscuits

4.3.3.1 Physical characteristics and color of biscuits

Table 11 illustrates the average values of the physical parameters of the biscuits.

Table 11. Physical indicators of biscuits with the addition of APP flour

Addition of APP, (%)	Diameter, (cm)	Thickness, (cm)	Volume, (cm ³)
0 (K)	4.10 ^a ± 0.07	2.51 ^a ± 0.01	34.5 ^a ± 0.55
4	4.15 ^a ± 0.02	2.30 ^b ± 0.02	31.4 ^{ab} ± 0.38
8	4.16 ^a ± 0.02	2.29 ^b ± 0.02	31.2 ^{ab} ± 0.77
16	4.17 ^a ± 0.02	2.16 ^c ± 0.22	29.3 ^b ± 3.00
24	4.17 ^a ± 0.02	1.84 ^d ± 0.02	24.9 ^c ± 0.12
32	4.19 ^a ± 0.02	1.69 ^e ± 0.01	22.3 ^c ± 0.93

Mean values were calculated from three replicates. Values in the same column with different exponents are statistically different ($p < 0.05$), based on Fisher's LSD test.

The addition of APP flour in the recipe of the biscuits leads to a significant reduction in their thickness and volume, but the diameter does not change.

Fig. 23 illustrates the color change of the resulting biscuits.

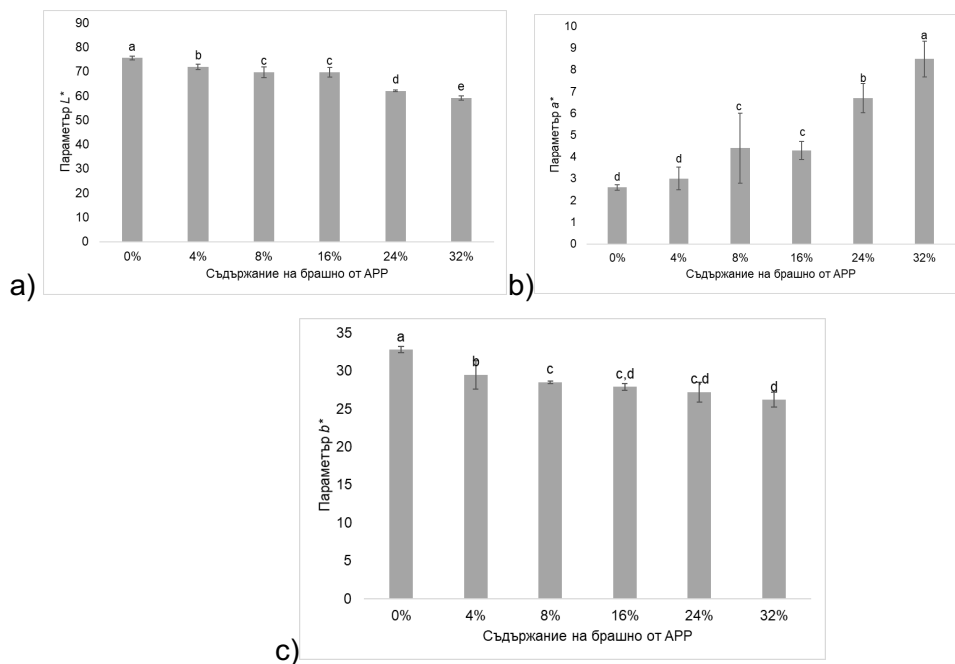


Figure 23. Color of biscuits with the addition of APP flour, as assessed by the CIE Lab system

Bars show standard deviations. Different letters indicate significant differences ($p \leq 0.05$) between samples.

As the amount of APP flour in the biscuits increases, they become darker in color.

4.3.3.2 Sensory characteristics of biscuits

Results of the sensory analysis of the six types of biscuits obtained are illustrated in Fig. 24a.

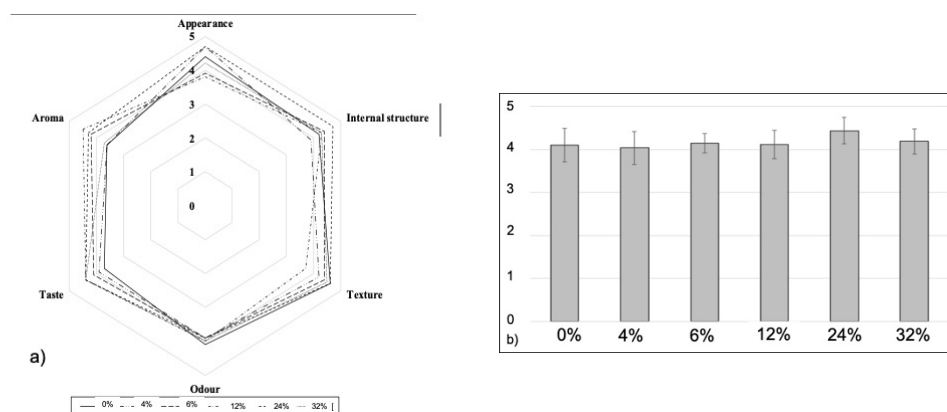


Figure 24. Sensory profile (a) and overall quality (b) of biscuits with the addition of APP flour

Consumers showed a preference for biscuits with a 24% addition of APP flour, as they have the best sensory qualities (appearance, internal structure, texture, taste, and aroma).

4.3.4 Determining the optimal amount of apple peel flour added in biscuits, through mathematical analysis

Fig. 25 illustrates the obtained weighting coefficients for the amount of residual products from apples using feature vectors.

