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Contents

Chemical constituents, antioxidant and anti-lipase activity of some wines produced in Georgia

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Abstract

Introduction. The purpose of this work was to investigate the composition, *in vitro* antioxidant and anti-lipase activity of different types of wine produced in Georgia and to identify the relationship, if any, between anti-lipase activity, polyphenol content and the antioxidant activity of the wines.

Materials and methods. Individual polyphenols were separated and quantified by HPLC analysis performed using a liquid chromatograph (Varian Prostar 500,Walnut Creek, California, USA). One unit of lipase activity was defined as that amount of lipase which hydrolyses 1.0 micro equivalent of fatty acid from a triglyceride in one hour at pH 7.2 at 37 °C. Ferric reducing ability of plasma (FRAP) assay was applied in order to determine antioxidant activity. All other methods used are standard biochemical methods.

Results and discussion. This study investigated the composition, antioxidant and anti-lipase activity of 6 different wines (Saperavi 2016, Saperavi 2017, Tavkveri 2017, Cabernet Franc 2017, 5. Cabernet Sauvignon 2017 and 6. Rkatsiteli 2017) produced in Georgia. Highest polyphenol content was found in Cabernet Sauvignon 2017 and Cabernet Franc 2017 (1843.13±92.15 and 1650.82±82.50 mg L^{-1}, respectively) while Rkatsiteli 2017 had the lowest polyphenol content (1046.42±52.30 mg L^{-1}). Malvidin-3-*O*-monoglucoside content, expressed as a percentage of total monoglucosides, ranged from 48.12 to 68.58%. Cabernet Sauvignon 2017 and Cabernet Franc 2017 had highest antioxidant (FRAP) activity, i.e., 2189.05±109.45 and 1973.09±98.65 mg ascorbic acid equivalents L^{-1}, respectively. Cabernet Sauvignon 2017 and Cabernet Franc 2017 also displayed the highest level of pancreatic lipase inhibitory activity (79.7 and 78.7% inhibition mL^{-1} of wine, respectively). Rkatsiteli 2017 and Tavkveri 2017 had the lowest anti-lipase activity (58.1 and 56.6% inhibition mL^{-1}, respectively).

Conclusion. Georgian wines represent natural sources of phytochemicals with high levels of antioxidant and anti-lipase activity.

Introduction

Obesity is a now a severe public health problem in all industrialised countries. According to the World Health Organization, worldwide obesity has nearly tripled since 1975. In 2016 it was shown that over 1.9 billion adults were overweight over 650 million of which were considered to be obese [1]. Obesity is frequently associated with the intake of a lipid-rich diet. Pancreatic lipase (triacylglycerol acyl hydrolase EC 3.1.1.3) is an enzyme which plays a central role in lipid digestion and subsequent absorption in humans. Consequently, dietary lipid absorption can be reduced by the partial inhibition of lipase activity and this is currently one of the main strategies used in the management and treatment of obesity [2–4]. Large numbers of plants have been screened for the purpose of discovering naturally occurring potent lipase inhibitors [5–7]. Foodstuffs such as cereals, soybeans, medicinal plants, grapes, green tea and leguminous plants have been shown to contain a range of phytochemicals with anti-lipase activity [8–15]. Phytochemicals such as alkaloids, carotenoids, glycosides, polysaccharides, saponins, terpenes and polyphenols have been shown to possess anti-lipase activity [4, 16–24]. Nevertheless, Orlistat® (Xenical), an hydrogenated derivative of lipstatin isolated from the Gram-positive bacterium *Streptomyces toxytricini*, is currently the only pancreatic lipase inhibitor in clinical use for the management and treatment of obesity. However, the ingestion of this compound is associated with a number of adverse effects such as liquid stools, diarrhea, steatorrhea fecal urgency, etc, which significantly limits its use as a general medication [25–30]. Therefore, a clear need exists to discover other naturally derived sources of phytochemicals with potent anti-lipase activity.

In this context, Georgian wines are known to contain high levels of polyphenols and therefore may be considered as potential natural inhibitors of pancreatic lipase. The total polyphenol content in Georgian white wines produced using the unique Kakhetian technology was reported to be between 2000 and 2290 mg L^{-1}. In red wines the total polyphenol content ranged between 2848–4416 mg per liter [31]. Winemaking in Georgia dates back to the early sixth millennium BC and Georgia is believed to be a cradle of wine [32].Wine consumption has traditionally played a significant role in the dietary regime of Georgians. Consumption of wine and its associated chemical constituents in the everyday diet of Georgians has been linked to many beneficial and well-known health promoting properties, particularly their anti-lipase activity [31, 33]. However, while a significant amount of research has been performed on Georgian wines [34–36], no data appears to exits on their anti-lipase activity. Therefore, the acquisition of detailed information about Georgia's traditional winemaking and wine consumption may be useful in revealing the role of wine consumption in reducing the consequences of high fat diets in humans. Additionally, it has been well documented that oxidative stress is associated with obesity [37]. Therefore, consumption of polyphenolic rich wine may also help alleviate the effects of oxidative stress.

The objective of this work was to investigate the composition, *in vitro* antioxidant and anti-lipase activity of different types of wine produced in Georgia and to identify the relationship, if any, between anti-lipase activity, polyphenol content and the antioxidant activity of the wines.

Materials and methods

Grapes and wines

Six wines produced in Georgia were chosen for investigation The grapes used for the manufacture of the different wines were harvested in September–October from the following locations in Georgia: Saperavi 2016 from Gurjaani (41°44'34.51" N 45°48'4.00" E) (Velistsikhe Microzone); Saperavi 2017 from Gurjaani (41°44'34.51" N 45°48'4.00" E) (Mukuzani Microzone); Tavkveri 2017 from Jighaura (41°55'10.5" N 44°47'17.84" E); Cabernet Franc 2017 from Tsinandali (41°53'46.77" N 45°34'30.39" E); Cabernet Sauvignon 2017 from Tsinandali (41°53'46.77" N 45°34'30.39" E) and Rkatsiteli 2017 from Gurjaani (41°44'34.51" N 45°48'4.00" E) (Velistsikhe Microzone).

Saperavi 2017, Tavkveri 2017, Cabernet Franc 2017 and Cabernet Sauvignon 2017 were produced according to the traditional Georgian technology as previously described Navarre et al, 2017 [38], at the experimental winemaking plant of the Agricultural University of Georgia. Saperavi 2016 was produced according to the Georgian Kakhetian technology and Rkatsiteli 2017 according to the Kakhetian Qvevri technology. Grapes along other parts of the grape, i.e., cluster (stem, skin, seeds) were crushed in a juicer and were then placed in a fermentation vessel. The traditional Qvevri technology involves placing a clay vessel in the ground following procedure are described by Shalashvili et al, 2012 [35].

Chemicals

Ascorbic acid, olive oil, sodium hydroxide, potassium dihydrogen phosphate, HPLC-grade ethyl acetate and methanol were purchased from Sigma Aldrich (Steinheim, Germany). 2,4,6-Tris (2-pyridyl)-s-triazine (TPTZ) was purchased from Sigma Aldrich (Steinheim, Germany). Folin-Ciocalteu reagent was from Appli Chem (Steinheim, Germany). Hydrochloric acid, formic acid and phosphoric acid were provided from Merck (Darmstadt, Germany). Sodium carbonate was from Chem Cruz Biochemicals (California, USA). Tween 80 detergent was obtained from Ferak Berlin GmbH (Berlin, Germany). Pancreatic plant lipase concentrate was purchased from Integrative Therapeutics, (Green Bay, USA). Orlistat® (trade name Xenical) manufactured by Roche (Italy) was purchased at a local pharmacy. All other reagents were commercially available at the local market and were of analytical grade.

Sample preparation for chemical analyses

Sample preparation for individual anthocyanin analysis. An aliquot (2.0 mL) of the different wine samples was carefully deposited onto a C18 solid phase extraction cartridge (Agilent, Bond Elut, USA). Sugars and more polar substances were eluted using 2.0 mL of ultrapure water through the cartridge. Polyphenols were eluted using 2.0 mL of ethyl acetate and finally anthocyanin pigments were eluted with 10 mL of methanol. Deionized water (DI, 10 mL) was added to the methanol extract and the methanol was then removed under vacuum in a rotary evaporator operating at < 30ºC.

Sample preparation for individual polyphenol analysis. An aliquot (4.0 mL) of the wine sample was carefully deposited onto a C18 solid phase extraction cartridge (Agilent, Bond Elut, USA). Sugars and more polar substances were eluted using 2.0 mL of ultrapure

water through the cartridge. Polyphenols were eluted using 2.0 mL of ethyl acetate. Ethyl acetate was evaporated under vacuum at 40-45 °C. Four mL of 50% ethanol was added to the dry extract. The extract was filtered through 45μm filter paper (Whatman, Maidstone, UK) and 20 μL was injected onto the high performance liquid chromatography (HPLC) system.

Titratable acidity. Titratable acidity (TA) was determined by titration with 0.1 N sodium hydroxide using an automatic titrator (ZDJ-4A, INESA Scientific Instrument Co., Ltd, Anting Shanghai, China). The TA results were expressed as g of tartaric acid equivalents 100 mL^{-1} of sample [39].

Total dry matter. For measurement of nonvolatile dry matter in wines a 50 mL sample of wine was aliquoted into a porcelain dish. The dish was then placed in a boiling water bath until evaporation of water, alcohol and other volatile compounds had occurred. Residual moisture was then evaporated from the samples by oven drying at 105 ^{0}C for 16h. Total dry matter was determined gravimetrically as the residue remaining after drying.

Alcohol content. The alcoholic strength by volume of the different wines was determined by distillation as described in Method OIV MA AS312 01A in the Compendium of International Analysis Methods [40].

Ferric reducing ability of plasma (FRAP) assay. The antioxidant capacity of the different wines was determined following the procedure described by Benzie *et al,* 1996 [41] with minor modifications. The FRAP reagent was freshly prepared by adding 10 mM 2,4,6-tripyridyl-s-triazine (TPTZ) (dissolved in 40 mM HCl), 20 mM of Iron (III) chloride in water and 300 mM of sodium acetate buffer (pH 3.6) in the ratio 1:1:10. The FRAP reagent was heated at 37 ^{0}C for 15 min. Then 100 μL of wine sample was added to 3.0 mL FRAP reagent (blank). The absorbance was recorded at 593 nm. The reaction was monitored for 4 min. FRAP values of the samples were compared to that of ascorbic acid and were expressed as mg of ascorbic acid equivalents (AAE) L^{-1} of wine.

Determination of total phenolic compounds (TPC). Determination of TPC was performed according the method of Bond *et al,* 2003[42]. The samples and standards (gallic acid standard solutions 10–50 μg mL^{-1}) were equilibrated at room temperature for 60 min prior to analysis. An aliquot of 1.0 mL of appropriately diluted (with DI water) sample was vortexed with 10 mL distilled water and 1.0 mL Folin-Ciocalteu reagent. DI water (1.0 mL) was used as a control. After equilibration at room temperature for 8 min, the solutions were mixed with 4 mL of 7.5% (w/v) sodium carbonate. The absorbance of the samples and standards were measured spectrophotometrically (UV/Vis spectrophotometer, AE – UV1609, A & E Lab Instruments Co., Ltd. Guangzhou, China) at 765 nm, with a 10 mm path length cell. TPC was calculated as mg of gallic acid equivalents (GAE) 100 mL^{-1} of sample.

Determination of individual polyphenols. Individual polyphenols were separated and quantified by HPLC analysis performed using a Varian Prostar 500 series liquid chromatograph (Varian Prostar 500,Walnut Creek, California, USA). Separation was achieved on a C18, 150 mm x 4.6 mm column (Waters Corporation, Milford, USA). Solvent A was 0.5% acetic acid and solvent B was 100% methanol. Separation was achieved using the following gradient: isocratic 0% B and 100% A for 0 min; isocratic 40%

B and 60% A over 40 min; 0% B and 100% A over 10 min; 0% B and 100% A over 10 min. The flow rate was 0.5 mL min^{-1} and eluent was monitored at 280 nm.

Determination of the content of monomeric anthocyanins. Anthocyanins were quantified using the pH differential method described by Giusti et al, 2001 [43]. Wine samples were diluted 1:50 in pH 1.0 and pH 4.5 buffers, and the absorbance measured at 520 nm and 700 nm in a UV -Visible spectrophotometer (A & E Lab Co Ltd., Guangzhou, China).The molar extinction coefficient used for cyanidin 3-glucoside was 26,900 ΔE/mole at 510 nm having a molecular mass of 449.2 g/mole The results were expressed in terms of mg of anthocyanin L[-1] of wine [43].

Determination of individual anthocyanins using liquid chromatography mass spectrometry (LC-MS). HPLC analyses was performed using a Varian Prostar 500 series liquid chromatography system. Separation was achieved using a C18, 150 mm•4.6 mm column (Waters Corporation, Milford, USA). Solvent A was0.1% aqueous formic acid (FA) and solvent B was100% methanol. Separation was achieved using the following gradient: isocratic 6% B for 5 min, 30% B over 10 min, isocratic 50% B for 15 min, 60% B over 5 min and 6% B over 10 min at a flow rate of 0.4 mL min^{-1}. Detector response was monitored at 518 nm. The MS was equipped with an electro spray ionization (ESI) source and an ion trap mass analyzer (Varian Prostar 500, Walnut Creek, California, USA). Mass spectra were recorded in positive ion mode at 3500 volts. The content of the different anthocyanin percentage was quantified based on the peak areas detected at 518 nm. Individual anthocyanins were identified according to their mass spectra.

Determination of lipase activity. The procedure employed for determination of lipase activity was essentially as reported by Stoytcheva *et al,* 2012 [44] with minor modifications. Briefly, the initial reaction mixture consisted of 2.5 mL deionized water, 3 mL of olive oil, 1 mL 200 mM Tris HCl buffer (pH 7.2) and 0.5 mL detergent (Tween 80). The mixture was mixed rigorously using a magnetic stirrer for 15 min in order to obtain a good emulsion. The lipase preparation (150 mg) was then added to the emulsified mixture and incubated at 37 ^{0}C for 30 min. At the end of incubation, 3 mL of 95% alcohol was added and the final reaction mixture was titrated with 50 mM NaOH using an automatic potentiometric titrator (ZDJ-4A, INESA Scientific Instrument Co., Ltd, Anting Shanghai, China). The end point for the titration was set at pH 9.0. A blank titration was carried out as above but without lipase. One unit of lipase activity was defined at that amount of lipase which hydrolyses 1.0 micro equivalent of fatty acid from a triglyceride in one hour at pH 7.2 at 37 °C. Lipase activity was calculated according to the following formula:

$$Lipase\ Units = (A - B) \cdot 1000 \cdot 2 \cdot DF$$

where A = volume of 50 mM NaOH consumed by the test sample in mL
B = volume of 50 mM NaOH consumed by the blank sample in mL
1000 = conversion factor from milli equivalents to micro equivalents
2 = time conversion factor from 30 min to 1 h
DF = dilution factor

The lipase inhibitory activity of the different wines was assessed following addition of 1 ml of wine to the reaction mixture described above. The reaction and subsequent titration was performed as described above for the determination of lipase activity. The percentage

inhibition was calculated from the lipase activity obtained in the presence and absence of wine and was calculated both per mL of wine as well as per mg of non-volatile dry extract of wine. Orlistat (20 mg) was used as a standard inhibitor compound. Lipase activity was measured in the presence of Orlistat and the percentage inhibition was calculated mg^{-1} of Orlistat.

Statistical analysis

The data presented represents the mean of three replicates±standard deviation (SD). Data were subjected to the one-way ANOVA and Tukey's HSD tests. All calculations were performed with Microsoft Excel 2007 (Microsoft Corp., Redmond, WA, USA) with PHstat 2 version 3.11add-in assistance.

Results and discussion

The wines studied herein are named according to the varieties of grapevine from which they were produced. Rkatsiteli, Saperavi and Tavkveri are native Georgian varieties of grapes *(Vitis vinifera)* [45]. On the other hand, Cabernet Franc and Cabernet Sauvignon were introduced to Georgia from France [46]. High quality red table wine is produced from Cabernet Franc and Cabernet Sauvignon in Telavi (Georgia). Rkatsiteli and Saperavi represent some of the oldest grape varieties and have consistently been the most important in Georgia's commercial winemaking industry. Rkatsiteli grapes are used for making European and Kakhetian-type white table wines as well as strong (12-13% (v/v) alcohol) and dessert wines. High quality red table wine is produced from Saperavi grapes while Tavkveri is an indigenous red grape variety of Georgia. Tavkveri grapes as well as being consumed as a fruit are associated with the production of bright red original wines [45,46].

Chemical constituents

Compositional analysis of the different wines showed significant variation in their constituents (Table 1). The total acidity of the wines varied between 4.85±0.24 g L^{-1} for Rkatsiteli 2017 and 6.31±0.30 g L^{-1} for Tavkveri 2017 (Table 1). According to Lučan and Palič the amounts of total acids in 38 different wines ranged between 3–11 g L^{-1}, [47].

The alcohol content of the tested wines ranged from 12.50±0.61 to 14.50±0.02 % (v/v). King et al., 2013 [30] reported that alcohol level in Cabernet Sauvignon wines ranged from 12% v/v to 16% v/v.

Cabernet Sauvignon 2017 and Cabernet Franc 2017 had the highest total polyphenolic content, i.e., 1843.13±92.15 and 1650.82±82.50 mg L^{-1}, respectively. Rkatsiteli 2017 had the lowest polyphenol content – (1046.42±52.30 mg L^{-1}). The polyphenol contents of the other wines ranged between 1087.63±54.35 and 1197.00±59.85 mg L^{-1} (Table 1). Cabernet Sauvignon 2017 also had the highest content of dry matter and monomeric anthocyanins, i.e., 26.50±1.32 g L^{-1} and 484.18±24.20 mg L^{-1}, respectively. The dry matter content of the other wines was found to be between 19.00±0.92 and 22.50±1.12 g L^{-1}. Tavkveri 2017 had the lowest level of dry extract 19.00±0.92 g L^{-1}. For comparison, analyses of Brazilian wines showed that dry extract content in average was 21 g/l. [48]. Cabernet Franc 2017 had the second highest level (426.12±21.30 mg L^{-1}) of anthocyanins. The lowest content of anthocyanin was observed for Saperavi 2016 (175.05±8.75 mg L^{-1}). Tavkveri 2017 and Saperavi 2017 had intermediate anthocyanin levels, i.e., 303.43±15.17 and 231.13±11.55

mg L^{-1}, respectively. These results are in good agreement with literature values which report that total polyphenol and anthocyanin content in wines ranges between 177–3477 mg L^{-1} and 11.25–1570 mg L^{-1}, respectively [49].

Proximate chemical composition of wines*

	1	2	3	4	5	6
TA, gL^{-1}	5.85 ±0.29[a]	4.89 ±0.24[b]	6.31 ±0.30[c]	5.41 ±0.26[d]	5.40 ±0.25[d]	4.85 ±0.24[b]
Non-volatile dry extract, gL^{-1}	22.00 ±1.10[a]	22.50 ±1.12[a]	19.00 ±0.92[b]	23.70 ±1.18[a]	26.50 ±1.32[c]	20.50 ±1.25[d]
Total polyphenols GAE, mgL^{-1}	1142.58 ±57.12[a]	1197.00 ±59.85[a]	1087.63 ±54.35[a]	1650.82 ±82.50[b]	1843.13 ±92.15[c]	1046.42 ±52.30[a]
FRAP, mg AAE · L^{-1}	1466.66 ±73.33[a]	1385.82 ±69.29[a]	1396.82 ±68.44[a]	1973.09 ±98.65[b]	2189.05 ±109.45[c]	1043.89 ±52.19[a]
Monomeric anthocyanins, mgL^{-1}	175.05 ±8.75[a]	231.13 ±11.55[b]	303.43 ±15.17[c]	426.12 ±21.30[d]	484.18 ±24.20[e]	N/A
Alcohol content, %	13.50 ±0.67[a]	14.00 ±0.71[a]	13.00 ±0.65[a]	14.00 ±0.70[a]	14.50 ±0.02[a]	12.50 ±0.612[a]

1. Saperavi 2016;
2. Saperavi 2017;
3. Tavkveri 2017;
4. Cabernet Franc 2017;
5. Cabernet Sauvignon 2017;
6. Rkatsiteli 2017.

*-Values within a row with different letters are significantly different by ANOVA with Tukey's HSD tests at $p < 0.05$.

Individual polyphenols

The individual polyphenolic compounds, caffeic acid, (-) epicatechin, (+) catechin and gallic acid, were chromatographically separated and quantified. A typical reverse-phase HPLC separation profile, in the case of Cabernet Franc 2017, is shown in Fig 1. Highly significant differences in the four individual polyphenolic compounds quantified were observed in the wine samples analysed in this study. The highest content of caffeic acid was present in Saperavi 2016 (17.3±0.86 mg L^{-1}) and the lowest was in Tavkveri 2017 (1.80±0.09 mg L^{-1}) and Rkatsiteli 2017 (2.00±0.10 mgL^{-1}). Cabernet Franc 2017, Saperavi 2017 and Cabernet sauvignon 2017 contained 3.50 ±0.017, 11.60±0.58 and 4.00±0.20 mg L^{-1} caffeic acid, respectively (Table 2). According to Šeruga *et al.* 2011 [50,] content of caffeic acid in some Croatian wines varied between 3–18 mg L^{-1}.

(-) Epicatechin was present in highest content in Cabernet Sauvignon 2017 (44.70±2.23 mg L^{-1}) and Cabernet Franc 2017 (36.60±1.83 mg L^{-1}). The lowest content of (-) epicatechin was found in Tavkveri 2017 (3.70±0.18 mg L^{-1}) and Saperavi 2016 (9.50±0.47 mg L^{-1}). Saperavi 2017 and Rkatsiteli 2017 contained 16.80±0.84 and 12.80±0.64 mg L^{-1} (-) epicatechin, respectively (Table 2) The same authors [50] reported that content of (-) Epicatechin in Croatian wines was in range of 7–37 mg L^{-1}.

Individual polyphenols in wines*

Individual polyphenols	mgL^{-1}					
	1	**2**	**3**	**4**	**5**	**6**
Caffeic acid	17.30 ±0.86[a]	11.60 ±0.58[b]	1.80 ±0.09[c]	3.50 ±0.17[d]	4.00 ±0.20[e]	2.00 ±0.10[f]
(—)-*Epycatechin*	9.50 ±0.47[a]	16.80 ±0.84[b]	3.70 ±0.18[c]	36.60 ±1.83[d]	44.70 ±2.23[e]	12.80 ±0.64[f]
(+)-Catechin	9.00 ±0.45[a]	11.80 ±0.59[b]	5.30 ±0.26[c]	11.70 ±0.58[b]	30.00 ±1.50[d]	46.20 ±2.31[e]
Gallic acid	4.80 ±0.24[a]	10.00 ±0.50[b]	3.50 ±0.17[a]	20.20 ±1.01[c]	21.00 ±1.05[c]	9.40 ±0.47[b]

1. Saperavi 2016;   4. Cabernet Franc 2017;
2. Saperavi 2017;   5. Cabernet Sauvignon 2017;
3. Tavkveri 2017;   6. Rkatsiteli 2017.

*- Values within a row with different letters are significantly different by ANOVA with Tukey's HSD tests at $p < 0.05$.

As to the (+) catechinen the authors [50] found it to be between 31-138 mg L^{-1}. According to our analyses the content of (+) catechin was highest in Rkatsiteli 2017 and Cabernet Sauvignon 2017 (46.20±2.31 and 30.00±1.50 mg L^{-1}, respectively). Tavkveri 2017 and Saperavi 2016 had the lowest content of (+) catechin (5.30±0.26 mg L^{-1} and 9.00±0.45 mg L^{-1}, respectively). Saperavi 2017 and Cabernet Franc 2017 had similar levels of (+) catechins, i.e., 11.80± 0.59 and 11.70±0.58 mg L^{-1}, respectively (Table 2).

The highest content of gallic acid was observed in Cabernet Sauvignon 2017 (21.00 ±1.05 mg L^{-1}) and Cabernet Franc 2017 (20.20±1.01 mg L^{-1}). Saperavi 2017 and Rkatsiteli 2017 had intermediate levels of gallic acid, i.e., 11.80 ±0.59 and 9.40±0.47 mg L^{-1}, respectively. The lowest content of gallic acid was found in Tavkveri 2017 (3.50 ±0.17 mg L^{-1}) and Saperavi 2016 (4.80±0.24 mg L^{-1}, Table 2). Gallic acid content in Chilean Cabernet Sauvignon was found to be 22.2 mg L^{-1}. In some other wines gallic acid content varied from 7.8 mg L^{-1} up to 70.8 mg L^{-1} [51].

Other individual polyphenols were not identified within this study due to a lack of corresponding standards.

Content of individual anthocyanins

As already outlined, individual anthocyanins were separated, identified and quantified using LC-MS. In concurrence with the observed differences in monomeric anthocyanins (Table 1) the content of the individual anthocyanins varied significantly depending of the wine sample analysed (Table 3).

Table 3

Individual anthocyanins in wines*

Anthocyanins	%				
	1	**2**	**3**	**4**	**5**
Delphinidin-3-*O*-monoglucoside	1.87 ±0.07[a]	1.61 ±0.04[b]	2.13 ±0.10[c]	1.41 ±0.06[d]	1.16 ±0.006[e]
Cyanidin-3-*O*-monoglucoside	0.15 ±0.01[a]	0.15 ±0.005[a]	0.14 ±0.001[a]	0.06 ±0.003[c]	0.18 ±0.008[d]
Petunidin-3-*O*-monoglucoside	4.50 ±0.10[a]	5.29 ±0.28[b]	5.67 ±0.27[b]	2.70 ±0.13[c]	2.07 ±0.10[d]
Peonidin-3-*O*-monoglucoside	3.04 ±0.09[a]	2.34 ±0.13[b]	2.50 ±0.12[b]	3.97 ±0.19[c]	2.51 ±0.12[b]
Malvidin-3-*O*-monoglucoside	60.67 ±3.45[a]	63.59 ±3.78[b]	68.58 ±3.43[c]	50.21 ±2.32[d]	48.12 ±2.40[d]
Delphinidin-3,5-*O*-diglucoside	7.91 ±0.28[a]	3.50 ±0.25[b]	2.13 ±0.01[c]	2.47 ±0.12[d]	2.31 ±0.28[d]
Petunidin-3-*O*-acetylmonoglucoside	0.77 ±0.03[a]	0.64 ±0.17[b]	0.24 ±0.01[c]	1.36 ±0.06[d]	2.30 ±0.13[e]
Petunidin-3,5-*O*-diglucoside	0.03 ±0.001[a]	0.05 ±0.002[b]	0.02 ±0.001[c]	0.10 ±0.005[d]	0.07 ±0.002[e]
Malvidin-3-*O*-acetylmonoglucoside	4.95 ±0.11[a]	5.55 ±0.26[b]	6.68 ±0.32[c]	19.44 ±0.97[d]	26.65 ±1.33[e]
Peonidin-3,5-*O*-diglucoside	0.06 ±0.003[a]	0.01 ±0.001[b]	0.02 ±0.001[c]	0.06 ±0.003[d]	0.26 ±0.01[e]
Malvidin-3-(6-*O*-caffeoyl) monoglucoside	1.68 ±0.08[a]	1.13 ±0.05[b]	0.40 ±0.02[c]	0.50 ±0.02[d]	0.47 ±0.02[d]
Petunidin-3-(6-*O*-p-coumaroyl) monoglucoside	0.32 ±0.01[a]	0.68 ±0.02[b]	0.74 ±0.03[c]	0.57 ±0.02[d]	0.34 ±0.01[a]
Malvidin-3-(6-*O*-p-coumaroyl),5-0-diglucoside	0.22 ±0.01[a]	0.31 ±0.01[b]	0.40 ±0.02[c]	0.43 ±0.02[d]	0.42 ±0.01[d]
Peonidin-3-(6-*O*-p-coumaroyl) monoglucoside	0.76 ±0.02[a]	1.25 ±0.06[b]	0.90 ±0.04[c]	1.05 ± 0.02[d]	0.50 ±0.02[e]
Malvidin-3-(6-*O*-p-coumaroyl) monoglucoside	7.18 ±0.37[a]	9.66 ±0.47[b]	5.26 ±0.25[c]	8.39 ±0.41[d]	6.29 ±0.30[e]
Delphinidin-3-(6-*O*-p-coumaroyl) monoglucoside	0.61 ±0.03[a]	0.85 ±0.04[b]	1.18 ±0.05[c]	1.81 ±0.09[d]	1.62 ±0.08[e]

1. Saperavi 2016;
2. Saperavi 2017;
3. Tavkveri 2017;
4. Cabernet Franc 2017;
5. Cabernet Sauvignon 2017

*- Values within a row with different letters are significantly different by ANOVA with Tukey's HSD tests at $p < 0.05$.

Overall, malvidin-3-*O*-monoglucoside was the main anthocyanin present in all the wine samples analysed herein. The percentage, in terms of monomeric anthocyanin content, of malvidin-3-*O*-monoglucoside varied from 68.58±3.43 % (Tavkveri 2017) to 48.12±2.40 % (Cabernet Sauvignon 2017). The other main anthocyanins detected in the wines were malvidin-3-(6-*O*-p-coumaroyl) monoglucoside, malvidin-3-*O*-acetylmonoglucoside, petunidin-3-*O*-monoglucoside and peonidin-3-*O*-monoglucoside). Other anthocyanins were present in minor quantities. Similar results were obtained by María José Noriega and Ana Casp: 15 anthocyanins were identified in young red wines from appellation of origin Navarr (Spain). The 3-monoglucoside of malvidin was the major component in all of the wines. Its contribution to the total anthocyanin content ranged from 39,07 % to nearly 70 % [52].

Lipase inhibition

Cabernet Sauvignon 2017 and Cabernet Franc 2017 showed the highest level of lipase inhibition, i.e. 79.66±3.98 and 78.79±2.45 % per of mL of wine, respectively. These values were not statistically significantly ($p < 0.05$) different (Table 4).

Table 4

Lipase activity and its inhibition by wines*

	1	2	3	4	5	6
Inhibition % based on 1 mg dry matter	3.20 ±0.16[a]	3.05 ±0.14[a]	2.97 ±0.14[b]	3.32 ±0.18[c]	3.00 ±0.15[a]	2.83 ±0.14[b]
Inhibition %	70.57 ±3.52[a]	68.80 ±3.44[a]	56.55 ±2.82[b]	78.79 ±2.45[c]	79.66 ±3.98[c]	58.05 ±2.90[b]
Enzyme activity (Unit)	2234.00 ±111.7[a]	2369.00 ±118.45[a]	3299.00 ±164.95[b]	1544.00 ±77.20[d]	1610.00 ±80.5[c]	3185.00 ±159.25[e]

1. Saperavi 2016;
2. Saperavi 2017;
3. Tavkveri 2017;

4. Cabernet Franc 2017;
5. Cabernet Sauvignon 2017;
6. Rkatsiteli 2017.

*- Values within a row with different letters are significantly different by ANOVA with Tukey's HSD tests at $p < 0.05$.

Saperavi 2016 and Saperavi 2017 showed the next highest level of lipase inhibition, i.e. 70.57±3.52 and 68.80±3.44 % per of mL of wine, respectively (again these values were not statistically significantly differeent). Rkatsiteli 2017 and Tavkveri 2017 had similar ($p > 0.05$) and the lowest anti-lipase activity, i.e., 58.05±2.90 and 56.55±2.82 %, respectively. Orlistat® (20 mg) showed 83% inhibition of lipase activity. Furthermore, the r^2 correlation value between the polyphenol content and anti-lipase activity was 0.77 (Figure 1). A similar correlation was found between the decrease in *in vivo* lipid levels promoted by red wine (Cabernet Franc, Meriot, Sangiovese and Syrah 2006 and 2007 from southern Brazil) consumption and the content of stilbens and tyrosol, a special class of polyphenols [53]. Some differences in the results for anti-lipase activities were observed when calculated per mg dry extract. Cabernet Franc 2017 and Saperavi 2016 showed the highest anti-lipase activity, i.e., 3.32±0.18 and 3.20±0.16 %, respectively. Tavkveri 2017, Saperavi 2017 and Cabernet Sauvignon had approx. 3% lipase inhibitory activity. Rkatsiteli

2017 possessed the lowest anti-lipase activity, i.e., 2.83±0.14 %. The anti-lipase activity of Orlistat® calculated per mg of the preparation was equal to 4.2 %. These data show that the anti-lipase activity of Cabernet Franc 2017 and Saperavi 2016 was only 21.4 % less than that of Orlistat®. According to Jaradat et al., 2017 [54] the aqueous extract of *V. vinifera* had lipase IC_{50} value of 14.13 μg mL^{-1} while Orlistat had a IC_{50} value of 12.38±2.3 μg mL^{-1}.
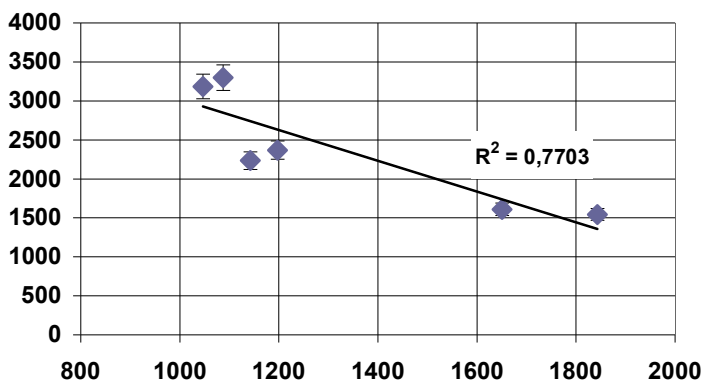
Figure 1. Correlation between enzyme activity and TPC
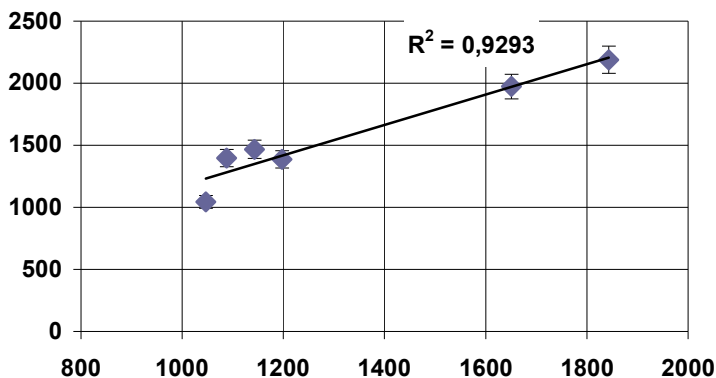
Figure 2. Correlation between FRAP and TPC

Antioxidant activity

According to literature reports, the antioxidant activity of wine varies between 879.12 - 2304.36 mg AAE·L^{-1} [55-56]. For the wines studied herein, Cabernet Sauvignon 2017 and Cabernet Franc 2017 displayed the highest antioxidant activity i.e., 2189.05±109.45 and 1973.09±98.65 FRAP mg AAE·L^{-1}, respectively. Rkatsiteli 2017 contained the lowest antioxidant activity (1043.89±52.19 FRAP mg AAE·L^{-1}). The observed higher level of antioxidant activity in red as opposed to white wine is in agreement with the trends reported in the literature [57]. There were no statistically significant differences (p>0.05) between the antioxidant activities of Saperavi 2016, Saperavi 2017 and Tavkveri 2017. Their antioxidant activities ranged from 1385.82±69.29 to 1466.66±73.33 FRAP mg AAE·L^{-1}.

There was a good correlation (r^2=0.93) between the polyphenol content in wines and their antioxidant activities (Figure 2). For comparison, a significantly positive correlation was reported between the antioxidant activity of Spanish wines and the total phenols or the total anthocyanins [49].

Conclusion

The red and white wines produced in Georgia from different varieties of *Vitis vinifera* have high anti-lipase activity when compared to Orlistat®, a synthetic drug compound used in the treatment of obesity. A correlation appeared to exist between the anti-lipase and antioxidant activity of the wines and their polyphenol content The main anthocyanin present in red wines wass malvidin-3-*O*-monoglucoside. Georgian red and white wines may be considered as a suitable natural sources for the extraction of compounds with high anti-lipase activity. The potential anti-obesity properties of these compounds merits further study *in vitro* and ultimately *in vivo*.

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Application of computer vision and image analysis method in cheese-quality evaluation: a review

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Abstract

Introduction. This review paper deals with literature analysis of modern computer vision and image analysis methods in cheese-quality evaluation.

Materials and methods. In this paper several cheese types made from cow's milk were analyzed: soft, semi-hard, and hard cheese. All images shown in this paper were scanned with a flatbed scanner, and then processed using ImageJ software.

Results and discussion. Because with the most part of the external quality attributes evaluation is time-consuming, due to visual inspection, computer vision provides a means to perform this task automatically. To evaluate various cheese external quality properties (color), and defects (mechanical openings – gas holes; rind defect – formation of calcium lactate crystals and excessive rind halo; amount and distribution of added ingredients; meltability and oiling-off) computer vision system has been successfully applied. Image analysis was used for measurement of the normal amount of gas production, and abnormal shape or distribution of eyes throughout the structure of Emmental and Tilsit cheese. Image analysis was used to determine the presence of rind halo cheese defect and to measure the area occupied by calcium lactate crystals on surfaces of naturally smoked Cheddar cheese samples. To improve empirical methods (Arnott and the Schreiber test) and to offer a new approach for evaluation of meltability and oiling-off of Mozzarella cheese, computer vision and image analysis method was applied. In addition, digital image analysis is used for evaluation of the addition of some ingredients and evaluation of the amount and distribution of added ingredients into the semi-cooked cheese with added paprika and herbs.

Conclusion. Computer vision and digital image analysis represents an efficient and non-invasive technique able to investigate the cheese optical properties and give information concerning their composition and structure.

Introduction

Trained human inspectors usually perform food-quality inspection. This method is highly variable and decisions are not always consistent between inspectors from day to day. Because instruments reduce variations among individuals and are more precise, instrumental measurements are preferred over human inspectors. Instruments can be designed to imitate human testing methods or may be statistically related to human perceptions and judgments to predict quality categories. Researchers have been working to find techniques for evaluating the external and internal quality attributes of agricultural and food products non-destructively [1–5]. Size, shape, and color of food are considered as external quality attributes. Internal quality attributes are texture (firmness, hardness, crispness, tenderness, and juiciness), proximate composition, and nutritive value (carbohydrates, proteins, and vitamins) and defects like pest infestation, internal cavity, frost damage, rotten, etc. While external quality attributes are evaluated by visual judgment, internal quality attributes are difficult to access by visual appearance and there is a need for technology that can determine them. In order to perform objective and reliable food inspection methods suited for routine inspection and quality assurance tasks, the application of non-destructive optical devices is considered ideal [4, 6–11]. Non-destructive optical techniques include computer vision systems (CVS) with online digital cameras/scanners, light and confocal laser scanning microscopes (CLS), the near-infrared (NIR) imaging systems, spectroscopy and hyperspectral imaging systems (HIS), X-ray imaging and ultrasonic devices [1-14]. Over the past few decades, CVS, including traditional CVS, hyperspectral CVS, and multispectral CVS, has been widely used in the food industry for the automatic external quality inspection of food and agricultural products [12–15]. The aim of this paper is to give a comprehensive overview on the principles and applications of computer vision method and image analysis to the assessment of visual parameters in the quality evaluation of cheese, which correlates with quality and safety characteristics. Computer vision method was used routinely in the quality assessment of several dairy products like whey, desiccated milk, yoghurt, and cheese [19–31]. CVS with image analysis are being developed to assess the appearance criteria of cheese, such as color, shreddability, gas holes and mechanical openings, and oiling-off [26–27, 29–30, 32–34]. Furthermore, CVS can be applied in the quality evaluation of cheese during cooking for the determination of browning and melting properties [35], as well as for prediction of shelf life and the determination of color changes during storage with the use of computer vision and artificial neural network (ANN) [24,29].

Materials and methods

Materials

In this paper, several cheese types made from cow's milk were analyzed: Mozzarella (soft cheese), Emmental (hard, cooked pressed cheese, Swiss-type cheese,), Cheddar (semi-hard, uncooked pressed cheese) and Tilsit (semi-hard smear-ripened cheese) and semi-cooked cheese with added paprika and herbs respectively.

Method

Literature referenced in this review article was obtained from bibliographic information in Google Scholar, Web of Science, ScienceDirect, Scopus, SpringerLink,

EBSCO host, Wiley online library, PubMed, DOAB (directory of open acces books), OvidSP database and CAB abstracts.

Getting of the figures. All images shown in this paper are the result of unpublished research of authors of this review paper. Cheese samples were scanned with a flatbed scanner EPSON Perfection V500 Photo (Epson America Inc., USA), and images were processed using ImageJ 1.48v software (Wayne Rasband, National Institute of Health, Maryland, USA). To avoid external light conditions, scanner was placed in black box and samples were illuminated with scanner bottom LED light (ReadyScan LED). Scanned 24-bit images of 300 dpi with dynamic range 3.4 were digitalized and stored in TIFF format.