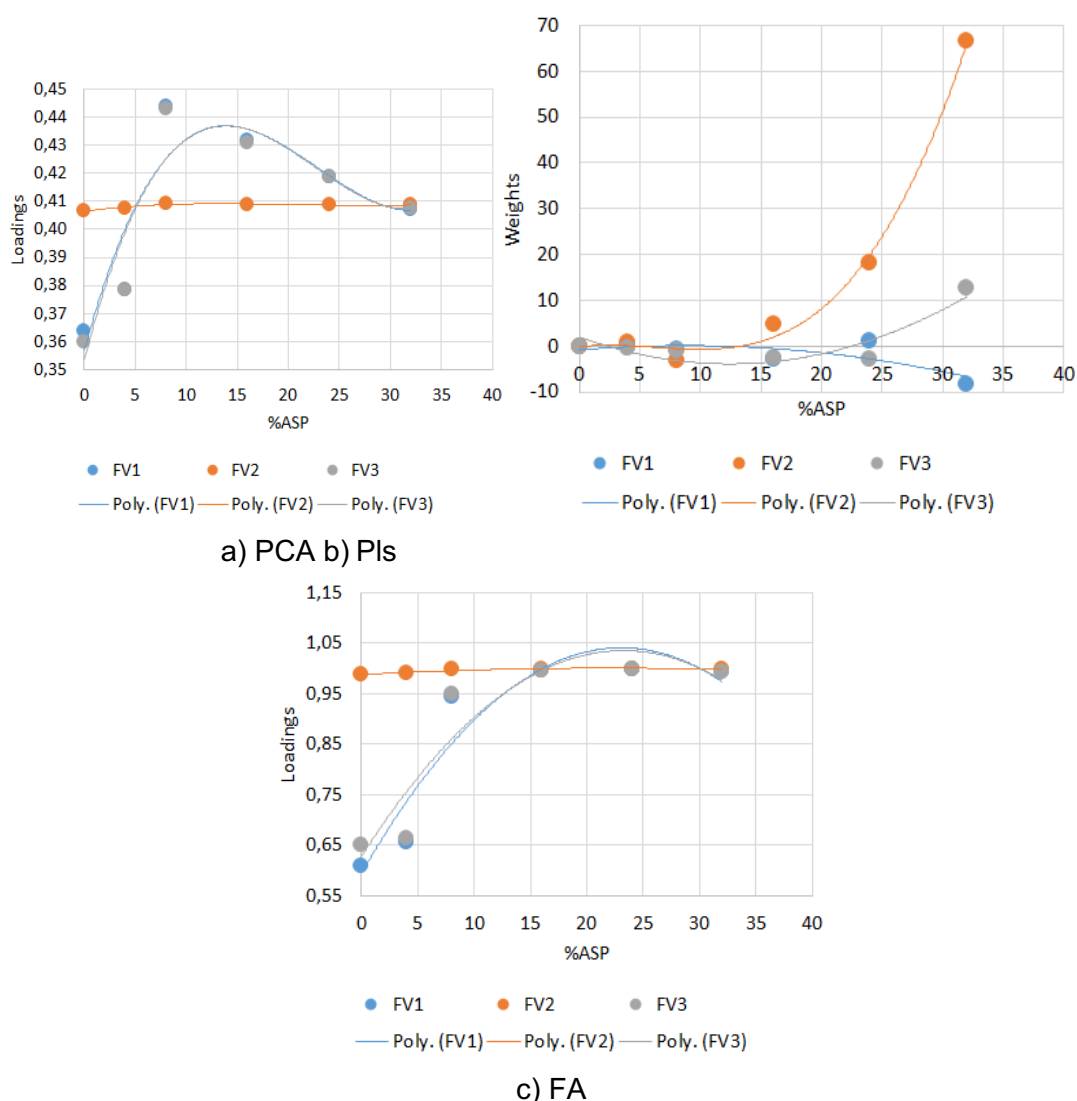


Figure 25. Weighting factors for the amount of APP flour residues

The optimal added amount of APP flour in the biscuits, determined by mathematical analysis, should be 23.58%, which confirms the conclusions drawn from the sensory analysis. Comparing these results, it is affirmed that the

FA method yields the most accurate determination of the optimal amount of APP flour in biscuits.

4.3.5 Example diagram of the technological operations for the utilization of tomato presses and obtaining crackers

As a result of the conducted research in this dissertation, a scheme of the technological operations for the utilization of apple peels and the production of biscuits is proposed (Fig. 26).

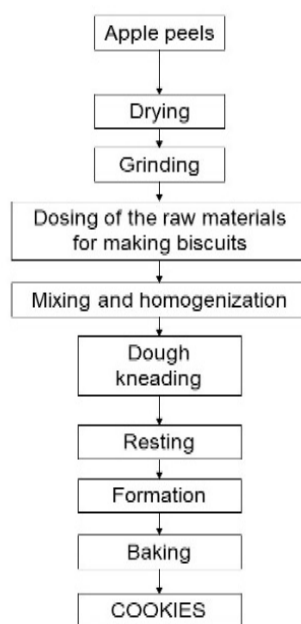


Figure 26. Example scheme of technological operations for the utilization of apple cores and obtaining biscuits

4.4 Investigation of the possibilities of obtaining cakes with the addition of flour from grape pressings

4.4.1 Investigation of the properties of wheat flour, grape pomace flour and flour mixtures

4.4.1.1 Chemical characterization and antioxidant activity of wheat flour and grape pomace flour

The results of the chemical analysis of the wheat flour and the flour from grape pressings are presented in Table 12.

Table 12. Chemical composition and antioxidant activity of wheat flour and grape pomace flour

Indicators, %	Wheat flour	Flour from grape pomace
Moisture content	13.40±0.08	4.04±0.06
Mineral substances	0.53±0.03	6.51±0.01
Fats	1.39±0.01	14.95±0.06
Proteins	13.21±0.60	12.48±0.98
Soluble dietary fiber	4.00±0.10	3.24±0.11
Insoluble dietary fiber	2.48±0.06	51.16±1.32
Total dietary fiber	6.48 ± 0.25	54.4±1.46
Total carbohydrates	84.87 ± 1.11	66.06 ± 1.01
arabinose	0.1±0.00	2.1±0.01
fructose	0.2±0.01	1.8±0.00
sucrose	1.1±0.01	-
lactose	0.2±0.00	-
Total phenols, (µg GAE/100 g CB)	100.2±17.41	5373.36±15.462
DPPH, (µg TE/L CB)	10.06±0.02	336.62±0.24
FRAP, (µg TE/g CB)	272.50±12.49	24985.00±20.45

GPP flour has significantly higher mineral matter, fat, insoluble and total dietary fiber, total phenolics and antioxidant activity than white wheat flour.

4.4.1.2 Amylographic characteristics of wheat flour and flour mixtures

Table 13 presents the values of the analyzed amylographic indicators of wheat flour and of mixtures enriched with GPP flour.