Results and discussion

Computer vision – basics

Computer vision system (CVS) is an engineering technology that combines mechanics, optical instrumentation, electromagnetic sensing, digital video, and image processing technology [36], or a shortly integrated mechanical-optical-electronic-software system. CVS provides suitably rapid, economic, consistent, and objective assessment for the food and agricultural industry. CVS is a non-contact and non-destructive optical technique suitable for online inspection, quality evaluation of food products, and for ensuring the safety and reliability of the product [28]. Food appearance is detected instrumentally by measuring electromagnetic, usually optical, properties. According to the sensor by which images can be generated, optical techniques can be divided in spectroscopy and image analysis methods. Computer vision includes several operations: capturing, processing, and image analysis. Images are formed when light (in the visible spectrum) falls on a partially reflective and partially absorptive object surface, with the scattered photons being gathered up in the camera lens (which is a light collector) and converts to electrical signals by image sensor [37]. After image capturing, the process of converting images into numerical form is called digitization [38-39]. In digitization, the image is divided into a two-dimensional grid of small regions containing picture elements defined as pixels by using a frame grabber (digitizer) and stored in the form of matrices. As a technique, CVS is able to measure the external features of products, to recognize objects and extract quantitative information from digital images [40]. Currently, the main application of CVS occurs in automated inspection and measurement, allowing manufacturers to keep control of product quality. Configuration of CVS is relatively standard; basic components are illumination device (lights), a device for image acquisition (digital camera/scanner), a frame grabber (in the case of an analogue camera), and computer hardware and software (algorithms for image analyzing and pre-processing) to provide disk storage of images and computational capability [26,41].

The illumination device is used for object illumination under test. There are many properties of illumination (light angle of incidence, light source color, direct/diffuse light technique), which must be selected in such a way that a perfectly evaluable image is generated in combination with the material properties of the object under inspection [37,39,41]. Image analysis can be easier with good illumination by reducing noise, shadow, reflection, and enhancing image contrast. Factors that influence the choosing of suitable illumination are object geometry under inspection (flat or curved), nature of object surface (absorbing, transmissive or reflective), and the nature of the object feature (opaque, semi-transparent or translucent) to be imaged in comparison with the background (backlighting is usually used for detecting objects that are translucent) [38,43]. Light at different

wavelengths carries different levels of energy; all possible wavelengths we call the electromagnetic spectrum. The electromagnetic spectrum consists partly of a visible and nonvisible range [37]. According to the operating range of the spectrum, we distinguish different type of cameras: CCD camera (400–700 nm), near-infrared (NIR) camera (900–1700 nm), near ultraviolet (UV) camera (300–369 nm). Cameras that operate in the visible part of the spectrum are analog and digital cameras. Digital cameras can be equipped with a CCD (charged coupled device) or CMOS (Complementary metal-oxide-semiconductor) sensor arrays [44]. In an analog camera, first the images are recorded, transformed into the analog signal, and then transferred to a digital data-stream in the computer with a frame grabber. In digital cameras, a frame grabber is not needed because the analog signal is sent directly to the computer via a USB or FireWire adapter [45]. Furthermore, the employment of 3-dimensional cameras may help to improve analysis, provide more information and allow the study of complex or irregular-shaped materials with fewer errors and less time [46]. Scanners are usually used for specialized tasks and specific use (extreme resolution, large numbers of output channels or extreme wavelengths). Flatbed scanners are devices that optically scan images and convert it to a digital image. It is a promising analytical instrument suitable for measurements of the colorimetric parameters of colored objects. Flatbed scanning is fast, easy to use, cheap, robust, independent of external light conditions, and with good accuracy. The scanner head (includes mirrors, lens, filter, and CCD array) move over the sample line by line, by a belt attached to a steep motor. Qualifying specification parameters for a scanner are bit (color) depth, resolution, and dynamic range. The higher the scanner's bit-depth, the more accurately it can describe what it sees when it looks at a given pixel. Resolution relates to the fineness of detail that a scanner can achieve and is usually measured in dots per inch (dpi) [47].

The computer hardware and software, which imitates the human brain, is another key component of the computer vision system. Hardware includes a personal computer and color monitor. The personal computer provides disk storage for images and computational capability with vendor-supplied software and specific application programs. A high-resolution color monitor enables the visualization of captured images and the effects of various image analysis [17,28,41,48].

Image processing and analysis

Image processing involves a series of image operations that enhance the quality of an image in order to remove defects such as geometric distortion, improper focus, repetitive noise, non-uniform lighting and camera motion. Image analysis is the process of discriminating the objects (regions of interest) from the background and producing quantitative information, which is used in the subsequent control systems for making decisions. Image processing and analysis steps can be divided into three levels: low, intermediate, and high [28,36]. Low-level processing includes image acquisition and pre-processing. Image acquisition encompasses images capturing, with a digital camera, and digitization with a frame grabber (if an analog camera is used). The pre-processing purpose is to improve image quality. The pre-processed image is enhanced in terms of the correction of geometric distortions, the removal of noise, grey level correction, and correction for blurring. Intermediate-level processing involves image segmentation, representation, and description. Image segmentation can be achieved by threshold, edge-based, and region-based segmentation [28]. The main aim is to divide an image into regions that have a strong correlation with objects of interest. High-level processing involves recognition and interpretation, using statistical classifiers or multilayer neural networks of the region of

interest. Neural network and fuzzy logic operations have been implemented successfully with computer vision in the food industry [49].

The core technique in computer vision is always related to image processing and analysis. The primary types of object measurements (size, shape, color, and texture) can be acquired from any images [50-51]. In computers, images are stored and processed in the form of matrices whose elements are pixels. Two types of information are stored in pixels; geometry information (location of pixels in the image) and surface information (intensity values associated with pixels). From the geometry information, the size and shape of the object can be obtained. Color and texture can be extracted from the object surface information.

CVS and color determination

Instrumentally, color measurement can be carried out using conventional or digital (CVS and image analysis) instruments. Instruments for the conventional color measurement are colorimeters, spectrophotometers, and spectroradiometers [52]. Commonly-used colorimeters are Minolta Chromameter, Hunter Lab colorimeter, and Dr. Lange colorimeters [53], which measure color only over a very few square millimeters, and thus their measurements are not very representative in heterogeneous materials such as most food items [53]. Because of this, the need for developing an automatic pixel-based color measurement process, using computer vision, increased. CVS has been used to objectively measure the color of different foods, analyzing each pixel of the entire surface of the food even when it is of non-uniform shape and color [53-54]. The CVS technique works by acquiring the image of an object, analyzing the image to extract the desired image attributes (color data) and presenting them numerically in a particular color space [55]. Colorimetry is used to explain how colors can be measured and specified in a scientific way. Color may be expressed in subjective (responses of the observer) and objective (measured by instruments) attributes. There are three psychological attributes for color description: hue, lightness, and chromaticity. Hue (h) is a color appearance parameter to which colors are described as red, green, blue, and yellow. Lightness (L^*) is a parameter for color brightness by which we can distinguish light and dark color. Chromaticity (C^*) or colorfulness describes the color sensation; when color is fully saturated, the color is considered in its purest version. Color measurement instruments transform or filter reflected spectra to produce reproducible color space coordinates, like L^*, a^*, b^*, R, G, B, h, C^*, V [56-59]. Color can be numerically represented by numerous color spaces. Generally, there are three types of color spaces, namely hardware-oriented space, human-oriented space, and instrumental space [60]. Hardware-oriented spaces are used in hardware processing, such as capturing, storing, and displaying (e.g. RGB and CMYK spaces). These color spaces can sense even a very small variation in color and are, therefore, popular in evaluating color changes of food products during processing [61]. RGB (red, green, blue) space is the most popular hardware-oriented space [52], in which color is defined by coordinates on three axes. Human-oriented spaces are linear with regard to the visual perception of human eyes and include HSI (hue, saturation, and intensity), HSV (hue, saturation, value) and HSL (hue, saturation, and lightness). They are not sensitive to a small amount of color variation, and not suitable for evaluating changes of product color during processing. Instrumental spaces are used for color instruments, such as the colorimeter and colorimetric spectrophotometer [62]. Instrumental spaces are CIELab, and CIELu*v*, and CIEXYZ spaces. The CIELab color space is an international standard for color measurements and the most used one due to the uniform distribution of colors that is close to the human perception of color [35,63].

Euclidean distance between two different colors corresponds approximately to the color difference perceived by the human eye [53].

Applications of computer vision method for cheese-quality evaluation

With numerous types of cheese and foods containing cheese available on the market, the necessity for the evaluation of cheese-quality properties continues to grow. Consumers' first impression of the cheese quality and desirability of the food is from its appearance. As a highly-versatile dairy ingredient, cheese can be used directly (unheated cheese) or indirectly (cooked cheese). Direct use is as table, sliced or shredded cheese and indirect use is in the form of cheese ingredients in numerous food products. Generally, cheese-quality characteristics can be observed as appearance attributes of unheated cheese at surface and appearance attributes of cooked cheese at the surface. Appearance attributes of unheated cheese are surface uniformity and smoothness, dimensions of shreds, extent of sticking and balling of shreds, size and uniformity of crumbled cheese pieces, level of curd fines, sharpness and uniformity of appearance of cut edges and corners of portions, degree of bending, drying or cracking of exposed slices, and the opacity or translucence. Cheese used as an ingredient in cooking applications attains a temperature of approximately 80–100°C. Although the appearance attributes of cooked cheese include visual uniformity, gloss, opacity/translucence, color, oiling-off, flow/surface coverage, shred identity, browning, crusting or burning, a key aspect of the cooking performance of cheese is the heat-induced functionality, which is a composite of different attributes, including softening (melting), stretchability, flowability, apparent viscosity, and tendency to brown. Examples of cheese-cooking applications are grilled cheese sandwiches, pizza pie, cheeseburgers, pasta dishes and sauces. Cheese-quality attributes can be grouped into microbial, chemical, physical, and functional categories. Attributes of interest for CVS are mostly physical, sensory, and cooking. According to Peri [64], cheese quality may be defined as the degree of acceptability of the product to the end user. Quality criteria involves different types of characteristics, including:
- − sensory (taste, aroma, texture, and appearance);
- − physical (sliceability, crumbliness, hardness, springiness, mouth-feel);
- − cooking (extent of flow, stringiness, browning);
- − compositional/nutritional (contents of protein, fat, calcium, lactose, sodium);
- − chemical (intact casein, free fatty acids, free amino acids);
- − safety (absence of pathogens, toxic residues, foreign bodies and conformity to approved levels of substances such as biogenic amines).

Cheese color

Color is an indicator of food freshness, ripeness, desirability, and safety [58,65-66]. Thus, color is an important sensory attribute of dairy products. Many factors can affect the color of dairy products like the composition of milk, food additives, manufacturing technology, natural milk microflora activity, maturation techniques during manufacturing, etc. The measurement of color allows for the detection of certain anomalies or defects that food items may present [53]. Color measurements are mainly carried out in two ways: sensory visual evaluation and instrumental analysis [67]. Increased requirements for quality by consumers require the color evaluation of food products to be more rapid, objective, and quantifiable. Sensory visual evaluation is laborious, time-consuming, costly, and tedious. For these reasons, it is recommended to determine color using color-measuring

instrumentation [53]. The color of cheese ranges from white to orange. A color measurement is used routinely in quality control and product development to assess the color of curd and cheese. The natural milk microflora activity, the technological processes, and the maturation techniques can change cheese color. Color is related to the diet of a cow, with the addition of coloring and cheese variety. Recent studies also highlight the potential role of colorimetry in assessing the ripening of smear-ripened cheese [69, 68] and for measuring defects, such as browning, during cheese maturation [70]. The yellowness of cheese is affected by the presence of carotenoid in the milk, which is dependent on the composition and the type of feed. Research on cheese color as a function of ripening time by Rohm and Jaros [71-72] reported a decrease of L^* value and an increase of a^* and b^* values during the ripening of Emmental cheese. Ginzinger et al. [73] reported that the yellowness index, a one-dimensional measure of cheese color highly correlated with b^*, increased as cheese aged. Other than traditional color preferences, such as orange Cheddar and white goat's cheese, the most important color parameter is uniformity (no uniform cheese color may signal a manufacturing defect). Buffa et al. [74] investigated the color change of cheese made from raw, pasteurized, and pressure-treated goat's milk. Color was measured using the HunterLab spectrocolorimeter in L^*, a^* and b^* values. Color evaluation demonstrated significant differences between cheeses due to milk treatments and ripening time. The a^* value did not show a definite trend throughout ripening, the L^* value decreased and the b^* value increased as the cheese aged. Contrary to these results, Marchesini et al. [75] reported that crude protein and fat significantly increased through the period of ripening, and led to a significant decrease of the L^*, a^* and b^* values of Asiago cheese color. Through ripening time, there is a high rate of increase in water-soluble nitrogen in a raw milk cheese. Lower moisture and the higher water-soluble nitrogen content could cause an increase of mechanical openings in the cheese surface and the formation of a less homogeneous and less compact protein matrix, resulting in a reduction of lightness values. Food coloring is also added to make certain cheeses appear distinct. For example, the orange color of Cheddar cheese is due to the addition of annatto, a yellow/orange colorant, which is added to achieve a consistent color over seasonal changes [76]. Poltorak et al. [77] measured the color of selected cheeses available in the Polish market with different fat contents, as well as cheeses containing vegetable oil as the milk fat substitute. Color attributes L^*, a^*, b^*, h and C^* were measured using a chromameter. They observed that the cheeses with reduced milk fat content were significantly lower in C^* and b^* than the full-fat cheeses. Similarly, b^* of cheese made with canola oil, substituting for milk fat, was significantly lower. This was attributed to the fact that the vegetable oils could not markedly affect the intensity of yellow color in cheeses.

Cheese defects

Mechanical openings (gas/eyeholes; slits)

Changes in mechanical properties during cheese ripening are major factors contributing to obtaining the desirable openings (eyeholes) instead of slit formation. The eye (gas) holes size, number, distribution, and shape contribute to the typical features of each cheese variety. When the size, number, distribution, and shape of the eyeholes is correct throughout a cheese block, eyeholes are considered as a desirable feature of the Swiss-type cheese (Emmental), Gouda, Ragusano, and Edam cheese. Eye formation due to gas production (CO_2 and N_2) is a major sign of the quality of some types of cheese (Swiss-type

cheese). Gas holes formed in other cheeses (Tilsit and Havarti) are not called eyes but are typical of these cheeses [78]. In contrast, in other cheese varieties (Cheddar) gas production is considered as a defect [79]. Even in cheeses where eyes or holes are expected and accepted, slits or cracks are formed under certain conditions. The gas holes are normally round shaped and shiny eyes. A good close-knit texture will allow for eye formation and hole growth in Swiss cheese. The negative impact of gas production in cheese can be manifested as an undesirable and atypical appearance and texture with gas holes, and undesirable or atypical aromas and flavors. The negative impact of gas production can be caused by clostridia or excessive CO_2 production. Defective eye formation, white spots and a putrid smell in Swiss-type cheese caused by clostridia reported Le Bourhis et al. [80]. Excessive CO_2 production in Swiss-type cheese in a later stage of ripening (after warm room) with a formation of oversized eyes and cracks or splits is referred to as late or secondary fermentation [81]. Caccamo et al. [32] investigated the use of image analysis to measure the amount of the surface area of cheese slices occupied by gas holes for Emmental, Ragusano, and Cheddar cheese. Slice thickness of Ragusano and Cheddar was 1 cm, and 1 mm for Emmental cheese. The aim of image processing was to determine the intensity of the red, green, and blue (RGB) channel of each pixel. The channel that produced the best contrast between holes and areas of the cheese with no holes were applied for further analysis. For the Ragusano and Emmental cheeses, the blue channel was best, while the red channel was best for the Cheddar cheese. Threshold method was used to measure the percentage of the total area occupied by gas holes. Image analysis could be a useful tool for quantitative measurement of the normal amount of gas production, for variation in the amount of gas production across time, and abnormal shape or distribution of eyes throughout the structure of Emmental cheese. Melilli et al. [82] reported the development of early gas defects in a brine-salted pasta-filata Ragusano cheese. In brine-salted cheeses, made from raw milk, early gas formation is typically the result of poor milk quality, poor hygienic conditions during cheese making, slow acid production during cheese making, and slow uptake of salt from brine. Coliform bacteria are a major contributor to early gas production in raw milk cheeses [83], which enter into the cheese from the raw milk and from the environment during cheese making. Because of slow salt uptake by cheese during brining, early gas formation occurs in the form of small numerous holes. Melilli et al. [82] investigated the combined impact of pre-salting the curd before stretching, brine concentration (saturated vs. 18% salt brine), and brine temperature (12, 15, and 18°C) on coliform count and the development of early gas defects in Ragusano cheese. Results showed a reduction in coliform bacteria in pre-salted Ragusano cheese as a result of a 3-way interaction effect between salt and stretching temperature and curd pH that significantly reduced the survival of coliform in the cheese.

Some cheeses have a characteristic open texture, with many mechanical openings called slits (Samsoe, Havarti, and blue varieties) [79]. Undesired gas production can result in the appearance of slits, cracks or huffy packages, which are problems in Cheddar cheese [84]. Slits is a term to describe fissures or cracks in the body of the cheese that can be longer than 3.5 cm. The formation of slits has been attributed to a wide variety of causes and interactions (trapped air, refrigerated storage, early and late abnormal gas production). Air entrapped during the compression of curd is thought to be responsible for open texture. The isolated pockets of trapped air form numerous small irregular holes in the cheese (slits). Slit defect can appear during refrigerated storage after the eyes have fully developed and the cheese is moved from the warm room. Early abnormal gas production is typically produced by coliforms, while late gas production is typically caused by Clostridium tyrobutyricum [79,85]. White et al. [86] and Dorge et al. [87] have explored the

development of slit openings during ripening by nonstarter bacteria. Fox et al., [79] indicate that one of the least-controlled defects in round-eye cheeses is the development of slits that appear during refrigerated storage after cheese is removed from the warm room. Cheddar cheese should not have gas defects. In Cheddar cheese, slit formation is due to gas production from citrate-fermenting lactobacilli. This defect manifests itself at about 90 to 120 d of aging [79]. There is a high demand for the non-destructive monitoring of eye formation in cheese during and/or after ripening (Figure 1). The image analysis approach was capable of distinguishing slits from areas with no slits and could provide a quantitative estimate of the percentage of area represented by slits. Caccamo et al. [32] developed an image analysis method to analyze the SEM images of cheese microstructure in routine production. Guggisberg et al. [88] used the X-ray CT measurements – as a non-destructive technique – of the cheeses during their ripening for monitoring of eye formation and growth. Schuetz et al., [89] reported computed tomography measurements as a useful and non-destructive tool to monitor the size of individual eyes in cheese and to investigate the overall mechanism of eye formation in cheese. The CT technology distinguishes materials of different density and, therefore, cheese eye volumes can be quantified without destruction of the cheese.
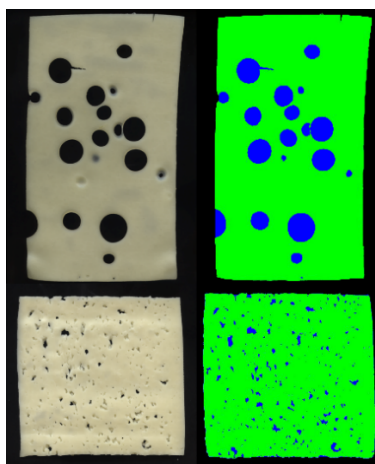
Figure 1. Emmental and Tilsit cheese – images prepared for image analysis of gas holes

Rind defect (formation of calcium lactate crystals and excessive rind halo)

The formation of calcium lactate crystals has been attributed to the supersaturation of the serum phase of the cheese with calcium and lactate ions, which crystallize and eventually grow into larger aggregates [25,90]. When present on the surface of Cheddar cheese, the calcium lactate crystals form white specks or a haze on the surface of the cheese. Even if they are not harmful, they constitute a significant quality problem for producers of Cheddar, as a microbial problem [91]. Rajbhandari and Kindstedt [25] reported the use of the digital photography and image analysis to measure the area occupied by calcium lactate crystals on surfaces of naturally-smoked Cheddar cheese samples (Figure 2). Results show that image analysis may serve as a useful tool for quantitatively evaluating the effects of factors such as cheese composition, packaging conditions, and

storage temperature on rate of the crystal growth and time of crystal appearance during storage.