Table 13. Amylographic indicators of wheat flour and flour mixtures with the addition of flour from GPP

Addition of GPP, [%]	Maximum viscosity, [BU]	Viscosity reduction, [BU]	Viscosity Recovery, [BU]	Final viscosity, [BU]	Gelatinization temperature, [°C]
0 (K)	628.0 ^d ±3.84	327.5 ^b ±0.54	451.5 ^d ±0.65	777.5 ^c ±2.02	61.1 ^a ±0.28
4	735.0 ^c ±1.31	328.0 ^b ±0.73	487.5 ^c ±0.71	880.5 ^b ±0.71	62.5 ^b ±0.35
6	795.5 ^b ±2.19	319.0 ^c ±1.31	495.0 ^{bc} ±1.41	961.5 ^a ±3.44	62.5 ^b ±0.35
8	823.5 ^b ±0.71	296.0 ^d ±1.01	507.0 ^{ab} ±0.90	968.0 ^a ±0.00	62.8 ^b ±0.42
10	884.5 ^a ±6.36	331.5 ^a ±1.62	523.8 ^a ±0.30	971.0 ^a ±1.41	63.0 ^b ±0.35

Mean values were calculated from three replicates. Values in the same column with different exponents are statistically different ($p < 0.05$) based on Fisher's LSD test.

As the amount of GPP flour in the flour mixtures increases, the maximum and final viscosity of the slurry increases as well.

4.4.1.3 "Falling number" of wheat flour and flour mixtures

Fig. 27 illustrates the values of the "falling number" of wheat flour and of flour mixtures with different contents of GPP flour.

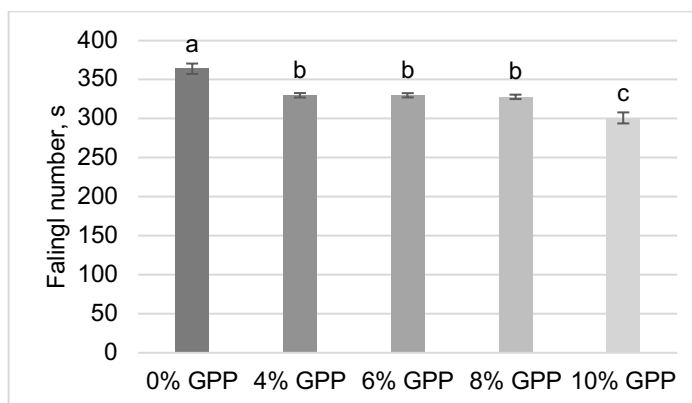


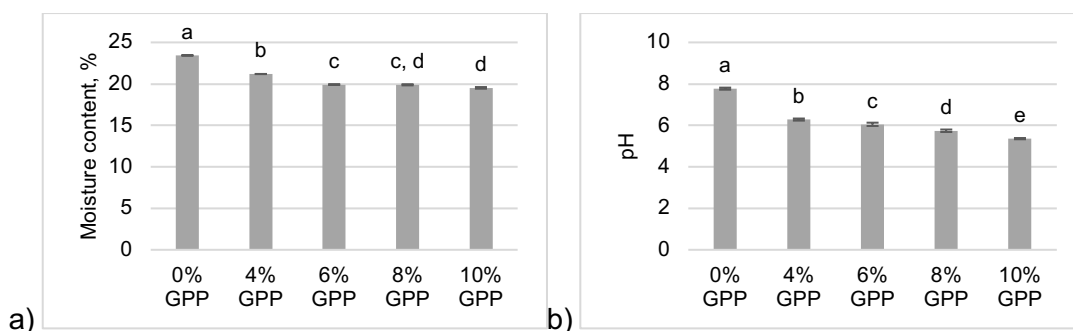
Figure 27. "Falling number" of wheat flour and flour mixtures with addition of GPP flour

The results presented in Fig. 27, showed that wheat flour (control) had the highest value for FN (364 ± 6.66 s). Regarding flour mixtures, those containing 4% and 6% GPP flour had the highest FN (330 ± 2.83 s and 330 ± 2.73 s, respectively).

4.4.2. Nutritional value and antioxidant activity of the resulting cakes

4.4.2.1 Chemical characterization of cakes

The results of the chemical composition of cakes with different GPP flour content are presented in Fig. 28.



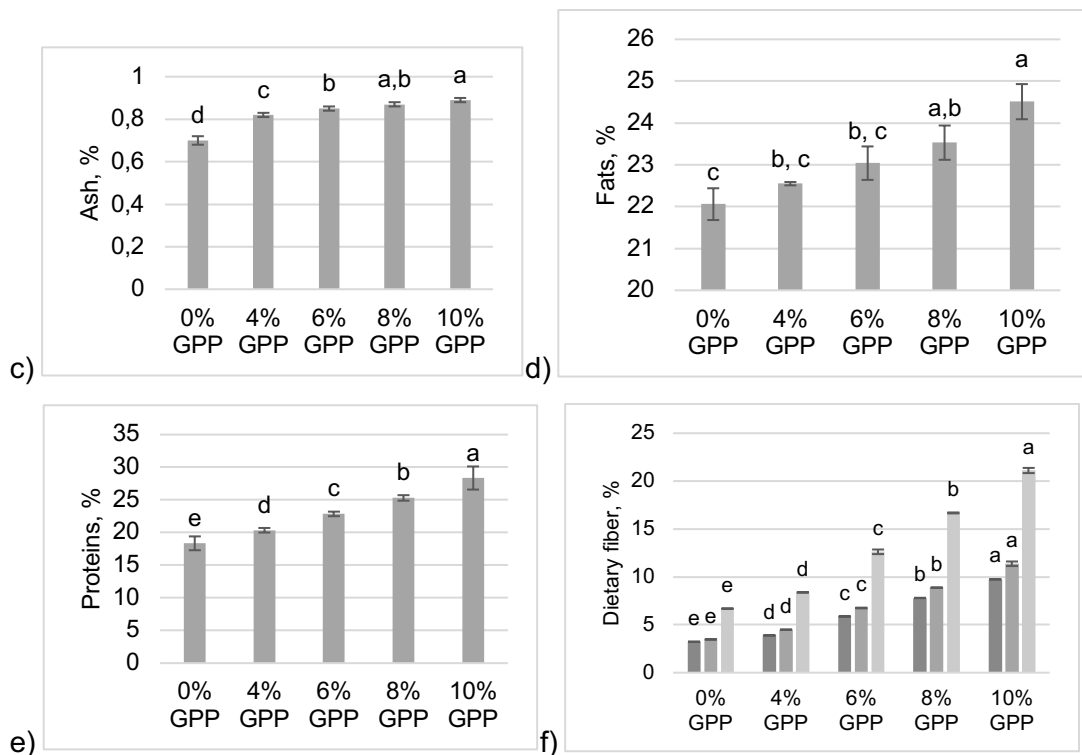


Figure 28. Chemical composition of cakes with addition of GPP flour
Bars show standard deviations. Different letters indicate significant differences ($p < 0.05$) between samples.

Grape pomace flour has a significantly better nutritional value compared to white wheat flour. The addition of GPP flour in cakes leads to an increased content of: mineral substances by approximately 27%; proteins by about 54%; fat by about 11%; total, soluble and insoluble dietary fibers by about 215, 201 and 227%, respectively. Muffins with a 10% GPP flour content have the best nutritional qualities. Fig. 29 presents the results for the carbohydrate fractions determined in the cakes with varying GPP flour content.

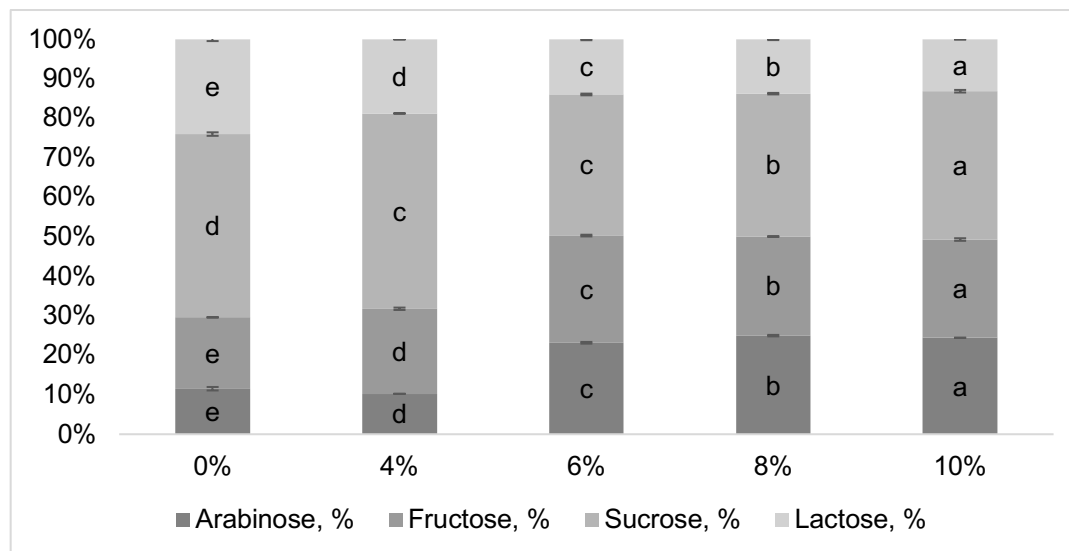


Figure 29. Carbohydrate fractions in cakes supplemented with GPP flour. Bars show standard deviations. Different letters indicate significant differences ($p < 0.05$) between samples.

The figure illustrates that the amount of carbohydrate fractions arabinose, fructose, sucrose and lactose in the cakes increases progressively as the GPP content of the flour increases.

4.4.2.2 Energy value of cakes

Fig. 30 presents the data on the energy value of cakes with different GPP flour content.

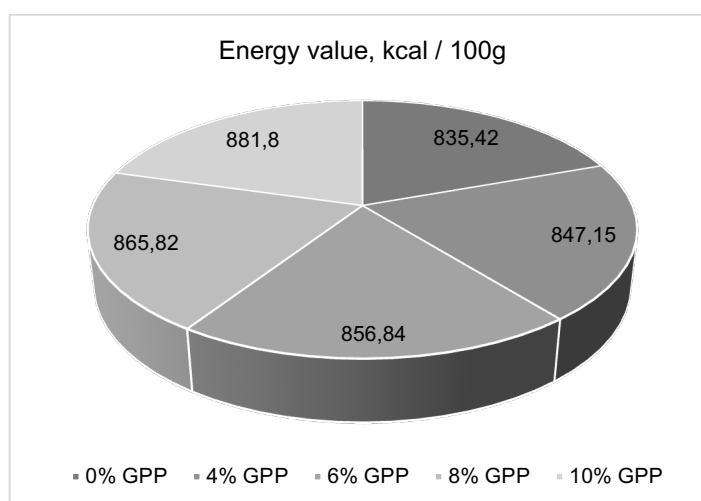


Figure 30. Energy value of cakes with the addition of GPP flour

Biscuits containing 10% GPP flour have the highest energy value – 881.8 kcal/100g, representing a difference of 46.38 kcal/100g compared to the control.

4.4.2.3 Phenolic compounds in cakes

The free phenolics identified in GPP flour and cakes are detailed in Table.

14.