Ripening influences the development of sensory characteristics of cheeses due to its effect on the chemical composition. The problem of abnormal coloring in the rind (black spots, unwanted yellow and orange colorations, and tray marks) may be due to colonization by yeasts, molds or bacterial populations influenced by environmental factors, especially in the airing area and ripening chambers [92–93]. During ripening, cheese loses moisture and the color of the paste becomes darker. Many parameters can cause a dark paste color of cheese, e.g. an excess amount of salt or an inadequate ripening, with high temperatures or excessive air velocity. The presence of an excessive rind halo, an irregular color, and a too dark or too white paste color is one of the main paste color defects. Figure 2 shows the application of image analysis of cheese defect named as excessive rind halo. Zabaleta et al. [94] investigated the sensory quality control of a semi-hard sheep's raw milk cheese variety over five consecutive years (2006–2010) and tried to describe the main sensory defects (eyes, paste color, rind, flavor, texture, and shape) that appear in semi-hard sheep raw milk cheese. One of the investigated cheese defects reported in their paper is an excessive rind halo, described as a too dark or wide paste border. Obtained results showed that medium- and long-ripened cheeses presented a higher percentage of an excess of rind halo with a darker paste color, animal flavor, and marks in the rind.
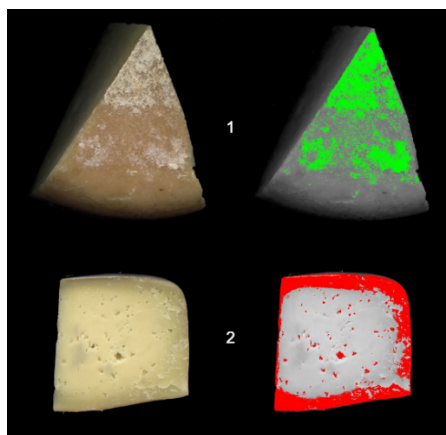
Figure 2. Cheese defects analysis:
1 – Formation of calcium lactate crystals; 2 – Excessive rind halo.

Visual texture

Image texture analysis is a characterization of visual texture (e.g. rough or smooth), estimated from the digital analysis of an image, enabling information on surface characteristics (shape, dimensions). Image analysis has the potential for analyzing cheese surfaces for features of relevance to quality control, such as roughness, smoothness, shininess, graininess, veins, cracks and slits. Image texture analysis has acquired a wide variety of imaging techniques in the food industry, like online digital cameras or scanners, light and confocal laser scanning microscopes, hyperspectral imaging systems, X-rays, and ultrasonic devices.

Amount and distribution of added ingredients

Many cheesemakers add flavor ingredients to cheese. Instead of smoked cheese, they produce cheese with added herbs (e.g. parsley, chives, and garlic) or spices (e.g. chili, cumin, black pepper, dried fruits, lavender or truffles). Digital image analysis can be used for evaluation of the addition of some ingredients (herbs, spices, vegetables, etc.) and evaluation of the amount and distribution of added ingredients into the cheese (Figure 3). Pasteurized cheese with vegetable ingredients is one of the new products that may be added to sandwiches, salads, sauce, toast, and pizza. Jelinski et al. [65] used computer vision to determine the distribution and amount of ingredients (garlic, parsley, and pepper) in pasteurized cheese. For localization and extraction of the ingredients, they used a threshold algorithm. An algorithm for image pre-processing was developed in order to extract the area of the edge of the cheese and then to extract the ingredients, using, for that purpose, the quantification of color and localization of the ingredient. It was found that the distribution and amount of ingredients in the samples were determined within a high accuracy when compared with the results of a sensory method. Cheese with garlic and parsley showed 88% accuracy, and cheese with pepper and parsley showed 81% accuracy. The results found in this study were promising, and the algorithms developed may be applied in the inspection of different kinds of cheese with ingredients. Different backgrounds were tested, with the black background presenting the best results. It should be highlighted that, for the image acquisition of the analyzed cheese, a scanner was used rather than a camera, the latter being the most usually used equipment in similar studies.
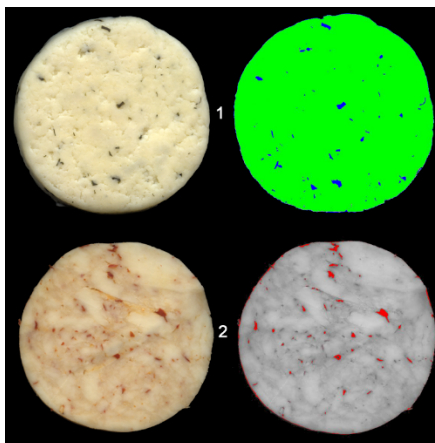
Figure 3. Image analysis of cheese ingredients
1 – herbs; 2 – red paprika.

Shreddability

Good shreddability is characterized by the free flow of the shredded cheese and a low tendency of the cheese shreds to stick together to form balls or clumps. Cheese with relatively low moisture, high protein, low proteolysis, and a high calcium-to-casein ratio tend to have a better shreddability (Emmental, Gruyere, low-moisture Mozzarella, Gouda, young or medium aged Cheddar and Provolone), than cheeses that have relatively high

moisture, a high degree of proteolysis, low calcium, and low protein-to-fat ratio (Tetilla and Fontina) [95]. Other factors that are conducive to the clumping of shredded cheese include longer shred length and shred diameter, and free fat content. A computer vision method was used for determining the length of Mozzarella cheese shreds [96]. An image processing algorithm was developed to analyze the image of cheese shreds without manually separating them and to quantify morphological features to characterize the lengths of individual cheese shreds. The developed method was successful in recognizing individual shreds, even when shreds were touching or overlapping [29]. Current shred evaluation methods are manual, which is an extremely time-consuming process. Ni and Gunasekaran [30], for cheese shred length measurements, used a robust and efficient algorithm, the X–Y sweep method. Obtained results showed an accuracy of 99%, and the X–Y sweep method can work correctly with all the shred-shaped objects. The X–Y sweep measurement data can be used to compute certain quality indices to characterize the degree of free-flowing and the degree of matting of the shreds.

Cooking properties

Process cheese is made by further processing, which involves the blending and shredding of finished natural cheese. Meltability is a major functional property of cheese, especially in the applications of cheese as toppings or ingredients in prepared consumer foods. The CVS method was employed to analyze the characteristics of Cheddar and mozzarella cheeses during cooking and the results showed that the method provided an objective and easy approach for analyzing the functional properties of cheese.

Meltability (Flowability), Browning and blister formation, Oiling-off

The meltability (flowability) is the extent in dimension to which melted cheese flows and spreads upon heating, expressed as a percentage of the dimension in the unheated sample. The uniform melting quality of processed cheese is considered as a desirable property [97[. The ability to soften on heating is had by most cheeses, e.g. Cheddar, Gouda, Emmental, Mozzarella, Raclete, and Blue cheese. Various tests have been described in the literature to measure flowability: Arnott test, Schreiber test, Price-Olson test [97-102]. The melting quality of cheese is defined as the property of cheese shreds to fuse together upon heating. Several papers reported on the melting properties of Mozzarella cheese. The most popular empirical methods to measure or quantify Mozzarella-melting properties are the Arnott test [97] and the Schreiber test [99–100]. In these tests, a thin disk of cheese is heated at a pressed temperature and duration (Arnott test: 100°C for 15 min; Schreiber test: 232°C for 5 min) and the change in sample height (Arnott test) or diameter (Schreiber test) is measured and used as an index of cheese melting. Melting quality was expressed as a percentage of the dimension in the unheated sample [97-100]. Olson and Price modified the Arnott test to measure the melting behavior of pasteurized processed cheese. A thin disk of cheese (25 mm diameter, 40 mm height) is placed in the closed end of a glass tube (30 mm diameter, 250 mm height) placed horizontally on a baking sheet in the pre-heated oven (at 180°C) and heated for 15 minutes. At the end, the flow distance was measured with a ruler and expressed in millimeters [102]. Muthukumarappan et al. [99] investigate the effect of the different oven temperatures and different heating surfaces (glass Petri dish, aluminum plate, and stainless steel) on the area of melted cheese. The meltability of Mozzarella

cheese was measured using a computer-imaging system with a CCD video camera. According to results, all the three surfaces can be used in evaluating the sample meltability at 90°C. For an index of cheese meltability, authors recommend the measurement of a sample melt spread area, rather than its change in height or diameter. Wang and Sun [26-27,33] applied a similar procedure to measure the cheese spread area upon melting. The meltability was calculated as the final area minus the original area of the cheese sample. The attractiveness of a pizza comes from its toppings. Mozzarella is used mainly as a pizza topping, based on its functional properties: meltability and stretchability (ability of heated cheeses to form strings and/or sheets when extended uniaxially). With the aim to determine pizza topping percentage and distribution Sun [28] and Du and Sun [51] developed a computer vision method. In order to determine the topping distribution, they developed a new region-based segmentation technique that can effectively group pixels of the same topping together. The method is based on dividing a pizza image into several equal-area partitions and was developed for measuring topping distribution evenness. Results showed that the new algorithm could reach an average accuracy of 90% and is capable of processing different types of pizzas. Wang and Sun [33] used CVS to measure the melting properties of Cheddar cheese. Melting property was expressed as the area expansion of the Cheddar cheese slices after cooking. Wang and Sun [26] reported that the melting characteristics of Cheddar and Mozzarella cheese were determined with a computer vision system and compared with those obtained from the Arnott and Schreiber tests. The meltability of Cheddar and Mozzarella cheese, determined with the CVS method, correlated well with the results obtained from the Arnott and Schreiber tests (Figure 4 and Figure 5). They concluded that the CVS method offers a promising new approach in cheese meltability determination. Wang and Sun [26], in their study, reported that the dimensions of cheese slices play an important role in measuring the melting property of cheese, irrespective of cheese variety. This implies the need for standardizing sample dimensions in the measurement of melting characteristics. Employing CVS as an instrument provides a solution for determining the meltability of cheese accurately and reliably. The method is capable of handling specimens in a wide range of sizes, thus, it is more flexible. Everard et al. [103] use a computer vision method to measure the effects of inorganic salt content, moisture/fat ratios and aging on Cheddar cheese meltability.
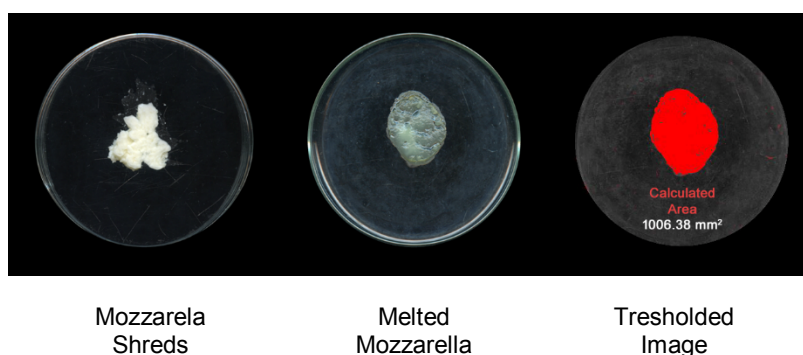

Mozzarela
Shreds

Melted
Mozzarella

Tresholded
Image

Figure 4. Mozzarella flowability – Schreiber Test
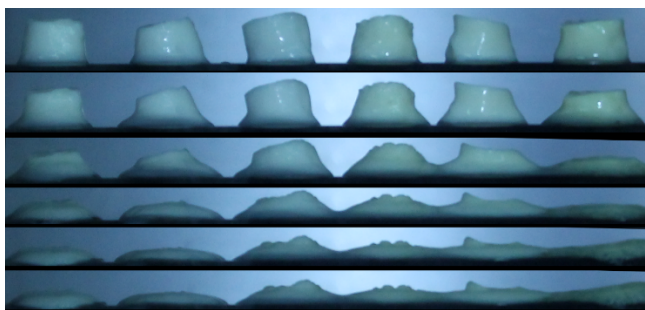
Figure 5. Mozzarella flowability – Arnott Test

Browning and blister formation

CVS and digital imaging technology have been applied to quantify the pizza-baking properties and performance of different cheeses (Mozzarella, Cheddar, Colby, Edam, Emmental, Gruyere, and Provolone [104], including the browning and blistering [105]. Light-brownish discoloration is observed on the cheese surface after cooking cheese and cheese-containing foods. Browning property is the overall color evaluation of the cheese after pizza baking. Mild browning is acceptable and even desirable, while excessive browning is undesirable [106]. CVS technology has been used successfully to assess the browning of cheese during heating. Compared with conventional methods using colorimeters, the computer vision method is efficient and provides more information on the color change of cheese by making continuous measurements possible. It also has the advantage of handling surfaces with uneven color distributions, such as cooked Mozzarella cheese. Wang and Sun [34] investigated the browning properties of Cheddar and Mozzarella cheeses. Browning results from Maillards reactions of sugars with amino acids at high temperature. This can come from residual lactose or galactose after cheesemaking, or when ingredients such as skim milk powder are added to the hot cheese as part of the cooking/stretching process. Browning can be controlled by varying the content of galactose and amino acid [34,105]. Browning can be considered as a defect in processed cheese, or as desirable property when it is used as cheese toppings. The preferred appearance for Mozzarella cheese baked on a pizza is the formation of evenly spread brown blisters over the white/yellow surface of the cheese, rather than a general browning. Blister formation can be evaluated by measuring the size and the shape of cheese blisters on pizza, and browning can be quantified using computer visioning [33-34,104,107]. The blistering and browning of cheese during baking results in a nonhomogeneous color distribution on pizzas. The blister color of pizza cheese can be assessed directly on baked pizza or indirectly by heating the cheese in a boiling water bath [105]. Blister formation occurs during pizza baking. Blisters are trapped pockets of heated air and steam that may be preferentially burned during baking, and blistering has been suggested to be affected by cheese-melt properties. During the heat treatment of a pizza surface, evaporating water and air are trapped between cheese shreds, and collected in bubbles under the melting cheese surface. Steam and air expand. A thin layer of cheese is lifted off the rest of the pizza, initiating the blister formation. The top of the blister becomes thinner during cheese rising. Liquid fat at the surface flows down the sides of the forming blister, moisture is lost from cheese at the top surface of the blister, and the top of the blister turns brown. At other

locations on the surface of the pizza, the cheese retains its white color because the free oil present there prevents excessive moisture loss from the surface. Mozzarella is the most prone to blister formation, especially when baked on a pizza [104,107-108]. Large blisters are usually less circular than smaller blisters, and cheeses with lower elasticity or stretching resistance can form larger blisters [108]. Cheeses with higher salt content have smaller blisters and this was thought to relate to the softening temperature increasing at higher salt levels.

Oiling-off

Oiling-off is the tendency of heated cheese to exclude oil. This ability is typical for most rennet curd varieties. The conventional method for oiling-off the properties of cheese determination is with a fat-ring test using filter paper [109], or a quantitative test using centrifuges [110]. A fat-ring test considers placing a cheese disc of specified dimensions on a circular filter paper, heating under defined conditions of time and temperature and cooling. Computer vision method was developed as an effective and efficient method for determining the oiling-off property of cheese (Figure 6). The oiling-off (free oil formation or fat leakage) property of cheese is the separation of liquid fat from the melted cheese body into oil pockets, particularly at the cheese surface.
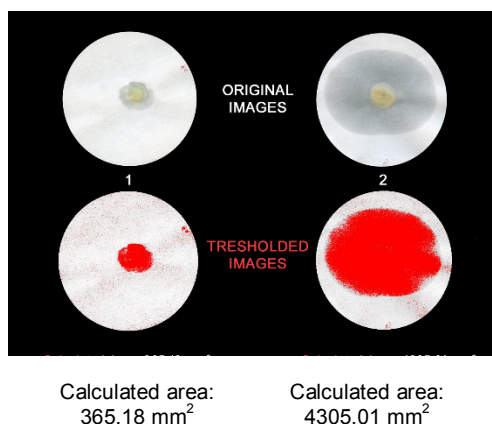
Figure 6. Mozzarella samples with small (1) and large oiling-off effect (2).

Oiling-off property can be considered as a desirable quality when is used as cheese toppings (provides the pizza with a shining appearance) or as an unacceptable defect in processed cheese [110–111]. The moderate release of free oil from cheese during heating is desirable in most cooking applications. Wang and Sun [112–113] studied the oiling-off property of cheese with computer vision. Free oil released on heating was absorbed by the filter paper forming a ring, the diameter of which was indicative of the extent of oiling-off. Wang and Sun [112] investigated the impact of the dimensions (area and thickness) of cheese samples on the oiling-off property of Mozzarella and Cheddar cheese, and a wide range of image features extracted from images of cheese (before and after cooking). Extracted image features were luminance, histogram-related and percentage oil area features. The results showed a temperature-dependent relationship between image

parameters and fat leakage. The change of percentage oil area upon cooking was in good accordance with the oiling-off property of cheese as observed, presenting a proper description of the oiling-off property of both Cheddar and Mozzarella cheeses. Along with its significant correlation with fat leakage, the percentage oil area was considered as a suitable oiling-off index. Correlation between CVS and traditionally fat-ring tests for evaluation of the oiling-off property of cheese (Cheddar and Mozzarella) was significant, as reported by Wang and Sun [112]. The results showed that it is possible to determine the oiling-off property of cheese with computer-vision image features. For determination of the oiling-off property of cheese, image features were extracted from segmented images. All cheese discs were melted into an uneven area and produced an oil ring around them. The oil area was segmented by a threshold method and their total area was measured with the computer-vision system. Extracted image attributes from images of cheese before and after cooking were luminance features, histogram-related features, and percentage oil area. The histograms of cheese discs were extracted in order to compare the gray-level distribution of cheese pixels before and after cooking. Luminance features were extracted from segmented cheese images on the gray values base. The results showed a good and temperature-dependent correlation between luminance features, percentage oil area, and fat leaking. Therefore, the number and intensity of gray-level pixels are the most promising image feature for the evaluation of the oiling-off properties of cheese, indicating excellent oiling-off representation by careful thresholding and appropriate parameter definition.

Advanced use of computer vision in cheese-quality evaluation

Curd moisture content in cheese is determined by syneresis of curd. In the cheese industry, syneresis is empirically controlled, and there are no technologies available for the online monitoring of curd syneresis to assist the cheesemaker [114]. Continuous measurement of curd moisture during syneresis is challenging, which limits the precision and accuracy of all reported methods [115-117). Increasing temperature (cooking) of the curd/whey mixture enhances syneresis, which is reflected in a lower moisture content of cheese after pressing. The control of syneresis is important because curd moisture content has an impact on cheese ripening. Computer vision and colorimetric techniques were investigated as a potential means of monitoring the gravimetric measurements of curd and whey during the syneresis phase of cheese manufacture in a stirred-curd context. Computer vision techniques distinguished the effects of pH and stirring speeds, and it was shown that, with the inclusion of known factors and calibration to a range of operating conditions, there is the potential for predicting a syneresis endpoint. It was found that the accuracy of a computer-vision system for monitoring syneresis improves with size of field of view [22, 103, 114, 118–119]. Syneresis was studied using images captured of the surface of the curd/whey mixture, using five image texture analysis techniques by Fagan et al. [120]. A wide variety of approaches is emerging for image texture analysis, as illustrated by the fact that five different techniques were compared in that study. Mateo et al. [119] reported the comparison of two online optical sensing systems for monitoring syneresis during cheese manufacture, with a digital camera and online visible-near infrared (NIR) sensor. Digital cameras capture spatial information and store images of the curd/whey mixture. The shrinkage of curd pieces is measured using image analysis. An online visible-near infrared (NIR) sensor was used for predicting syneresis indices and it was concluded that this technique was adequately robust to be implemented in the cheese industry to facilitate information about critical steps of production. An online visible-near infrared spectroscopy

has potential as a useful process analytical tool for better online process control and to provide benefits to the cheese industry. The hyperspectral imaging (HSI) combines conventional spectroscopy and imaging techniques to acquire both spectral and spatial information from an object simultaneously. A typical HSI system consists of a high-performance camera with a large dynamic range, low noise level, good quantum efficiency, an imaging spectrograph, and a stable light source [121]. The result of the measurements with HSI is a three-dimensional data structure or a hyperspectral data cube ('hypercube') in which each pixel of a hyperspectral image can be interpreted as a spectrum [122–124]. Gowen et al. [125] reported on the potential applications of HSI for quality control in dairy foods. HIS technique could be able to detect the presence of starch, incorporated as an adulterant, in fresh cheese [14], quantization of sugar, citric acid, and salicylic acid in different types of cheese, for classification of cheese according to protein, fat, and carbohydrate content [126–127] and detecting water in cheese in an individual sample. The detection of contamination on cheese, in this example a slice of cheese with plastic contamination, was imaged using the NIR HSI system. Gunasekaran and Ding [128] reported the three-dimensional analysis (3-D) of microstructure characteristics of fat globules in Cheddar cheese using confocal laser scanning microscopy (CLSM) and image analysis. 3-D information is important to evaluate accurately microstructural characteristics of cheddar cheese. CLSM as an alternative way to observe food structure with high resolution, without disturbing the internal structure. Image analyses were used to evaluate the number, size and shape characteristics of fat globules in the samples as the process parameters and fat levels may be changed to achieve the required textural qualities. This method enables the in situ 3-D evaluation of fat globule characteristics. Recently, image analysis has been applied for analysis of the SEM images of cheese microstructure [129].