Table 14. Phenolic acids, phenylethanoids and flavonoids (mg/kg CB) in GPP

Indicators	GPP	0%	4%	6%	8%	10%
<i>Phenolic acids</i>						
Gallic acid	40.1 ± 3.09	4.1 ± 0.66 ^d	4.7 ± 0.13 ^{cd}	5.6 ± 0.19 ^{ab}	6.4 ± 0.06 ^{ab}	7.4 ± 0.89 ^a
Protocatechinic acid	53.8 ± 33.85	n.d	1.9 ± 0.06 ^d	2.6 ± 0.01 ^b	3.1 ± 0.15 ^b	4.2 ± 0.11 ^a
Ellagic acid	32.2 ± 3.07	n.d	n.d	n.d	n.d	n.d
<i>Phenylethanoids</i>						
Tyrosol	74.3 ± 0.93	68.9 ± 5.04 ^a	64.5 ± 0.06 ^{ab}	60.3 ± 0.66 ^{BC}	57.9 ± 2.24 ^c	49.9 ± 0.36 ^d
<i>Flavonoids</i>						
Catechin	795.5 ± 63.35	nd ^e	12.8 ± 2.20 ^d	19.1 ± 3.93 ^c	25.2 ± 1.04 ^b	32.0 ± 0.65 ^a
A catechin derivative	11.3 ± 1.51	nd ^e	0.6 ± 0.07 ^d	0.8 ± 0.03 ^c	1.3 ± 0.01 ^b	1.9 ± 0.09 ^a
A catechin derivative	34.7 ± 9.27	nd ^e	0.4 ± 0.03 ^d	0.7 ± 0.01 ^c	1.0 ± 0.08 ^b	1.5 ± 0.02 ^a
A catechin derivative	51.6 ± 2.48	nd ^e	0.9 ± 0.01 ^d	1.1 ± 0.10 ^c	1.4 ± 0.03 ^b	1.6 ± 0.03 ^a
A catechin derivative	91.6 ± 3.49	nd ^e	0.6 ± 0.02 ^c	1.0 ± 0.08 ^b	1.0 ± 0.22 ^{ab}	1.3 ± 0.06 ^a
A catechin derivative	70.9 ± 1.08	nd ^e	0.1 ± 0.01 ^d	0.33 ± 0.03 ^c	0.67 ± 0.02 ^b	0.87 ± 0.06 ^a
A catechin derivative	13.0 ± 3.42	nd ^e	0.73 ± 0.02 ^d	1.14 ± 0.00 ^c	1.53 ± 0.01 ^b	1.95 ± 0.02 ^a
A catechin derivative	25.7 ± 6.80	nd ^e	0.6 ± 0.06 ^b	0.8 ± 0.10 ^b	1.0 ± 0.08 ^a	1.2 ± 0.01 ^a
A derivative of epicatechin	224.5 ± 24.69	nd ^e	2.0 ± 0.42 ^d	3.8 ± 0.14 ^c	4.9 ± 0.05 ^b	7.0 ± 0.20 ^a
Myricetin	8.4 ± 0.97	nd ^e	n.d	n.d	n.d	n.d
Quercetin	56.3 ± 10.17	nd ^e	2.3 ± 0.28 ^b	2.9 ± 0.39 ^b	3.6 ± 0.32 ^a	4.1 ± 0.04 ^a
Apigenin	38.9 ± 8.51	nd ^e	0.8 ± 0.02 ^c	1.0 ± 0.06 ^b	1.3 ± 0.04 ^a	1.3 ± 0.12 ^a
Kaempferol	39.1 ± 10.89	nd ^e	1.0 ± 0.04 ^d	1.2 ± 0.06 ^c	1.4 ± 0.11 ^b	1.7 ± 0.04 ^a
Total phenolic acids	126.1 ± 10.9	4.1 ± 0.7 ^d	6.6 ± 0.2 ^c	18.2 ± 0.2 ^b	9.5 ± 0.1 ^b	11.6 ± 1.0 ^a
Common phenylethanoids	74.3 ± 0.9	68.9 ± 5.0 ^a	64.5 ± 0.1 ^{ab}	60.3 ± 0.7 ^{BC}	57.9 ± 2.2 ^c	49.9 ± 0.4 ^d
Total flavonoids	1461.5 ± 66.2	nd ^e	33.0 ± 2.9 ^d	34.3 ± 5.2 ^c	44.4 ± 1.8 ^b	56.3 ± 0.6 ^a
TOTAL:	1661.9 ± 78.0	73.0 ± 5.7 ^d	94.1 ± 3.1 ^{cd}	102.9 ± 6.1 ^{BC}	111.7 ± 3.9 ^{ab}	117.7 ± 1.3 ^a

flour and cakes with addition of GPP flour

nd: not found i.e. below the detection limit; Index values for cakes in the same order, with different exponents, are statistically different (p < 0.05) based on Fisher's LSD test.

Catechin and its derivatives were the most abundant phenols in the GPP flour (1094.3 mg/kg BM, i.e. 65.8% total), but they were not present in the control sample. All phenolics present in GPP flour (except for ellagic acid and myricetin) were detected in cakes enriched with GPP flour. Their concentrations increased proportionally with the amount of GPP flour added. Consequently, the total phenolics content GPP flour-enriched products significantly surpassed that of the control product. This confirms the usefulness of this by-product in improving the nutritional value of bakery products.

4.4.2.4 Anthocyanins, total phenolics and antioxidant activity of cakes

Fig. 31 illustrates the total content of anthocyanins and phenols, along with the antioxidant activity (DPPH and FRAP methods) in cakes with varying amounts of GPP flour.

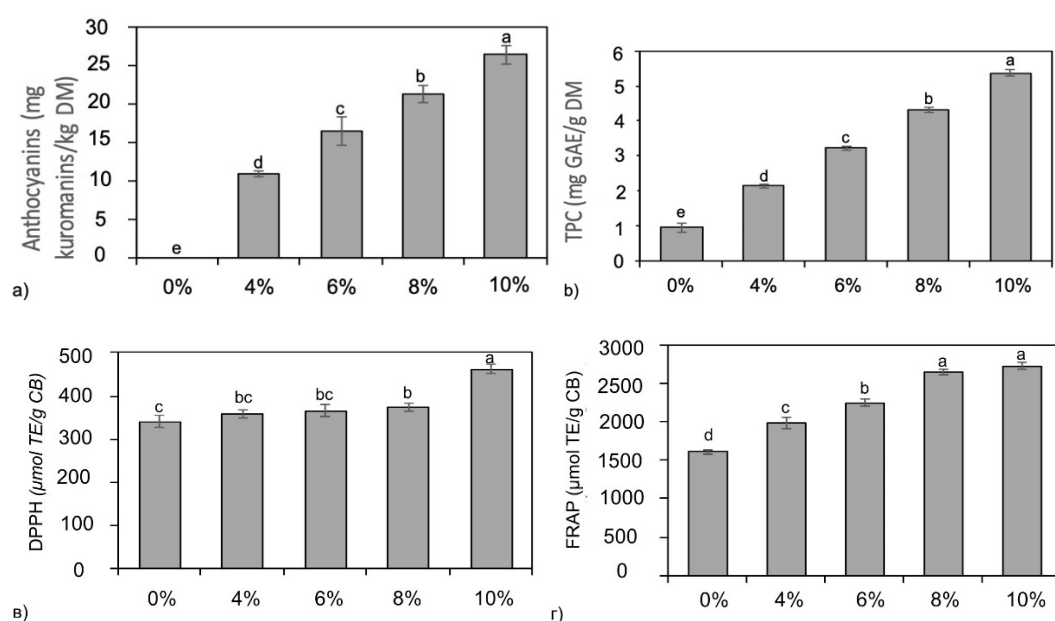


Figure 31. Anthocyanins (a), total phenolics (b) and antioxidant activity: (c) DPPH method, (d) FRAP method, in cakes supplemented with GPP flour. Bars show standard deviations. Different letters indicate significant differences ($p < 0.05$) between samples.

Statistical analysis of the data (ANOVA) determined significant differences between the cakes for all the characteristics studied.

4.4.2.5 Fatty acid composition of cakes

Table 15 presents the fatty acid composition of cakes with varying amounts of GPP flour.

Table 15. Fatty acids in cakes with the addition of grape pomace flour

Fatty acid, %	0% GPP	4% GPP	6% GPP	8% GPP	10% GPP
Palmitic (C16:0)	25.21 ^c ± 0.31	25.75 ^b ± 0.21	26.08 ^{ab} ± 0.04	26.26 ^a ± 0.01	26.47 ^a ± 0.03
Stearic (C18:0)	4.90 ^d ± 0.01	5.03 ^c ± 0.04	5.16 ^b ± 0.04	5.20 ^b ± 0.01	5.28 ^a ± 0.01
Oleic (C18:1)	43.61 ^b ± 0.86	45.20 ^a ± 0.28	45.06 ^a ± 0.06	45.30 ^a ± 0.01	45.63 ^a ± 0.10
Linoleic (C18:2)	20.35 ^c ± 0.21	21.06 ^b ± 0.03	21.70 ^a ± 0.28	21.80 ^a ± 0.28	21.95 ^a ± 0.14
MUFA	48.70 ^a ± 0.43	49.03 ^{ab} ± 0.04	49.96 ^d ± 0.04	49.66 ^{cd} ± 0.06	49.38 ^{bc} ± 0.10
PUFA	20.15 ^{is} ± 0.37	23.18 ^d ± 0.03	24.55 ^c ± 0.01	25.9 ^b ± 0.03	27.30 ^a ± 0.01
SFA	30.80 ^e ± 0.13	31.29 ^d ± 0.01	31.61 ^c ± 0.01	31.90 ^b ± 0.01	32.20 ^a ± 0.01

Cake values in the same row, with different exponents, are statistically different ($p < 0.05$) based on Fisher's LSD test.

Statistical analysis of data (ANOVA) determined significant differences between products for all fatty acids identified. The content of palmitic, stearic, oleic and linoleic fatty acids increased as the amount of GPP flour increased.

4.4.3 Quality of the resulting cakes

4.4.3.1 Physical, textural characteristics and color of cakes

Table 17 illustrates the main physical parameters of cakes with different contents of GPP flour.

Table 17. Physical parameters of cakes with the addition of GPP flour

Addition of GPP, (%)	Diameter, (mm)	Thickness, (mm)	Volume, (cm ³)
0 (K)	57.25 ^a ±0.21	34.05 ^a ±0.64	128.00 ^a ±1.41
4	57.10 ^a ±0.57	33.40 ^{ab} ±0.42	127.00 ^a ±0.10
6	56.80 ^a ±0.71	32.20 ^{bc} ±0.42	126.50 ^a ±0.71
8	56.50 ^a ±0.14	31.05 ^c ±0.49	123.50 ^b ±0.71
10	55.05 ^b ±0.21	30.80 ^c ±0.71	120.50 ^c ±0.71

Mean values were calculated from three replicates. Values in the same column, with different exponents, are statistically different ($p < 0.05$) based on Fisher's LSD test.

Increasing the amount of GPP flour in the cakes results in a slight decrease in the diameter, thickness and volume of the products. The hardness, elasticity, density and chewiness of the resulting cakes are presented in Table 18.

Table 17. Textural parameters of cakes with the addition of GPP flour

Addition of GPP, (%)	Hardness, (N)	Elasticity, (mm)	Density	Chewability, (N)
0%	35.48 ^{is} ±0.50	0.84 ^{and} ±0.01	0.58 ^a ±0.01	17.19 ^d ±0.25
4%	44.15 ^d ±0.37	0.83 ^{ab} ±0.01	0.55 ^b ±0.01	19.97 ^c ±0.97
6%	52.47 ^c ±0.69	0.82 ^b ±0.01	0.53 ^b ±0.01	21.87 ^b ±0.78
8%	57.35 ^b ±0.68	0.79 ^c ±0.01	0.53 ^b ±0.01	22.95 ^b ±0.23
10%	63.88 ^a ±0.09	0.79 ^c ±0.01	0.51 ^c ±0.01	26.67 ^a ±0.11

Mean values were calculated from three replicates. Values in the same column, with different exponents, are statistically different ($p < 0.05$) based on Fisher's LSD test

The firmness of cakes increases significantly with increasing the amount of GPP flour in products. Chewiness increases slightly, but elasticity and density decrease. Color parameters L*, a*, b* change when GPP flour is added (Table 18).

Table 18. Color of cakes with addition of GPP flour

Addition of GPP, %	L^*	a^*	b^*
0 (K)	58.17 ^a ±1.22	43.11 ^a ±1.43	71.29 ^b ±2.17
4	55.32 ^b ±0.88	35.61 ^b ±0.91	72.15 ^b ±1.52
6	54.72 ^b ±0.28	32.07 ^c ±0.62	74.11 ^a ±0.10
8	53.60 ^b ±0.42	31.26 ^c ±0.14	74.18 ^a ±0.21
10	50.73 ^c ±0.52	29.41 ^d ±1.33	74.39 ^a ±1.41

Mean values were calculated from three replicates. Values in the same column, with different exponents, are statistically different ($p < 0.05$) based on Fisher's LSD test

The control cakes exhibited the highest lightness ($L^* = 58.17$), while those with 4%, 6% and 8% GPP flour addition showed relatively equal brightness. However, the cakes with 10% GPP flour addition had a darker color ($L^* = 50.73$).

4.4.3.2 Sensory characteristics of cakes

The sensory analysis showed that the cakes with the addition of 4% GPP flour received the highest ratings (Fig. 32a) for all five sensory parameters examined (appearance, texture, smell, aroma and taste). While the control sample had a satisfactory number of points, the results were lower compared to the other samples.