Conclusion

CVS is primarily a substitute for human vision. Digital image analysis represents an efficient and non-invasive inspection technique able to investigate the food optical properties and, when combined to suitable classification models, to give information concerning their composition and structure. This technique has been successfully applied to the study of the optical properties of various dairy products.

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The use of enzyme preparations for pectin extraction from potato pulp

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Abstract

Introduction. The use of enzyme preparations at various stages of the technological process of extracting pectin from potato pulp and their influence on yield and purity of pectin has been studied.

Materials and methods. The hydrolysis of potato pulp's protopectin was carried out in various ways using hydrochloric acid, enzymatic preparations of cellulolytic and amylolytic activity at different stages of the technological process and in a combined method.

Results and discussion. The effect of a complex enzyme preparation of cellulase on the final produce yield and quality has been researched. It was stated that adding the enzyme preparation at the stage of preliminary treatment of raw materials in an amount of 0,1% of the total dry matter mass (accordingly 9 CU/g of raw material) in combination with acid-thermal hydrolysis leads to an increase in the recovery of alcohol-sugared potato pectin from 7% to 13,6%.

The positive influence of amylolytic enzyme preparations on the physical and chemical properties of potato pectin has been proved. Dosage of the enzyme was carried out in the amount of 3 AU/g of absolutely dry starch. The use of amylolytic enzyme preparations in order to process potato pulp in combination with acid hydrolysis raised the uronide component of potato pectin from 27.4% to 42%.

The study of the structure of potato pectin samples, extracted under different conditions, by comparison of infrared spectra has been carried out. We have used the method of X-ray diffraction analysis to investigate changes in the structure of potato pectin obtained by different methods and compared it with potato starch. It is proved that the use of enzymes at the stage of preliminary processing of raw materials increases the yield, purity and complexing ability of pectin.

Conclusions. The use of cellulolytic enzyme preparations and α-amylase in the technology of pectin extraction from a potato pulp in combination with acid-thermal hydrolysis leads to an increase in the yield and purity of potato pectin.

Introduction

Potatoes are grown in more than 130 countries of the world and ranked fourth in the world in terms of growing (after rice, wheat and corn). The average world annual potato harvest is 367.75 million tons. A large part of the potato is used for the production of potato starch [1], which in turn is widely used in the food and pharmaceutical industries.

Annually the mass of waste products of starch production – potato pulp – only in European countries is more than 1 million tons [2, 3], including about 40 thousand tons in Ukraine. Basically, these wastes are fed to cattle [2], but they may be an industrial source of such a valuable nutritional supplement as pectin.

One can trace investigations on the use of potato pulp as a source of bioethanol [4,5], edible fibers [2, 6–8], alcohol [9] and pectin [10–15].

Potato pulp consists mainly of four types of polysaccharides: starch, cellulose, hemicellulose and pectin. Depending on the regulation of the technological process with potato pulp, three target products for the food industry can be obtained: pectin with starch, pectin and fiber. It is known from literary sources that potato pulp contains from 15% to 30% of pectin substances and is considered to be a potentially new raw material for their obtaining [7, 8, 16-19].

Pectic polysaccharides, which are the main polysaccharides of potato cell walls, have a unique structure [20], they are mostly rich in ramnogalacturonan I [18, 19] (RG I, 75%) and homogalacturonan (HG, 20%) [20].

Methods of pectin extraction from potato pulp by using chelating agent [12, 21], in an acidic or alkaline medium, using enzymes and under pressure [15] are currently known. To reduce the starch content, the raw materials are pre-treated with amylolytic enzyme preparations.

Potato pulp contains a large amount of "bound" starch. During the process of protopectin hydrolysis, the starch is partially hydrolyzed to dextrin, and passes into the extract. While coagulating pectin with ethyl alcohol, high molecular weight dextrins are also precipitated, thereby affecting the properties of pectin. A lot of scientific papers are dedicated to the optimal parameters of enzymatic hydrolysis of potato pulp [2, 5, 22]. The enzyme processing is carried out during the preliminary processing of raw materials / or after separation of the extract obtained.

The technology of potato pectin extraction has not yet been sufficiently investigated and studied for its industrial implementation in comparison with the technology of citrus, apple and beet pectin. Potato pulp is not currently used in industry to manufacture commercial pectin, although it meets all the requirements and has a high content of pectin [19].

The purpose of the research is to study the methods of pectin extraction using enzyme preparations and determining their effect on the yield and physical and chemical properties of potato pectin.

Materials and methods

Chemical reagents and enzymes

Apple, beet and citrus pectins were extracted in laboratory conditions by means of acid-thermal hydrolysis of raw materials by the methods.

Arabinoza, xylose, glucose, rhamnose, galactose, mannose, potato starch.

α-amylase BAN-480L (Novozymes), glucoamylase Optidex-400L (GENENCOR), complex enzyme preparation of cellulolytic action "Cellulade" (Enzyme).

Pectin extraction

Pectin extraction was carried out by implementation of successive technological stages of hydrolysis-extraction, separation of pectin extract, neutralization, coagulation of pectin with ethanol, fixation of coagulum, drying and grinding of the finished pectin.

To study the process of hydrolysis, the accuracy of the hydrolysis parameters was the determining factor: pH, temperature, and the duration of the process.

Sample 1. Potato pulp was mixed with an acid solution, preheated to a hydrolysis temperature. The concentration of the acid solution, as a hydrolytic factor, was calculated depending on the set pH value of the hydrolysis mixture and taking into account the hydrolysis hydromodule. The hydrolysis hydromodule ($q_г$), which is determined by the ratio of the mass of the acid solution to the mass taken on the hydrolysis of the potato raw material, is given equal to 2 (the ratio of pulp raw material (RM): water as 1:10).

Acid-thermal hydrolysis-extraction of potato pulp was carried out using chloride acid at a temperature of 72–75 °C, pH of a hydrolysis mixture of 1.3–1.6 (1,45% HCl to a hydrolysis mass) for 70 minutes. The liquid phase was separated, neutralized with NH_4OH solution to a pH of 3–4. Pectin coagulation was carried out by means of ethyl alcohol (80%) at a ratio of extract: ethanol as 1 : 2. Separated pectin coagulate was further washed (fixed) with 96% ethanol, after which it was dehydrated, dried, ground and sifted.

Sample 2. Pectin, obtained from potato pulp, which had previously been subjected to processing with enzyme preparations of α-amylase and glucoamylase followed by acid-thermal hydrolysis of the raw material. Processing of raw materials of α-amylase enzyme preparation (EP) "BAN 480L" was carried out at a temperature of 72–75 °C, pH 6.0 adding EP in the amount of 3 AU/g of raw material for 30–40 minutes. To inhibit this EP, the mixture was boiled for 3 minutes, after which it was cooled to 50 °C and the EP of the glucoamylase "Diazyme SG" was added in an amount of 3 units of activity/g of RM. Processing was carried out at 50 °C., pH 4.0–4.5 for 6 hours. After this HCl solution was added and acid-thermal hydrolysis, extract separation, neutralization and coagulation of pectin was carried out, as described in the method of sample №1 obtaining.

Sample 3. The potato pectin powder obtained by the method of acid hydrolysis described above (sample №1) was dissolved in water and processed with EP amylolytic action: α-amylase and glucoamylase as described in the method of sample №2 obtaining. At the same time, during the whole time of enzymatic hydrolysis, samples of a qualitative reaction on starch with iodine were made. Upon completion of enzyme processing, pectin was again precipitated with ethanol as described above (see sample №1).

Sample 4. Potato pectin is obtained from the raw material of preliminary processed cellulase and α-amylase enzyme preparation followed by acid-thermal hydrolysis. Enzyme preparation processing "Cellulad" was carried out in the amount of 9 CU/g (cellulose units per gram) of raw material pH 5.5–6.5, temperature 50 °C for 3 hours. After that the hydrolysis mass of the α-amylase enzyme preparation "BAN 480L" in the amount of 3 AU/g (amylase units per gram) of raw material was added and processed at a temperature of 72–75 °C., pH 6.0 for 30–40 minutes. Acid-thermal hydrolysis of the mixture and subsequent pectin extraction operations were carried out as indicated in the method of sample №1 obtaining.

Sample 5. Potato pectin obtained by preliminary processing of pulp of cellulose enzyme preparation in the amount of 9 CU/g of raw material at pH 5.5–6.5, temperature 50 °C for 3 hours followed by acid-thermal hydrolysis (as in the method of sample №1 obtaining). Separated pectin extract was processed with a pH of α-amylase "BAN 480L" in the amount of 3 AU/g of raw material at a temperature of 72–75 °C, pH 6.0 for 30 minutes.

Pectin coagulation was carried out by means of the method described above (see sample №1).

Sample 6. Potato pectin obtained by means of enzymatic hydrolysis of potato pulp without using acids and other reagents. Enzymic hydrolysis was carried out by EP of cellulolytic action "Cellulad" in the amount of 9 CU/g of raw material at a temperature of 50 °C, pH 5.5–6.5 for 3 hours. Pectin coagulation was carried out by means of the method described above (see sample №1).

Beet pectin. Fresh beet pulp was extracted with a solution of hydrochloric acid at a 1 : 1 ratio at a temperature of 80–85 °C, pH 0.8–1.0 for 1 hour.

Pumpkin pectin. Parameters of hydrolysis of pumpkin raw materials were selected on the basis of the study of literary sources: the temperature 70–75 °C, pH 1,6–1,8; hydrolysis duration – 1 hour.

Sunflower pectin. To extract pectin from inflorescences of sunflower baskets, the parameters were used: the ratio of solid and liquid phases as 1 : 4, temperature 80–85 °C, pH 0.7, hydrolysis duration – 1 hour.

Citrus pectin. Pectin was extracted from citrus peels dried and milled by a laboratory mill. Parameters of hydrolysis-extraction are as follows: raw material ratio: extractant as 1:10, temperature 90–92 °C, pH 1,0–1,2, duration of the process 30–40 min.

Apple pectin. Apple pectin was extracted from fresh apple marc at a temperature of 80 °C, pH 1.6 for 1 hour.

Pectin extract coagulation, coagulate consolidation and drying was performed as described for sample 1.

Physical and chemical properties of potato pectin

The content of ballast substances in dry potato pectin was investigated by weight method. Analytical characteristics: the content of methoxyl, carboxyl groups, the uronide component – by titerometric method, the complexing ability, respectively [23].

Investigation of sorption ability

The sorption properties were determined on a McBen sorption-vacuum unit, where on previously dehydrated samples at temperature of 20 °C and pressure of 0 to 18 Mmhg the sorption of water vapor was carried out until a hygroscopic state was achieved. After that, desorption was performed in equilibrium conditions. To evaluate the sorption characteristics of pectin, a method of constructing sorption-desorption isotherms was used. A study of the sorption characteristics was carried out for five samples of potato pectin (numeration of samples according to the preliminary subparagraphs).

Isotherms of adsorption-desorption of water vapor of potato pectin were determined as the ratio of partial pressure of water vapor above the surface of the sample to the partial pressure of a saturated vapor of pure water.

$$a_w = P/Ps \tag{1}$$

To confirm the model of water adsorption by hydrocolloids, the first portion of the adsorption curve is represented in linear coordinates $(P/Ps)/a = f(P/Ps)$ through the Langmuir equation:

$$a = a_m B(P/Ps)/(1 + B(P/Ps)) \tag{2}$$

where a is the amount of substance that is adsorbed at a certain activity of water; a_m – the amount of adsorbed material required to cover the surface with a dense monomolecular layer; B – a constant characterizing the energy of the interaction of the adsorbate and the adsorbent (the energy of adsorption); P/Ps – relative equilibrium pressure of water vapor. The value of the capacity of the monomolecular layer (a_m) was found for the studied samples of potato pectin as a catagan of the angle of inclination of the straight line to the abscissa axis, $a_m = ctga$.

To describe and analyze this zone, we used the Freundlich empirical equation:

$$A = \frac{a}{m} = k \cdot p^{\frac{1}{n}} \tag{3}$$

where a is the amount of adsorbed substance; m – mass of adsorbent; p – equilibrium gas pressure in the system; $1/n$ – characterizes the intensity of adsorption; k – constant.

For the convenience of experimental data processing, the logarithmic form of this equation is used:

$$\lg a = \lg k + \frac{1}{n} \lg p \tag{4}$$

IR spectroscopy

Investigation of the monosaccharide composition of potato pectin was carried out using IR spectroscopy. Infrared spectra are recorded in the range of 400–4000cm^{-1} on the Fourier spectrometer of FT-IR Spectrum BX-II, Perkin Elmer. Samples were prepared in the form of KBr tablets.

X-ray diffraction spectrometry

The phase structure of pectin samples was studied by using X-ray method. The diffraction curves were recorded in "reflection" mode on an X-ray diffractometer HZG4A (Carl Zeiss, Jena, Germany) using copper (CuK$_\alpha$) radiation, nickel-filtered.

Electronic scanning microscopy

Electronic micrographs are made using a scanning electron microscope LEO 1420 (Germany).

Results and discussion

Influence of cellulase concentration on the yield of potato pectin

It is known that even under harsh conditions of hydrolysis of plant raw material (low pH, high temperature), the process of hydrolysis of protopectin is incomplete. In order to increase the yield of pectin, the enzyme preparation of cellulolytic action was used at the stage of preliminary processing.

In order to increase the yield of pectic substances of potato raw materials, the domestic complex enzyme preparation "Celulad" was used, with an activity of 9,000 CU/g ("Enzyme").

In the process of preliminary processing, the enzyme was added in an amount of 0.1%, 0.5%, 1% to the RM mass (9, 45, 90 CU/g of raw material, respectively). Enzymatic hydrolysis was carried out for 3 hours at a temperature of 50 °C at a hydromodule of 1: 2. After that, acid-thermal hydrolysis with chloride acid was carried out under optimal conditions: pH 1.6, temperature 72–75 °C, duration 70–75 min [33]. Also, pectin sample was obtained by using enzymes only (0.1% / 9 CU/g of raw material). The results of research on the pectin yield are presented in Figure 1.

Pectin was used as the comparison sample, removed by acid-thermal hydrolysis of the raw material under similar conditions without adding enzymes (Figure 1, control).
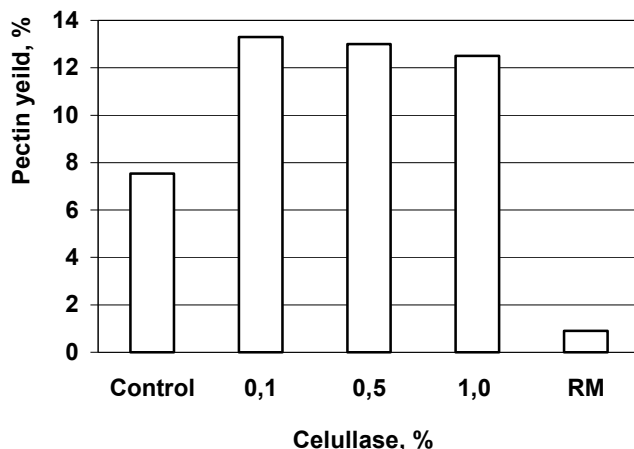
Figure 1. Dependence of the pectin yield on the enzyme concentration

Processing of potato pulp by cellulase leads to a significant increase in the yield of pectin, namely while adding EP in the amount of 0.1% in combination with acid-thermal hydrolysis, the yield is increased almost twice (from 7.54% to 13.3%). With a further increase in the amount of added enzyme preparation, there is no significant decrease in the pectin yield, and the use of only cellulases in the amount of 0.1% (9 CU/g of raw material) does not provide high results. Thus, the use of cellulolytic enzyme preparations at the stage of preliminary processing of plant raw materials in combination with acid-thermal hydrolysis allows a significant increase in the yield of pectin substances.

In order to obtain a pectin sample extracted without using acid and any other chemical reagents, we conducted a series of experiments using cellulase enzyme preparation to hydrolyze potato pulp (Figure 2). EP was added in the amount of 9, 18, 27, 36 CU/g of raw material.

The highest pectin yield (5.11%) was observed while using EP in the amount of 36 CU/g of raw material. It should be noted that despite the high yield of pectin substances in enzymatic hydrolysis, its coagulation structure is weak.

Figure 2. Pectin yield (% to the RM mass), depending on the dosage of cellulase enzyme preparation (CU/g of raw material)

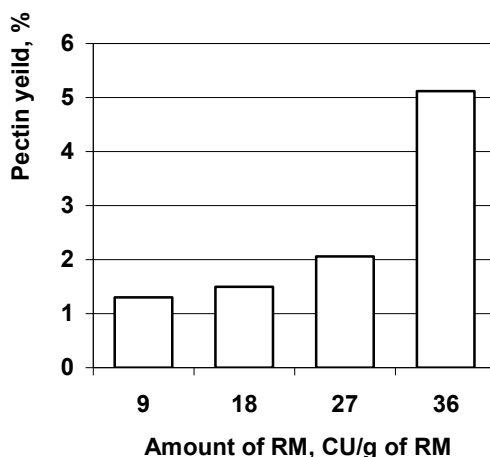Thus, on the basis of experimental researches it was established that the most effective use is the use of enzyme preparations of cellulase at the stage of preliminary processing of raw materials in the amount of 0.1% to the mass of RM under the conditions of enzymatic processing: pH 5.5–6.5, temperature 50 °C, duration 3 hours followed by acid-thermal hydrolysis of raw materials.

Influence of α-amylase enzyme preparation on pectin extraction from potato pulp

Using qualitative reaction to starch, it was found that the obtained potato pectin samples contain a certain amount of starch, which in a partially hydrolyzed state passes into the extract from the pulp and precipitates with ethanol. This is indicated by a blue color when adding an iodine solution to the obtained dry pectin sample.

In order to improve the pectin purity, we conducted a series of experimental studies on the methods of pectin extracting using amylolytic enzymes at different stages of the process, namely: use of α-amylase (AM) at the stage of preliminary processing of potato raw material (sample 4) and processing of the resulting pectin extract (PE) after acid-thermal hydrolysis (sample 5).

The bacterial α-amylase BAN-480L, with an activity of 1000 AU/g, was used for the research. Enzymatic hydrolysis of the pulp (sample 4) with this enzyme preparation was carried out at a temperature of 75 °C and a pH of the hydrolysis mass of 5.5–6.0, based on the specification of this EP. Dosage of the enzyme was carried out in the amount of 3 CU/g of raw material (in terms of starch). Enzymatic hydrolysis with amylase was carried out for 30–40 minutes.

The optimal duration of enzymatic hydrolysis and α-amylase enzyme preparation dosage was established by carrying out a series of studies on the accumulation of reducing substances in potato pulp hydrolysates, the concentration of which was determined by the Wiltshtetter and Schudl method. The results of the studies are presented in Table 1.

The content of reducing saccharides (in terms of glucose) in the hydrolyzate, depending on the amount of α-amylase added

Dosage of enzyme (amount of CU/g of raw material)	Hydrolysis duration, hour	Amount of glucose in the extractor, g	Glucose mass fraction, %
3,0	0,5	0,447±0,01	4,47
3,0	1,0	0,458±0,01	4,58
3,0	1,5	0,458±0,01	4,58
2,0	0,5	0,330±0,02	3,30
2,0	1,0	0,370±0,01	3,70
2,0	1,5	0,380±0,01	3,80
1,5	0,5	0,240±0,02	2,40
1,5	1,0	0,340±0,01	3,40
1,5	1,5	0,320±0,01	3,20
1,0	0,5	0,360±0,02	3,60
1,0	1,0	0,340±0,01	3,40
1,0	1,5	0,370±0,01	3,70

The dosage range of AM EP was chosen regarding previous studies. In addition, experiments were carried out with adding AM EP in the amount of AU/g of raw material, which showed that an increase in the number of enzyme preparation does not give high values – the glucose content was 4.16% to RM. While adding AM EP in the amount of 0,75 AU/g of raw material and 0.5 AU/g of raw material, glucose content in the hydrolyzates was 1.2% and 0.8%, respectively, indicating insufficient starch breakdown and is not effective.