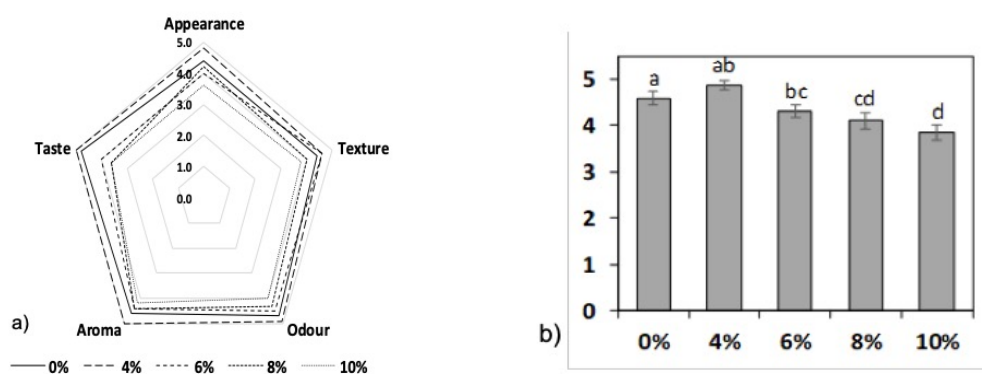


Figure 32. Sensory profile (a) and overall acceptability (b) of cakes with GPP flour addition

Different letters indicate significant differences ($p < 0.05$) between samples.

The bags enriched with 4% GPP flour achieved the best overall score (best overall acceptability) in terms of sensory analysis (Fig. 32b).

4.4.4 Determination of the optimally added amount of flour from grape pomace in cakes, by mathematical analysis

Applying a linear programming algorithm, the optimal amount of added flour from GPP was determined, which amounted to 4.72%. Fig. 33 graphically illustrates the resulting pattern and the recommended amount of GPP flour to be added to the cakes.

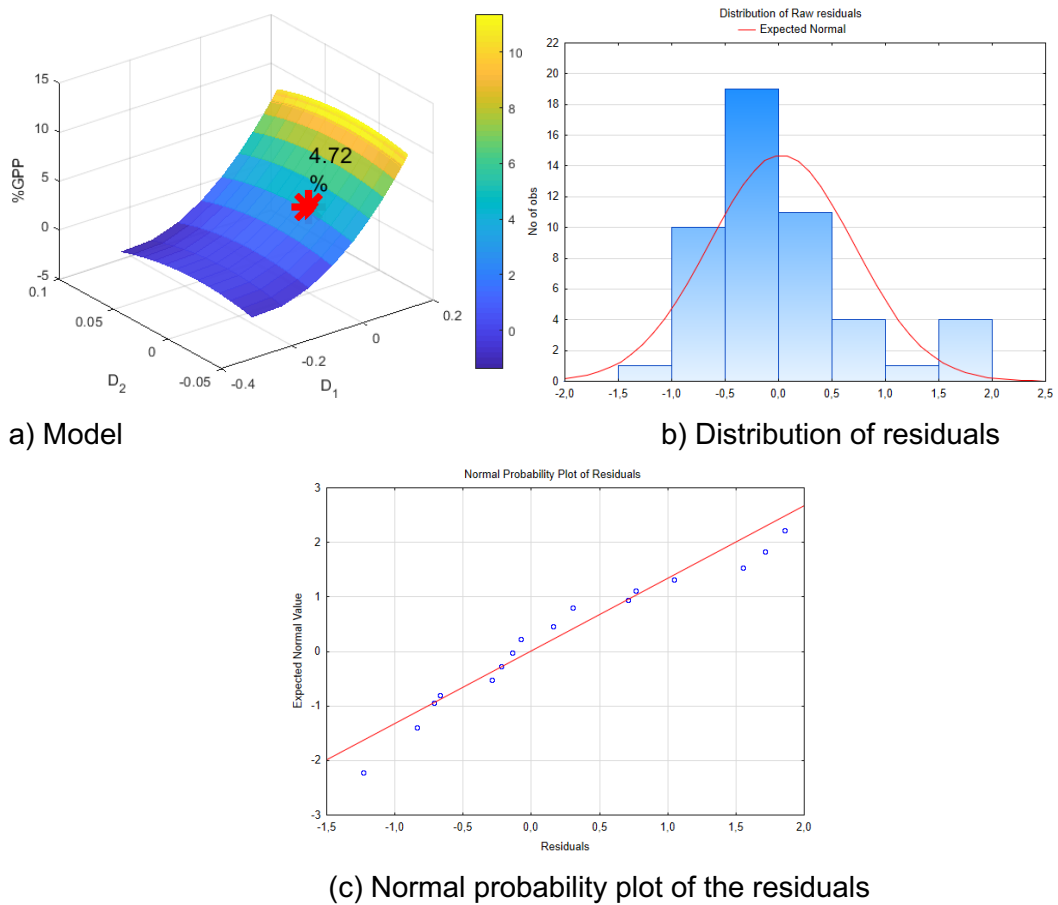


Figure 33. Determination of the optimal amount of GPP flour in cakes

The optimal added amount of GPP flour to the cakes, as determined by mathematical analysis, should be 4.72%, which confirms the conclusions of the sensory analysis.

4.4.5 Example scheme of technological operations for utilization of grape pressings and obtaining cakes

As a result of the research conducted in this dissertation, a scheme of the technological operations for the utilization of grape pressings and the production of cakes is proposed (Fig. 34).

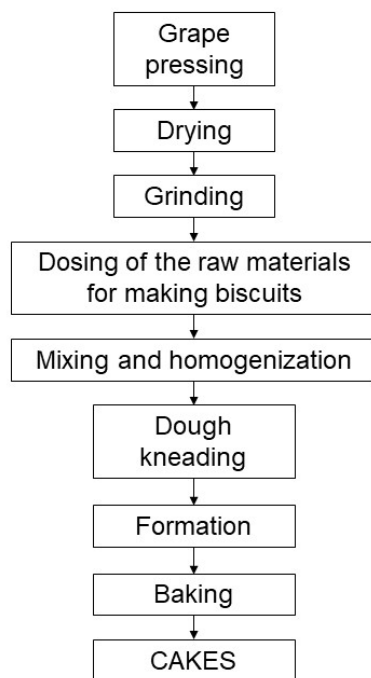


Figure 34. Example scheme of technological operations for utilization of grape pressings and production of cakes

5 Summary conclusions

The conducted research and the obtained results allow the following general conclusions to be made:

1. For the first time, the opinions of consumers from the Republic of Bulgaria, the Republic of Croatia, the Republic of North Macedonia and Bosnia and Herzegovina, regarding the management and utilization of waste from HVP, as well as the production of functional food products, were investigated. More than 70% of respondents have not found food products containing HVP waste, but if such a product were available on the market, they would buy it.

2. For the first time, valorization processes aimed at utilizing plant waste obtained during the processing of tomatoes, apples and grapes were investigated.

3. Based on comprehensive studies aimed at obtaining crackers with added flour from tomato presses, biscuits with added flour from apple peels, and cakes with added flour from grape presses, three types of functional bakery and confectionery products (crackers, biscuits and cake) were developed. These products are enriched with flour from tomato pomace, apple skins and grape pomace, respectively, demonstrating the possibilities of implementing waste-free technologies in HVP.

4. Flours from tomato pomace, apple peels and grape pomace have a very high nutritional value and antioxidant activity compared to white wheat flour. The content of mineral substances is extremely high (by 970%, 856% and 1128%, respectively, more than white wheat flour), total dietary fiber (by 856%, 374% and 739% more), and total phenols (by 20290 %, 971% and 5252% more).

5. Flour mixtures containing tomato pomace flour, apple peel flour or grape pomace flour are characterized by low α -amylase activity.

6. Through mathematical analysis, the optimal added amount of tomato pulp flour in crackers was determined to be 9.27% of the mass of white wheat flour. Similarly, the optimal added amount of apple peel flour in biscuits was found to be 23.58%, and for grape pulp flour in cakes, it was 4.72%.

7. A high nutritional value and antioxidant activity of the obtained crackers, biscuits and cake, with the addition of flour from tomato press, apple

skins and grape press was found, respectively, compared to the control samples, such as:

- the amount of mineral substances in enriched crackers increases by 77%, in enriched biscuits - by 22%, and in enriched cakes - by 27%;
- the amount of protein is 15% more in enriched crackers, 58% less in enriched biscuits, and 54% more in enriched cakes;
- the amount of soluble dietary fiber increases by 28% in crackers with flour from tomato presses, by 189% in biscuits with flour from apple peels, and by 202% in cakes with flour from grape presses;
- the amount of insoluble dietary fiber increases by 128%, 128% and 228%, respectively, in enriched crackers, biscuits and cakes;
- the amount of total dietary fiber increases by 91% in fortified crackers, by 373% in fortified biscuits, and by 216% in fortified cakes;
- the amount of total phenols in enriched crackers is 170% more, in enriched biscuits - by 352% more, and in enriched cakes - by 450% more;
- the antioxidant activity of enriched crackers is higher by 120%, in enriched biscuits by 50%, and in enriched cakes by 47%;
- enriched crackers have a significantly higher content of tocopherols (by 59%) and total carotenoids (by 1612%);
- in the oil of the enriched crackers, the following were found in the greatest quantities: linoleic acid - from 39.24 to 41.74%, oleic acid - from 32.04 to 33.10%, and palmitic acid - from 20.54 to 21.355 ; and in enriched cakes - from 21.06 to 21.95% linoleic acid, from 45.20 to 45.63% oleic acid, and from 25.75 to 26.47% palmitic acid.

8. The quality of the obtained three types of enriched bakery and confectionery products, compared to the control samples, is as follows:

- crackers with 8% tomato pulp flour addition are characterized by the best overall acceptability, texture, aroma, taste and smell. All types of enriched crackers have a darker color, significantly smaller volume (by about 50%), low hardness and high chewiness;
- biscuits with 24% apple peel flour addition have the best appearance, internal structure, texture, taste and aroma. All types of enriched biscuits have a darker color, significantly less thickness (by about 33%) and less volume (by about 35%);

- cakes with 4% grape pomace flour addition have the best appearance, texture, smell, aroma, taste and general acceptability. All types of enriched cakes are darker in color, and firmer.

9. Due to the elevated mineral content, increased dietary fibers, fats, proteins, phenolic compounds, tocols and carotenoids, and high antioxidant activity - proven to positively impact one or more functions in the human body - the resulting products (crackers, biscuits and cake) enriched with tomato, apple and grape by-products, respectively, can be classified as functional foods.

6 Dissertation Contributions

6.1 Scientific Contributions

1. A database was created, and mathematical models were derived to determine the optimal amount of added tomato pomace flour in crackers, apple peel flour in biscuits and grape pomace flour in cakes.

2. A high content of biologically active substances has been proven in the examined flours from tomato and grape pomace and apple peels, which makes them a valuable raw material for obtaining functional bakery and confectionery products.

3. It has been found that incorporated flours in flour mixtures increase the starch gelatinization temperature.

6.2 Scientific and applied contributions

1. For the first time, the most suitable mathematical models were selected, to determine the optimal amount of added flour from tomato pomace in crackers (9.27%), apple peel flour in biscuits (23.58%), and grape pomace flour in cupcakes (4.72%).

2. The high nutritional value and antioxidant activity of flour from tomato press, apple peel and grape press has been proven, which is why they are used as valuable raw materials for producing functional bakery and confectionery products (crackers, biscuits and cake).

6.3 Application Contributions

1. The possibility of utilizing by-products obtained from the processing of tomatoes, apples and grapes, and implementing waste-free technologies in HVP, through the production of bakery and confectionery products (crackers, biscuits and cakes) has been studied.

2. Three recipes and technologies were developed for the production of crackers enriched with tomato press flour, biscuits enriched with apple peel flour, and cakes enriched with grape press flour, respectively.

3 Three exemplary schemes of technological operations are proposed for the utilization of tomato pomace, apple skins and grape pomace in the production of crackers, biscuits and cakes.

4. Three types of functional bakery and confectionery products (crackers, biscuits and cakes) enriched with flour from tomato pomace, apple peel and grape pomace, respectively, were successfully obtained in the laboratory. It was determined that crackers with 8% added flour from tomato presses, biscuits with 24% added flour from apple peels and cakes with 4% added flour from grape presses have the best sensory quality.