Thus, enzymatic hydrolysis of potato pulp of α-amylase enzyme preparation should be carried out at a temperature of 75 °C, pH of a hydrolysis mass of 6.0, the EM dosage 3 AU/g of raw material for 30–40 minutes. An analysis of potato pulp micrographs of preliminary processed with amylolytic EP and without such processing, made using a scanning electron microscope on the content of starch grains (Figure 3) was carried out. Thus, in potato pulp, when using AM EP at the stage of preliminary processing of raw materials (Figure 3, c), there are no clearly expressed grains of starch in the field of view of the microscope comparing with the pulp, which was subjected to acid-thermal hydrolysis (Figure 3, b), grains of starch are outlined in the image. It should be noted that even under aggressive hydrolysis conditions, starch grains remain in the potato raw material. In the microphotography there is a significant amount of starch grains, which under these hydrolysis conditions are only partially hydrolyzed to dextrins and precipitated with ethanol. In the microphotography (Figure 3, a) of potato pulp, taken after the technological process of starch extraction, the starch grains are clearly visible among fiber particles. After enzymatic hydrolysis by α-amylase, the pulp does not actually contain starch grains (Figure 3, c), which confirms the effectiveness of the α-amylase preparations use for potato pulp preliminary processing before acid-thermal hydrolysis.
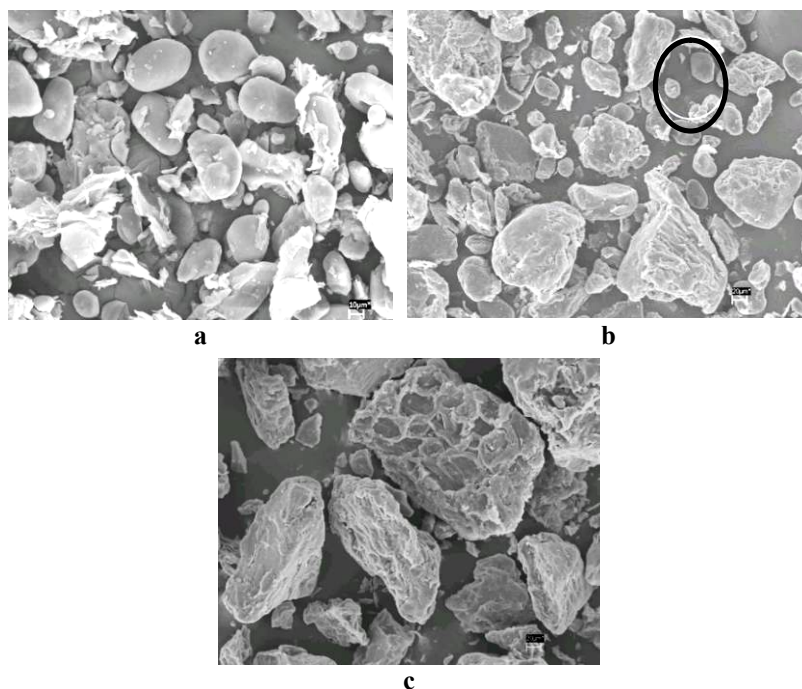
Figure 3. Electronic scanning microphotography of potato pulp:
a – after starch extraction (10 nm resolution);
b – after acid-thermal hydrolysis (20 nm resolution);
c – after the enzymatic hydrolysis of AM EP (20 nm resolution)

Enzymic processing of pectin extract (sample 5) was carried out after acid-thermal hydrolysis of raw materials, according to the following parameters: temperature – 75 °C, EP dosage – 3 AU/g of raw material, duration – 30 minutes, pH of the extract – 3–4. The extract neutralization to the pH value of 5.5–6.0 leads to deterioration of the final product quality – potato pectin. The potato pectin obtained in this way has better physicochemical parameters than potato pectin obtained only by acid-thermal hydrolysis, but somewhat worse than the pectin obtained in the above-described method (sample 4).

Physical and chemical properties of potato pectin, extracted under different technological conditions

Spheres of pectin use depend on its physical and chemical properties, namely, the content of the uronide component and the degree of esterification. These two indicators make it possible to recommend pectin to be used as a gelatinizer or stabilizer in the food industry, or as an enterosorbent in medicine. Pectin physicochemical properties to a large extent depend on the technological parameters of the basic processes – raw materials hydrolysis and pectin extraction. We obtained a number of potato pectin samples and determined their physical and chemical indices. Table 2 shows the most characteristic samples obtained by acid hydrolysis (Table 2, sample 1); combined hydrolysis involving enzyme preparations of cellulolytic and amylolytic action, and then chloride acid (Table 2, sample 4); combined hydrolysis with enzymatic preparations of cellulolytic action, then

hydrochloric acid followed by processing of the obtained extract with α-amylase (Table 2, sample 5); hydrolysis using only enzymatic preparations of cellulolytic and amylolytic action (Table 2, sample 5). Physico-chemical parameters of potato pectin samples obtained under different conditions are given in Table 2 (for the description of the methods for obtaining samples, see the section "Methods and Materials").

Table 2

Potato pectin physico-chemical parameters

Indices	Sample 1	Sample 4	Sample 5	Sample 6
Ash content, %	1,20±0,1	2,40±0,1	1,40±0,1	0,95±0,1
pH 1% solution of pectin	2,94±0,2	3,90±0,3	3,24±0,2	4,5±0,05
Mass fraction of ballast compounds, %	13,30±0,5	6,70±0,5	7,28±0,5	5,43±0,1
Content of free carboxyl groups, %	0,85±0,1	5,26±0,1	4,62±0,1	4,05±0,05
Content of esterified carboxyl groups, %	0,72±0,05	4,80±0,1	5,65±0,1	6,75±0,05
Uronide component, %	27,4±0,1	41,10±0,5	42±0,5	62,5±0,5
Esterification degree, %	45,86±0,1	47,70±0,1	55,0±0,1	44,5±0,1
Complex-forming ability, Pb^{2+} mg/g	104,0±0,5	310,0 ±0,5	83,0±0,5	325,0±0,1

The use of EP of amilolytic action leads to an increase in the uronide component comparing to the control by 1.5 times, which can be explained by a decrease in the content of starch hydrolysis products in the finished pectin powder.

One of the important properties of pectin substances is the complexing ability, due to which pectin is widely used in medicine, food industry and agriculture. This ability depends on the number of free carboxyl groups, that is, the esterification degree of carboxyl groups with methyl alcohol. The complexing ability also depends on the pH medium. The ability to form complexes for potato pectin at pH 3.9 (sample 4) is 310 Pb^{2+} mg/g. For example, for comparison, the beet pectin complexing ability at pH 5.0 is 505.0 Pb^{2+} mg/g, and apple pectin – 312.3 Pb^{2+} mg/g [15].

Potato pectin structure

Infrared spectra of pectin substances contain information on their composition and structure, purity, absolute and relative number of free and substituted carboxyl groups, and the presence of an ash component [15].

Although the composition and structure of pectin substances has not been fully established, today the monosaccharide composition of some pectins, determined by gas-liquid chromatography, is known: beet pectin contains galactose, glucose, arabinose and rhamnose [15]; apple pectin – galactose, glucose, mannose, xylose, arabinose and rhamnose; citrus pectin – galactose, xylose, arabinose and rhamnose [15], potato pectin – rhamnose, arabinose, galactose [18, 19, 27].

Pectin properties depend on its chemical composition, the degree of esterification, molecular weight, the ratio of the content of neutral saccharides and the uronide component.

In such a way, the study of the monosaccharide composition of pectin samples is extremely important, since they greatly affect the properties of the polysaccharide, thus defining the scope of its application, and comparing the structure of potato pectin with other

species makes it possible to evaluate the replacement of expensive imported pectin by domestic one.

Samples of all investigated pectins were extracted in laboratory conditions, in order to avoid the influence of extraneous sugars and stabilizers used in commercial pectin samples.

Spectra of pectin substances have a rather complex structure, therefore we considered only the bands, the identification of which coincides with other studies. Table 4 provides literature data on the position of the functional group peaks and the peaks of the pectin samples under study.

Table 4

Position of the characteristic bands (cm^{-1}) of infrared spectra

Types of fluctuations	Position of the characteristic bands	Sample № 4	Sample №6	Beet	Apple	Citrus
$v(OH)_в$	3600-3000	3420	3413	3433	3433	3394
					3068	3316
CH$_2$	2960-2926	2931	2925	2931	2931	2938
C-H	3000-2800	-	-	-	-	2899
		2364	-	-	-	2364
C=O	1750-1350	1739	1739	1745	1745	1745
	1640	1635	1648	1635	1635	1628
		1537	1537	1524	1524	
$\delta_{as}[(CH]_3)_E$	1442	1433	1433	1446	1446	1446
$\delta_s[(CH]_3)_E$	1378	1368	1374	1329	1361	1374
$\delta(CH)_K$	1331	-	-	-	-	1322
C-O-C	1300-1050	1244	1257	1287	1231	1231
(C–OH)$_C$, n(C–C, C–O)K		1153	1159	1153	1153	1146

All pectin samples (Figure 4) contain bands characteristic of pectin substances. The fluctuations of the OH group are manifested in the form of a wide band in the range 3200-3400 cm^{-1}, which corresponds to the primary hydroxyl groups. And in citrus pectin intensive peak around 3400 cm^{-1} passes into a slight shoulder of 3300 cm^{-1}. It should be emphasized that the OH-groups of pectin substances are shifted to the low-frequency area in comparison with the OH-groups of water. This is due to the participation of hydroxyls in the system of H-bonds [28].

The small band (shoulder) in the area of 2700-2500 corresponds to the valence fluctuations of the linked OH carboxyl group [28]. This shoulder is expressed more clearly in beet, apple and potato biopectin. All samples contain clear band within the limits of 1750-1735 cm^{-1}. The intensity and width of the strips are different for each pectin, which indicates a different degree of esterification. This area is one of the most important in identifying pectin substances. The coefficient of specific carbonyl content of carboxyl groups in a pectin molecule is calculated as the ratio of absorption at 1745 cm^{-1} (fluctuation of carbonyl carboxyl groups) to absorption at a length of 2940-2926 cm^{-1} (fluctuation of CH$_2$) [29]. The presence of a band in the area of 1640 cm^{-1} in all samples confirms the presence of ionized carbonyl and carboxyl groups, with the largest number in two samples

of potato pectin. In the analysis of pectins spectra it can be concluded that they contain a significant amount of polygalacturonic acid (intensive absorption bands in the area of 1010-1150 cm^{-1}) [29], and peaks in the area 1200-950 cm^{-1} correspond to the fluctuations of the skeleton of a molecule.
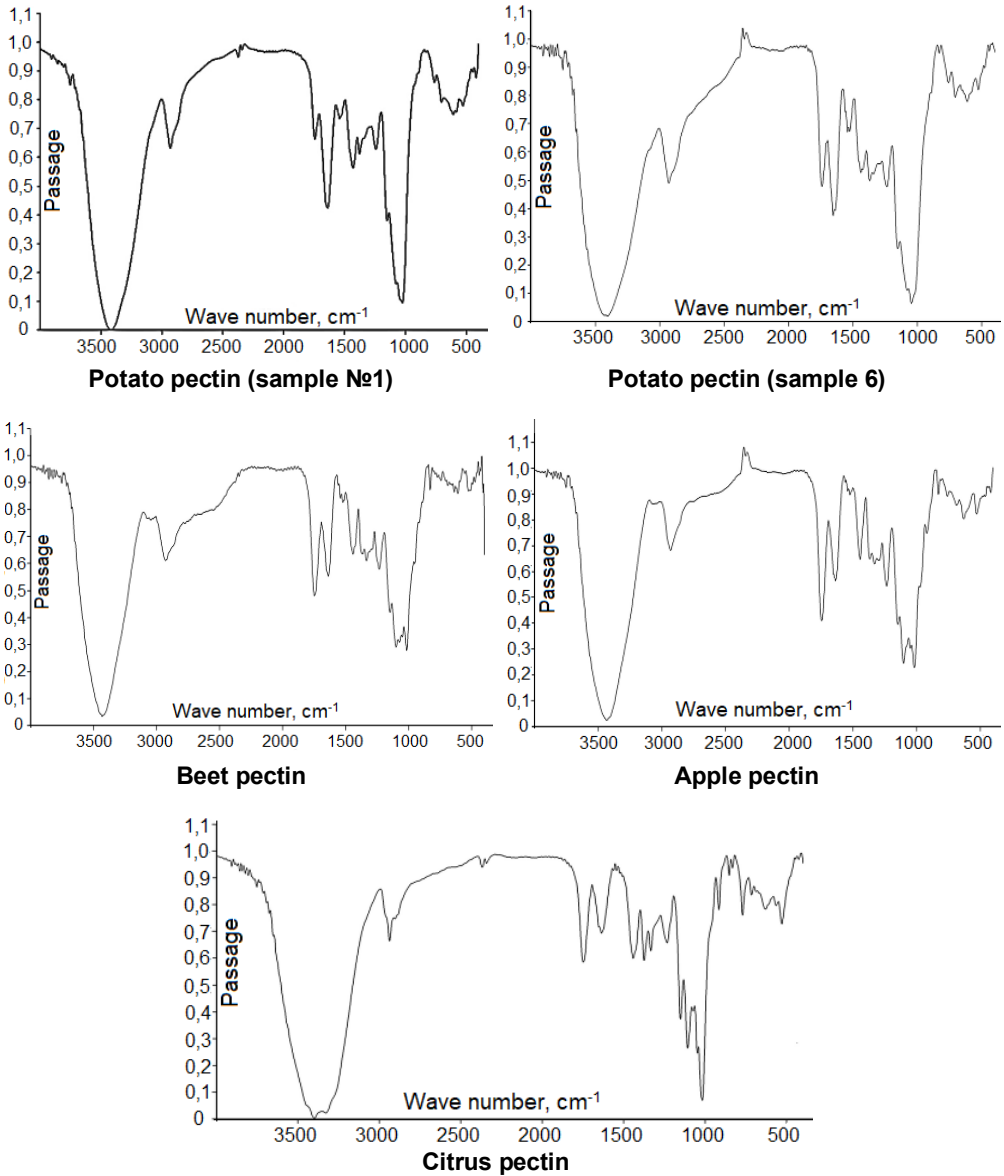
Figure 4. Infrared spectra of different types of pectin

To distinguish the potato pectin monosaccharide composition, spectral data on monosaccharides were collected: rhamnose, arabinose, galactose, mannose, xylose and glucose. There are no absorption bands characteristic of a particular monosaccharide and inherent only to it. Therefore, in order to identify, by comparing with the spectrum of the known compound, it is necessary to collect the IR spectrum in a wide frequency range, usually from 4000 to 650 cm^{-1}, with a particularly characteristic area of 1250-650 cm^{-1}, the so-called area of fingerprints. The coincidence of the frequency of saccharides fluctuations with the characteristic pectin frequencies at least at three peaks indicates the presence of a pectin molecule in a saccharide [26].

It is known that potato pectin is a rhamnogalakturonan I, which includes rhamnose, galactose, arabinose. This confirms the coincidence of a large number of peaks of these monosaccharides with the characteristic bands of both types of pectin: 3400, 2930, 2365, 1650, 1539 cm^{-1} – with galactose, 1430, 1370 and 1220, 1144, 1072, 1036 cm^{-1} – with rhamnose. Deviation of maximum peaks to 10 cm^{-1}.

However, having analyzed the positions of the maxima of the potato pectin characteristic bands extracted using EP and mannose, it follows that this monosaccharide is also present in a small amount. In particular, it's peaks: 2371, 2342, 1635, 1424, 1368, 1036 cm^{-1}. A slightly smaller amount of peak coincidence in potato pectin extracted by an enzymatic method, with xylose: 1240, 1151, 1042 cm^{-1}, which suggests that this monosaccharide is also present in a small amount of potato pectin molecules. The presence of xylene may result in reducing the pectin's degradation potential. The presence of a large number of coincident peaks of both pectins with glucose, which can explain the coprecipitation of starch hydrolysis products along with pectin during the process of coagulation with ethanol should be noted.

Method of X-ray diffraction

In the presence of crystalline formations in a polymer in their spatial lattice, it is possible to detect a large number of different parallel and equidistant mesh planes that cause X-rays diffraction. The diffraction patterns of three potato pectin samples extracted in various ways and potato starch are shown in Figure 5. The obtained diffractograms characterize the relationship between the pulse intensity and the interplanar distances in the structure of the sample [32]. It is known that pectin substances are not characterized by the structure orderliness (crystallinity), therefore the presence of peaks on x-ray films of pectins indicates the presence of residues of starch molecules in the samples.

In the first potato pectin sample, which was extracted without using enzymes, the number of peaks reflection is the largest, indicating a sufficiently high content of starch, which has the crystallinity of a structure of type B, which corresponds to the crystallinity of this pectin sample: 7.52°, 13.13°, 17, 17°, 20.17°.

In sample 4, which was extracted using α-amylase, the peak 17.17°, which is characteristic for starch, disappears [32]. The same thing happens in sample 2, that is, when enzymes are used, the number of reflections and, accordingly, the pectin crystallinity decreases due to the hydrolysis of starch co-precipitation, and pectin becomes more amorphous. On the diffractogram of the native potato starch (Figure 5) there are 2 main peaks of reflection: at diffraction angles 2θ = 17.2 and 22.2 degrees. In addition to discrete scattering from crystallites, a large fraction of diffuse scattering from the disordered starch phase, that is an amorphous halo, is present on the diffractogram.
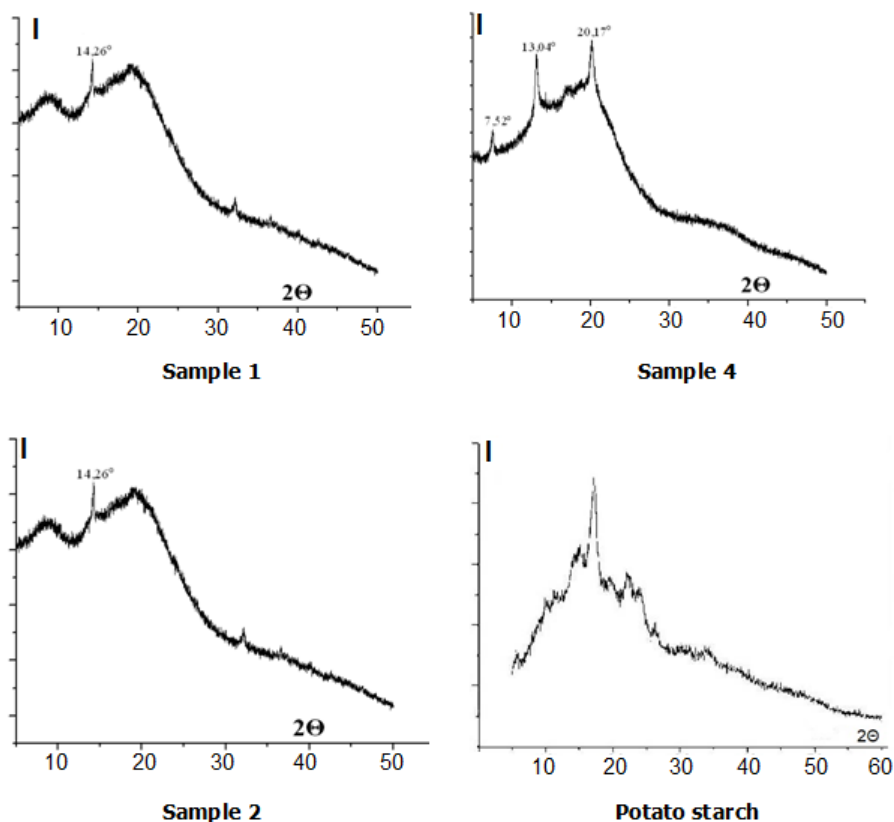
Figure 5. Diffractograms of potato pectin and starch

Sorption-desorption properties of potato pectin obtained in different ways

Pectin is a natural hydrocoloid, capable of sorbing water in large quantities and swelling with increasing mass. Pectin sorption properties contribute to the manufacture of adsorbents based on it, which are widely used in medicine. Food products enriched with pectin are related to healthy and preventive products. To evaluate the pectin sorption characteristics, a method of constructing isotherms of sorption-desorption is used.

The study of sorption characteristics was carried out for five samples of potato pectin:

1 – obtained by acid-thermal hydrolysis of raw materials;

2 – obtained by acid-thermal hydrolysis of raw materials, preliminary processed with enzyme preparations of amylolytic action (α-amylase + glucoamylase);

3 – pectin, additionally processed with enzyme preparations of amylolytic action;

4 – obtained by acid-thermal hydrolysis of raw materials, preliminary processed with cellulase and α-amylase enzyme preparations;

5 – obtained by acid-thermal hydrolysis of raw materials, preliminary processed with cellulase enzyme preparation, and the resulting extract was processed with α-amylase.

Pectin sorption properties were investigated by means of a Mac-Ben sorption-vacuum unit, where at 20 °C and at a pressure from 0 to 18 mm Hg sorption of water vapor of pre-

dehydrated samples were carried out until the hygroscopic state was reached. After that, desorption was performed in equilibrium conditions.

Adsorption isotherms are S-shaped (Figure 6), which is typical for polymolecular adsorption, at which the interaction of water vapor and adsorbent with the formation of polymolecular layers take place. The isotherms of all samples are hysteresis, the emmergence of which indicates that the system under investigation is fine-porous [30]. Isotherms of adsorption-desorption of potato pectin water vapor are shown in Figure 6 in coordinates: the amount of water adsorbed (a) – the water activity a_w), which was defined as the ratio of the partial pressure of water vapor above the surface of the sample to the partial pressure of a saturated vapor of pure water – $a_w = P/Ps$.
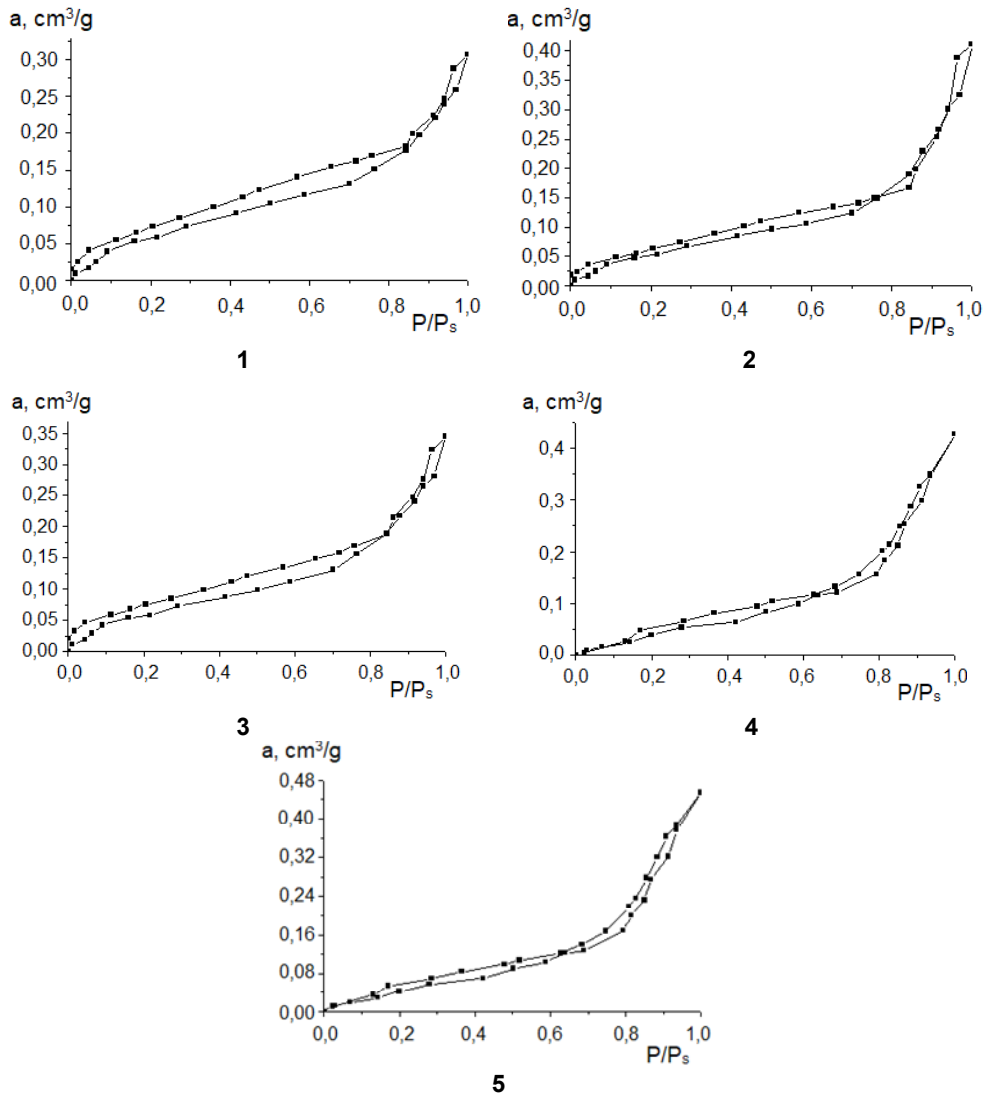

Figure 6. Isotherms of adsorption-desorption of potato pectin samples

Pectin hydration capacity depends on its chemical composition, molecular mass, mutual spatial arrangement of individual chains, dispersion, porosity and other factors. In order to explain the adsorption processes of fine-porous solid adsorbents, the theory of polymolecular adsorption of BET and other scientists is most often used. However, in the case of water vapor adsorption by hydrocolloids, the porous structure is labile (varies in the process of swelling), so the data of the theory cannot be applied [31]. In a detailed analysis of the adsorption isotherms form shown in Figure 6, we can note the wave-like character of the adsorption curves in the pressure range = 0.0 – 0.9. The complex nature of the curves can be explained by the gradual development of the Langmuir isotherms of adsorption, which correspond to the formation of the first and second hydrated shells around the active surface pectin centers.

From Figure 6 it is seen that desorption isotherms (dehydration) for all samples are located above adsorption isotherms (moisture). On the graphs of all samples, the hysteresis loopis small in width, but does not end at zero, which is evidence of partial chemisorption, that is, some of the chemically bound water remains in the pectin and is not removed by desorption.

Differential curves of pore distribution by magnitude are presented in Figure 7.

On the graphs of the pores distribution by radius, we see that different types of potato pectin are similar to each other. Micropores, the radius of which is ≤20 A are the most uniformly distributed. Since the size of the micropore is close to the size of the molecules, substances can be adsorbed in the form of individual molecules [30]. All samples in the area up to 10 A have the mostly pronounced peak. However, samples № 4 and № 5 have the largest number of pores of this size. Also, pectins contain mesopores. The diameter of such pores is from 20 to 200 A. It should be noted that these pores play an important role in the adsorption and encapsulation of low-molecular substances, since they can accommodate large molecules while maintaining a high adsorption potential [30]. All pectin samples have no macrospores. To assess the capillary-porous structure of potato pectins, the structural characteristics described in Table 6 were determined.

Table 6

Structural characteristics of potato pectin

Sample	Sample specific surface, S, m^2/г	Sorption pores volume, Vs, cm^3/g	Sample pores diameter D,A	R^2
1	219	0,31	57	0,9210
2	188	0,41	87	0,9363
3	204	0,34	67	0,9547
4	184	0,35	76	0,8419
5	186	0,39	84	0,9048

Where, D is the sample pore diameter which is calculated by the formula: $D = 4Vs/S$, A; R^2 is the square of the calculation error of the sample specific surface.

The obtained data testify that potato pectin is an effective sorbent, and the presence of a large amount of mesopor indicates the possibility of using this pectin as an encapsulating agent for various low molecular weight substances.

Potato pectin, obtained as a result of acid-thermal hydrolysis of potato meats preliminary processed with enzyme preparations has the best sorption properties.
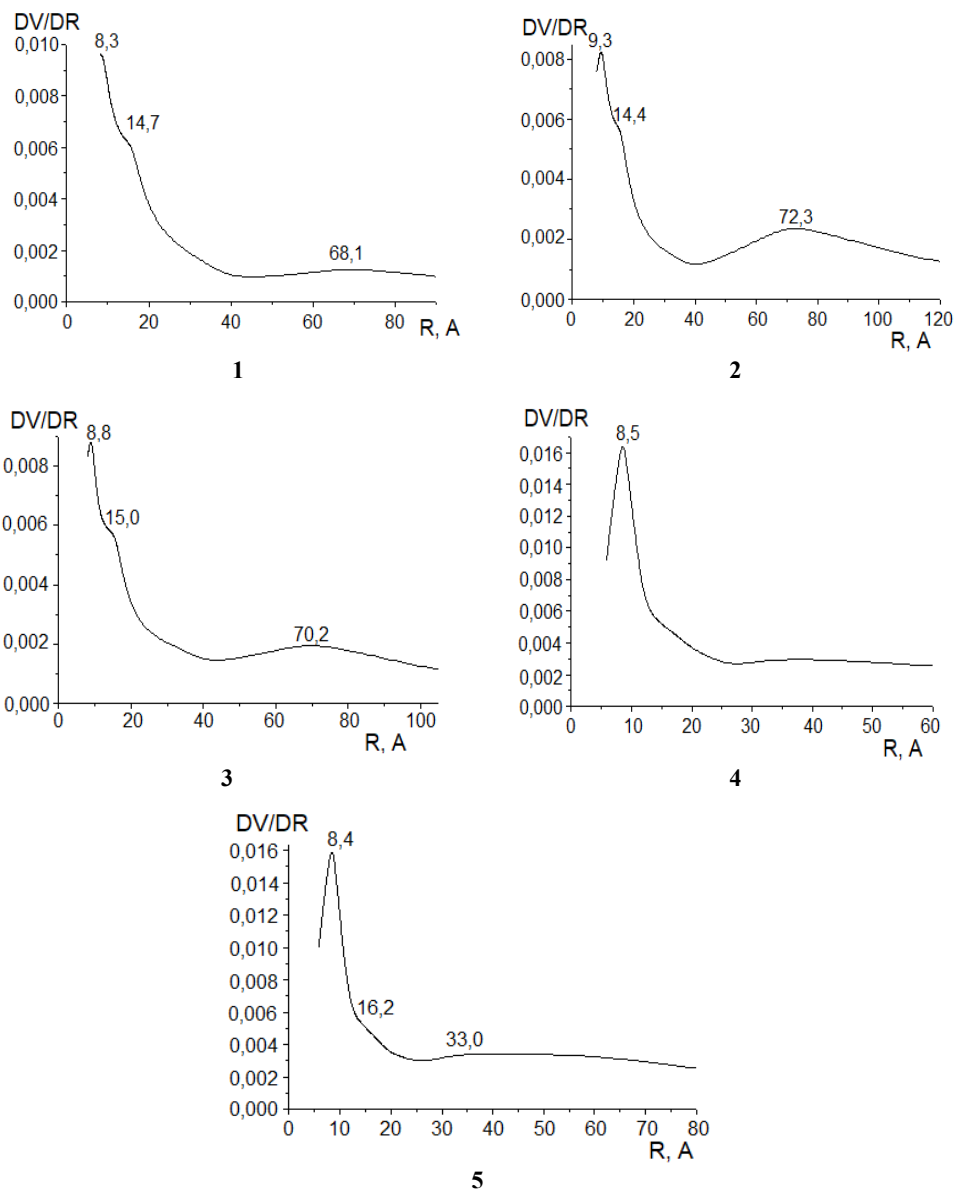
Figure 7. Differential curves for pore distribution by radius for different potato pectin samples

Conclusions

Based on the analysis of the physicochemical parameters of pectin obtained with the use of enzyme preparations and without them it has been proved that the use of EP of amilolytic action leads to an increase in the pectin purity (uronide component) compared with control in 1,5 times. For the first time, the potato pectin complexing ability has been

studied. The results of the studies showed that the potato pectin complexing ability is 310 Pb^{2+} mg/g, which indicates the possibility of its use in health products as an enterosorbent.

It has been established that potato pectin has a high sorption capacity with respect to water, with the greatest hydration ability being possessed by pectin samples obtained using cellulase and α-amylase enzymes. The amount of water sorbed with pectin is from 17 to 25%. And the presence of a large number of mesopores makes it possible to recommend this pectin as an encapsulating agent for various low molecular weight substances.

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Influence of commercial refining on some quality attributes of sunflower oil

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Abstract

Introduction. The research was carried out to check the impact on the commercial refining of sunflower oil such as crude, neutralization, bleaching and deodorization on some specific physicochemical attributes that are essential for quality point of view and health.

Materials and methods. Sunflower (SFO) oil samples (crude, neutralized, bleached and deodorized) were collected from the processing line unit from industrial oil company. In this study physicochemical parameters of SFO have been determined by official IUPAC and AOCS methods, while fatty acid composition was checked on GC-MS.

Results and discussion. The obtained outcome of physical parameters showed that neutralization, bleaching and deodorization steps of crude SFO considerably decreased the moisture content (0.46–0.04%), color (2.8–1.1R, 28.0–11.0Y), freezing point (3.2–2.3) and smoke point (226.0–219.0), while some lesser change in refractive index was also observed. Moreover, in the case of chemical parameters for instance free fatty acids, saponification value and peroxide value were reduced from 0.56 to 0.06%, 178.5 to 177.2 mg KOH/g oil and 3.2 to 0.9 $mEqO_2$/Kg oil, correspondingly. On the other hand refining steps did not showed significant impact on the iodine value (126.0–125.2 gI_2/100g of oil) and fatty acid composition (total unsaturated fatty acids 89.06–90.91%). The most important influence during industrial processing was noted in soap contents, as these are generated during second step of refining. In present study soap content were reduced from 121.0 to 30.4 ppm during neutralization to deodorization steps.

Conclusions. Among industrial process, deodorization step has greater influence on physicochemical attributes on the quality and stability of processed SFO.

Introduction

The cultivated sunflower (Helianthus annuus L.) dicotyledonous plant is one among 67 species in the genus Helianthus [1]. It is one of the four most essential annual crops within the global grown for edible oil [2]. Generally, the oil content present in the sunflower seeds ranges from 16-24% [3]. The world's whole production of sunflower oil is nearly 16 million tonnes annually with Argentina, Ukraine, Russia and China as the largest producers [4]. Sunflower oil contain valuable components such as soluble vitamins (A, D, E and K), phytosterols, natural pigments and phospholipids (1 to 5%) [5]. This oil plays an essential role in the diet and provides energy [6].

Crude oil obtained from sunflower seed needs refining before the utilization in order to eliminate unwanted compounds (free fatty acids and color pigments). The objective of refining is to take away those impurities with the least possible impact on desirable compounds present in the crude vegetable oils in order to obtain bland, odorless and oxidative stable refined vegetable oils [7] that are acceptable to consumers.

Presence of typical compounds such as waxes, odiferous volatiles, metal traces and pigments impacts negatively on the appearance, taste, smell and storage consistency of the refined oils. These compounds must be eliminated from edible oils to yield a stable product with a pleasant flavor [8]. The presence of phospholipids can cause the oil discoloration, act as a precursor of off-flavors and contribute to the loss of impartial lipids in the course of neutralization [9]. In additionally, phospholipids are naturally exists as emulsifiers, which bind oil molecules collectively leading to extended viscosity and refining [10]. There are three main processes involved during chemical refining such as neutralization, bleaching, and deodorization. During alkali neutralization process most of the free fatty acids are removed. On the other hand during physical refining, free fatty acids are removed through deodorization process instead of alkali neutralization [11]. Even though both physical and chemical refining processes are efficient to keep up the quality of oil, but in these processes some nutritionally valuable components are also drive out from the oil as well [12].

This research study is aimed to check the impact on the commercial refining of sunflower oil such as crude, neutralization, bleaching and deodorization on some specific physicochemical attributes that are essential for good health. To the best of our expertise no any research work has been mentioned to date on the physicochemical parameters of sunflower oil during industrial processing.

Materials and Methods

Reagents and oil samples collection

All the chemicals and reagents used in the present research work were purchased from E-Merck (Dermastd, Germany). Sunflower oil samples (crude, neutralized, bleached and deodorized) were collected from the processing line unit from industrial oil company located at Hyderabad, Pakistan. Collected samples were stored at 4°C in amber colored bottles and purged with nitrogen gas stream to decrease the oxidation of oil.

Physicochemical parameters

Physicochemical parameters of industrially refined sunflower oils were measured according to standard American Oil Chemists Society (AOCS) methods [13]. For instance,

moisture, color, freezing point °C, smoke point °C, refractive index (40°C), free fatty acids, saponification value, iodine value, peroxide value and fatty acids composition.

Moisture

Moisture content within the processing steps of sunflower oil was checked through oven standard method at 105°C ± 1°C for 1 hour using Moisture Analyzer MX-50 (SHS) Super Hybrid Sensor by using AOCS method Da 2a-48 [13].

Color

The color of industrially processed sunflower oil was determined by Lovibond Tintometer (Model F) according to AOCS method Cc 13a-43 [13]. Before checking of color, glass cell (1 inch and 5 ¼ inch) was cleaned and dried. The color was matched by different colors of sliding yellow, red and blue color till an excellent match was obtained.

Freezing and smoke point

For freezing point, about 50g of oil sample was taken and kept for half an hour at 2 to 3°C in the refrigerator using Cc 9a-47 AOCS method [13]. While, smoke point was measured by using AOCS Cc 9a-48 method [13]. In brief 50 mL of oil was kept at above 175 °C for 1 hour on heating mental.

Refractive Index
The refractive index is the ratio of the speed of light within the substance to the speed of light in a vacuum. The refraction index of sunflower oil at 40°C±1 was carried out by AOCS Cc-7-25 method [13], and use of the Refractometer.

Free fatty acid

Free fatty acid in refined steps of sunflower oil was determined as reported in the AOCS method Da 14-48 [13]. In detail oil was solublized in warm neutralized ethyl alcohol and vigorously shaken. The mixture solution was titrated with 0.1N sodium hydroxide with the presence of phenolphthalein (indicator).

Saponification value

Approximately 2 g of oil was weighed in a round bottom flask and added 25 mL of alcoholic potassium hydroxide. The material was refluxed for one hour till reaction completed. Following cooling of mixture, 1 mL of phenolphthalein indicator was poured to it and titrated with 0.5 N of hydrochloric acid till end point showed with the disappearance of pink color. Likewise, a blank test in same manner was also carried except of adding oil as reported in the AOCS method Da 16-48 [13].

Iodine value

According to procedure approximately 0.1g of oil was taken in the flask and added carbon tetrachloride (7.5 mL) and Wijis reagent (12.5 mL) to dissolve oil. The mixture of solution was shaken vigorously and placed for 1 hour in the dark. Later on added 75 mL

water and 7.5 mL fresh solution of potassium iodide and starch indicator. The iodine was liberated from sample mixture and titrated against standard sodium thiosulphate (0.1 N) solutions till the blue color was disappeared at end point. In the same way, a blank test was also carried out with in the absence of oil using AOCS Cd Ib-87, method [13].

Peroxide value

Around 2g of oil was weighed in conical flask and added chloroform (10 mL). The content in the flask was shaken vigorously. Then 0.5 mL of potassium iodide and 15 mL of glacial acetic acid was mixed and stirred for a minute, in the end solution was kept for 5 minute in dark. Flask was removed from the dark place and added (75 mL) water along with 2 to 3 drops of starch indicator. The content was titrated against sodium thiosulphate (0.01 N). Likewise, a blank test was also carried out exception of the oil by Cd 8- 53 AOCS method [13].

Soap content

About 10g of oil in conical flask was weighed, added acetone (10 mL) and bromophenol indicator 3 drops. The sample mixture was titrated with hydrochloric acid (0.01N) until reddish green color altered to yellow color and soap contents were measured by the formula as mentioned in AOCS method Cc 17-95 [13].

Fatty acid composition analysis

Fatty acid methyl esters (FAMEs) were prepared by using standard IUPAC 2.301 method [14]. Analysis of FAMEs was carried out by the gas chromatography instrument coupled with selective mass detector (GC-MS) model 6890 N from Agilent equipment. The chromatographic peaks were analyzed by using the ChemStation 6890 Scale Mode software. For the separation of fatty acids A capillary column HP-5MS (5% phenyl methylsiloxane) (30 m x 0.25 mm ID x 0.25 μm film thickness) was used. The oven initial temperature was 150°C; it was held for 2 min then increased to 230°C with 4°C/min of ramp rate. Helium gas was used as the carrier gas with a flow rate of 0.8 mL/min. Temperature was set at 240°C and 260°C for injector and detector temperature. 1 μL of FAME was injected in the (50:1) split mode ratio. All analysis was carried out triplicate.

Statistical analysis

The samples of sunflower oil were analyzed in triplicate. Data were reported as means ± Standard deviation (n=3×3).

Results and discussion

Physical parameters of industrially refined sunflower oil

The physical parameters of sunflower oil samples were checked including crude, neutralized, bleached and deodorized collected from the vegetable oil factory located at Hyderabad, Pakistan. After each processing stage the results of moisture, color, freezing point, smoke point and refractive index are shown in Table 1.

Physical properties of crude and industrial processed sunflower oils

Parameters	Crude SFO	Neutralized SFO	Bleached SFO	Deodorized SFO
Moisture, %	0.46±0.03	0.27±0.05	0.05±0.09	0.04±0.07
Color Red units Yellow units	2.8±0.19 R 28.0±0.21Y	2.0±0.22 R 20.0±0.25Y	1.6±0.19 R 16.0±0.17Y	1.1±0.74 R 11.0±0.71Y
Freezing point, °C	3.2±0.05	3.0±0.66	2.8±0.67	2.3±0.69
Smoke point, °C	226±0.87	223±0.95	221±0.89	219 ±0.99
Refractive index, 40 °C	1.4744±0.0016	1.4745±0.0018	1.4746±0.0019	1.4747±0.0021

Moisture

It is widely recognized fact that oil free from moisture has benefit due to the oxidative stability, while the lower storability and suitability owing to higher moisture content of oil for an extended period preservation. During process of neutralization, moisture in crude sunflower oil was reduced from 0.4 to 0.27% with the level of 41.30%. Within the stage of bleaching, moisture was similarly decreased from 0.27 to 0.05% from the level of 81.48%. Whereas, deodorization step reduced the moisture percentage of bleached oil from 0.05 to 0.04% with 20% reduction efficiency. Generally, the reduction performance of moisture level of neutralization, bleaching and deodorization was determined to be 18.6, 40.2 and 41.2%, respectively.

Color

Some pigments are accountable for the color of the oil such as carotenoids and chlorophyll. The color of oil distinguished in terms of red (R) and yellow (Y) units. Usually color of crude oil is evaluated in 1 inch cell, while color of bleached and deodorized oil is measured in 5.25 inch cell. The color significantly decreased from 2.8 to 2.0 R and 28.0 to 20.0 Y during alkali neutralization process, which showed that around 28.6% color loss in both units. In bleaching step, color changed from 2.0 to 1.6 R and 20.0 to 16.0 Y, which illustrated 20.0% color elimination during bleaching. Whereas the oil color again reduced in deodorization process from 1.6 to 1.1 R and 16.0 to 11.0 Y, which indicated 31.2% decrease in color. Overall results of industrial process on neutralization, bleaching and deodorization was established to be 21.65% R, 21.65% Y, 32.42% R, 32.42% Y and 45.93 % R, 45.93% Y, respectively. Color intensity of vegetable oils, mostly eliminated through bleaching and deodorization step. The light color intensity is accepted for vegetable oils to be highly attractive from marketable view-point [15].

Freezing point

Triglycerides and waxes with saturated fatty acids resist flowing oil smoothly due to sediment. Consequently it is a key sign to determine the freezing point. During sunflower oil processing, it was experimental observation that in neutralization, bleaching and

deodorization steps freezing point of crude oil reduced from 3.2 to 30 ^{o}C (6.25%), 30 to 2.8^{o}C (6.66%) and 2.8 to 2.3 ^{o}C 17.85%, respectively. Overall input of neutralization, bleaching and deodorization was determined to be 13.33, 26.67 and 60%, respectively, which obviously indentified that deodorization has high impact on freezing point.

Smoke point

Basically it could be described as the temperature at which oil produces thin stream continuously of the smoke by heating. Smoke point of oil characterizes suitability for frying point of view. During industrial refining, it was observed that smoke point of crude oil was reduced from 226 to 223°C for neutralization, 223 to 221°C for bleaching and 221 to 219°C in deodorization steps. Overall impact of neutralization, bleaching and deodorization was found to be 19.8, 32.9 and 47.3%, respectively.

Refractive index

The refractive index relies on the fatty acid composition and triglyceride of fat and oil. During all stages of the refining little impact was noticed. Small variation was observed from crude to neutralization and bleaching to deodorization from 1.4744 to 1.4745, 1.4746 to 1.4747, respectively. Overall influence on refractive index is shown in the percentage from 0.0067, 0.0135 and 0.0203%, respectively for neutralization, bleaching and deodorization.

Chemical parameters of industrially processed sunflower oil

Chemical parameters are very crucial for the quality parameters of oil. These parameters are mainly important for the edible and health point of view as well as for industrial purposes. Some different chemical parameters of SFO were measured during industrial refining processes as indicated in Table 2. These parameters which include free fatty acid, saponification value, iodine value, peroxide value and soap content.

Table 2

Chemical properties of crude and industrial processed sunflower oil

Parameters	Crude SFO	Neutralized SFO	Bleached SFO	Deodorized SFO
Free Fatty Acids, %	0.56±0.09	0.14±0.06	0.19±0.07	0.06±0.03
Saponification value, mg KOH/g of oil	178.5±0.78	178.2±0.78	177.5±0.84	177.2±0.73
Iodine Value, (gI$_2$/100g of oil)	126.0±0.61	125.8±0.66	125.5±0.72	125.2±0.71
Peroxide value, mEqO$_2$/kg of oil	3.2±0.46	2.9±0.54	2.3±0.44	0.9±0.33
Soap Content, ppm	–	121.0±0.88	60.8±0.99	30.4±0.84

Free fatty acids (FFA)

This parameter is very significant indicator to determine the suitability and edibility of oils. These fatty acids are not bound chemically to glycerol molecules and are recognized as FFA. The taste odor, and oxidative stability of oil negatively affected by increased FFA. During chemical or physical refining the high FFA contents in edible oil are removed [8]. During all refining steps, noticeable variation in the decrease of FFA was determined in neutralization, bleaching and deodorization steps. However, FFA in crude sunflower oil showed variation from 0.56 to 0.14% (75.0%) for neutralization stage, 0.14 to 0.19% (35.7%) for bleaching stage and 0.19 to 0.06% (68.4%) in deodorization stage. The effect on FFA during industrial refining stages has approximately 32.58, 28.68 and 38.74 % share reduction for neutralization, bleaching and deodorization, respectively.

Saponification value (SV)

The SV relies on the fatty acids (types) exists in the oil. Significance of this value is more essential for the production of soap. Through industrial processing the negligible impact on SV was determined from neutralization to deodorization process. SV increased slightly from crude to neutralized oil 178.5 to 178.2 mgKOH/g. While reducing trend of SV was observed in bleaching and deodorization process 178.2 to177.2mgKOH/g and 177.5 to 177.2mgKOH/g, respectively. The overall influence of refining stages was observed to be 11.72%, 38.63% and 49.65% for neutralization, bleaching and deodorization.

Iodine value (IV)

The IV explains the degree of unsaturation of fat and oil. It is recognized fact that least unsaturated oil shows lower iodine numbers, whereas reverse is true for highly unsaturated oil. The IV expressed the classification of oil as non-drying and drying oils. No any major influence was observed during refining stages. There was minor change noticed in IV from neutralization to deodorization 126.0 to 125.8gI$_2$/100g, 125.8 to 125.5gI$_2$/100g and 125.5 to 125.2gI$_2$/100g. Overall contribution of neutralization, bleaching and deodorization was observed to be 12.83, 33.33 and 53.84%, respectively.

Peroxide value (PV)

The degree of oil and fat oxidation is determined by the quantity of peroxides present. These are the primary compounds formed during the oxidation of unsaturated fatty acids, which may react further to form the compounds that can cause rancidity [16, 17]. In the neutralization stage there was no any major influence observed on PV. On the other side comparative study showed somehow positive outcome on PV among neutralization, bleaching and deodorization stages [18]. During the step of bleaching to deodorization, PV was decreased from 2.3 to 0.9 mEqO$_2$ /Kg. Overall the effect of industrial refining processes showed the removal of PV by following order 8.56, 25.71 and 65.72% neutralization, bleaching and deodorization, respectively.

Soap content (SC)

Salt of fatty acids in vegetable oil is known as soap content. Shelf life and stability is depends on the presence of soap content in the oil. It is well known fact that, lower the soap content higher the shelf life. Soap content was observed in the neutralization step (121.0 ppm). On the other side reducing trend of soap content was determined in the bleaching (121.0 to 60.8ppm) and deodorization (60.8 to 30.4ppm) steps. The processing efficiency on soap content showed following trend from 121%, 49.75% and 50%, respectively in the neutralization, bleaching and deodorization. Overall the input of each industrial refining step such as neutralization, bleaching and deodorization was observed 57.02, 28.65 and 14.33 %, respectively.

Fatty acid composition (FAC)

FAC of sunflower oil samples in all industrial processing steps including crude are indicated in Table 3.

Table 3

Fatty acid composition of crude and industrially processed sunflower oil

Fatty Acids (%)	Crude SFO	Neutralized SFO	Bleached SFO	Deodorized SFO
Myristic (C14:0)	0.52±0.02	0.48±0.01	0.46±0.06	0.45±0.07
Palmitic acid (C16:0)	5.31±0.66	4.95±0.77	4.94±0.72	4.23±0.68
Palmitoleic acid (C16:1)	0.92±0.05	0.85±0.08	0.84±0.03	0.82±0.04
Stearic acid (C18:0)	5.12±0.20	4.75±0.25	4.57±0.27	4.42±0.22
Oleic acid (C18:1)	45.08±0.56	46.48±0.68	46.62±0.88	46.58±0.62
Linoleic acid (C18:2)	42.33±0.66	42.39±0.63	42.85±0.77	43.99±0.75
Total saturated fatty acids	10.94	10.18	9.97	9.09
Total unsaturated fatty acids	89.06	89.82	90.03	90.91

There are six different kinds of fatty acids were determined in crude sunflower oil as shown in Figure 1. The total saturated fatty acids and unsaturated fatty acids in the last stage of refining accounted for sunflower oil as 90.91% and 9.09 %, respectively. The highest concentration of fatty acid in sunflower oil was found linoleic acid (C18:2) following by the oleic acid (C18:1), palmitic acid (C16:0), stearic acid (C18:0), palmitoleic acid (C16:1) and myristic acid (C14:0). The poly unsaturated fatty acids are significant fatty acids in vegetable oil, and also better liable to the oxidative rancidity [19]. The results of fatty acids showed that industrial refining treatment steps has no major impact [20], excluding some minor change in the relative proportion of fatty acids.
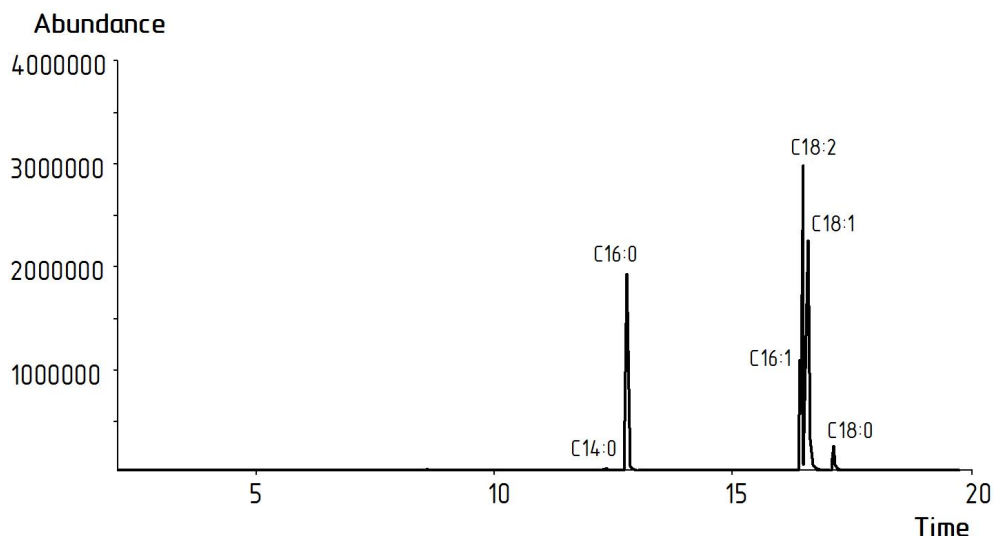
Figure 1. Fatty acid (GC-MS) chromatogram of sunflower oil

Conclusions

Commercial refining has showed major impact on some quality attributes of SFO. Among four different processing stages, the highly influenced change (reduction) was noticed in color, smoke point, soap content and peroxide value through neutralization, bleaching and deodorization. Whereas, considerable influence was observed on freezing point, smoke point, refractive index, free fatty acid, saponification value and iodine value. On the other hand negligible impact on the fatty acid composition was seen during refining of SFO. From this study, it could be conclude that among different refining stages deodorization step has greater influence on physicochemical attributes on the quality and stability of processed SFO.

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Research of physical and chemical parameters of the oil obtained from organic and conversion hemp seeds varieties "Hliana"

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Abstract

Introduction. The aim of the research is to confirm the literature data on the ratio of Omega-3 and Omega-6 unsaturated fatty acids in hemp oil – 1:3 ideal for human body absorption, recommended by the experts of the World Health Organization.

Materials and methods. The object of the study is the oil of conversion and organic seeds of industrial hemp variety "Hliana" of the crop of 2017. The content of tetrahydrocannabinol in this grade is zero. The fatty acid composition was studied using a chromatographic method, sensory characteristics, acidity and iodine number of hemp oil were also determined.

Results and discussion. The basic sensory characteristics of the experimental oil samples corresponded to the requirements of normative documentation. The acidity and iodine number of hemp oil from organic seeds of industrial hemp was 1.13% and 152 g/100 g respectively; with conversion seeds – 1.23% and 154 g/100 g respectively. According to chromatogram data the percentage content of acids in hemp oil was determined. Hemp seed variety "Hliana" contains approximately 55% of linoleic (Omega-6) acids, 16% oleic acid (Omega-9), 15% alpha-linolenic (Omega-3) and 2% gamma-linolenic (Omega-6) acid. The ratio of omega-3 and omega-6 fatty acids in hemp oil of the samples studied was approximately 1: 3.6. It is known that the human body needs about 2-3 grams of omega-3 and 4 grams of omega-6 each day. This amount of unsaturated fatty acids can provide 1 tablespoon of hemp oil per day.

Conclusions. For the first time the fatty acid composition of oil from hemp seeds of the variety "Hliana" was studied. It was confirmed that in hemp oil the ratio of essential fatty acids Omega-3 and Omega-6 is 1:3.6. The parameters of composition and quality of oil from organic and conversion seeds of hemp are almost identical.

Introduction

Health improvement of the population is an actual problem of power, doctors and food technologists of many countries of the world. It is proved that the prevention of an overwhelming number of diseases is a healthy lifestyle: a balanced diet and physical activity. Perspective are food products that have not only nutritional but also biological properties. To create such in different countries of the world hemp seeds are used [1].

Hemp seed is one of the best sources of easily digestible vegetable protein; phytonutrients, supporting the normal state of tissues, blood vessels, skin cells and internal organs; polyunsaturated fatty acids; vitamins A, D and E and group B, calcium, sodium, iron and dietary fiber [2].

According to the research of Canadian scientists, the content of lipids in hemp seeds is 26.9 – 30.6%, and of proteins 23.8 – 28.0%. Oil from hemp seeds mainly consists of unsaturated fatty acids, dominant is linoleic acid (Omega-6) – 59.7% and α-linoleic (Omega-3) – 17.0%. [3], their ratio makes it unique [4]. Especially valuable in hemp oil is the content of more than 2% of gamma-linolenic acid contained in human milk and is rarely found in nature [2, 5, 6]. Scientists of the world are studying the fatty acid composition of hemp seed varieties zoned in their country [4, 7, 8, 9, 10, 11, 12, 13, 14]. At present there is no information on the fatty acid composition of hemp varieties of Ukrainian breeding.

Recently the extraction of oil from non-traditional raw materials such as wheat germ, hemp seeds, flax seeds, pomegranate seeds, grapes, cherries, tomatoes, coffee beans, amaranth and many others has gained wide popularity [15].

It is known that the word "hemp" causes an ordinary citizen to associate with drugs. But hemp is a plant, and cannabinoids (marijuana) are a narcotic substance that is derived from cannabis. There are three main types of cannabis:

-Cannabis sativa – crop hemp;
-Cannabis indica – Indian hemp;
-Cannabis ruderalis – hemp garbage.

In sufficient quantities to obtain a drug (30% or more) cannabinoids are contained only in Indian hemp. Crop hemp and garbage hemp contain an extremely small amount of psychoactive substances which, it should be noted, are contained only in pollen, leaves, cones of an adult hemp plant. In seeds of hemp, there are no narcotic substances in principle.

Migal M. and Shulga I. studied the dynamics of accumulation of cannabinoids in vegetative and generative organs of hemp and established by thin-layer chromatography method that there are no cannabinoid cannabis seeds in the shell and embryo of the seeds [17].

Seeds of hemp practically one-third comprise of useful fats which can be used in cooking, and hemp oil in quality is not inferior to whale fat [18].

Hemp oil is a rich and balanced source of linoleic (Omega-6), alpha-linolenic (Omega-3) fatty acids. Impact on human health of these two polyunsaturated fatty acids consists in anti-inflammatory, anti-thrombotic, antiarrhythmic and hypolipidemic properties. Hemp oil also contains a significant number of tocopherols that exhibit antioxidant activity [19].

According to the literary data the fatty acid composition of hemp oil is as follows: Omega-6 (linoleic acid) – 40–60%, Omega-3 (alpha-linolenic acid) – 15–25%, Omega-9 (oleic acid) – 11% palmitic acid – 6%, stearic acid – 3% [2].

In addition to food, hemp oil is used in the manufacture of paints, shampoos, soaps, cosmetics, body care products, etc. [14].

The purpose of the research is to determine the physico-chemical parameters and fatty acid composition of organic and conversion seeds of hemp variety "Hliana", confirmation of the literature data on the ideal ratio of Omega-3 and Omega-6 unsaturated fatty acids – 1 :3 recommended by the experts of the World Health Organization. The quality of the seeds (including the content of unsaturated fatty acids) depends on the method and conditions for the hemp growing.

Materials and methods

Materials

The object of the study is conversion oil (3 years conversion) and organic seed of industrial hemp "Hliana" of the 2017 crop grown by the agro-industrial group "Arnika" (Poltava region, Ukraine). This variety is selected at the Institute of bast crops and is universal in use (for the production of fiber and seeds), the content of tetrahydrocannabinol in it is zero. Organic hemp seed meets the requirements of the EU certificate [20]. The organic olive oil of hemp was 33.45% and the conversion value was 33.60%.

Methods

Determination of sensory indicators of oil quality

Determination of the sensory characteristics such as taste, smell, color and transparency was carried out at 20 °C.

To determine the color of 50 cm^3, the oils were poured into a chemical glass and looked in the light that passed and reflected on a white background. In the presence of chlorophylls the color should be greenish.

To determine the transparency the oil was poured into a measuring cylinder per 100 cm^3 and left at rest for 24 hours at temperature of 20 °C. In the settled oil in the light that passed and reflected on a white background the transparency was determined. The oil was considered transparent in the absence of weighed flakes as well as mesh (the net is due to the presence of tiny waxy substances in the oil that add turbidity). After defending the oil the presence of damp was determined in it.

The smell was determined in oil which was applied to a glass plate with a thin layer. For the most distinctive recognition of the smell the oil was heated in the water bath to 50 °C.

Taste specific, inherent in hemp oil was determined sensoryally in the oral cavity.

Determination of acidity and iodine number of hemp oil

The acidity was determined according to ISO 729:1988 – "Seed oil – Determination of oil acidity".

We took a dry and clean flask with an oil sample of 5 g and dissolved it in 50 cm^3 neutral mixture of diethyl ether with ethyl alcohol, shake until dissolved. To the solution an indicator (5 drops of a 1% alcohol solution of phenolphthalein) was added. After that the solution was titrated with stirring with 0.1 mol / dm^3 alcoholic solution of potassium hydroxide until the indicator changed its color to bright pink. Carried out two definitions in parallel.

Oil acidity (%) was calculated by the formula 1.

$$X_1 = (V \cdot C \cdot M) / 10 \cdot m,\qquad(1)$$

where C is the exact concentration of the standard solution of potassium hydroxide, mol/dm^3;

V is the volume of the standard solution of potassium hydroxide expended on titration, cm^3;

M is the molar mass of acids taken to express the analysis results, for coconut oil and palm kernel oil – 200 g / mol, for all other oils – 282 g / mol;

m is the weight of the sample.

For the result of determining the acidity the arithmetic mean of two parallel measurements was taken which is rounded to decimal.

The iodine number was determined according to ISO 3961:2013 – "Animal and vegetable fats and oils – Determination of iodine value".

0.1 g oil sample was placed in a flask and added 500 cm^3 20 cm^3 solvent (a mixture of 50 cm^3 of cyclohexane and 50 cm^3 of anhydrous acetic acid) and 25 cm^3 Viysa reagent with a pipette. The Viase reagent contained monohloride iodine in acetic acid (I / Cl ratio 1.1). The flask was closed with a stopper, the contents were stirred in circular motions and placed in a dark place for 2 hours. After completion of the reaction, 20 cm^3 of potassium iodide and 150 cm^3 of water were added. The contents of the flask were titrated with a standard solution of sodium thiosulfate (concentration 0.1 mole / dm^3) until the yellow color disappeared. A few drops of starch were added and the titration continued until the blue color disappeared. To prepare the starch solution, 5 g of starch was added to 30 cm^3 of water, added to 1 liter of boiling water and boiled for 3 minutes, cooled. In parallel, titration of the blank sample was carried out according to the above procedure only without the addition of oil.

Iodine number (g / 100 g) of oil was calculated by the formula 2.

$$W_1 = (12{,}69 \cdot C \cdot (V_1 - V_2)) / m,\qquad(2)$$

where C is the concentration of sodium thiosulfate solution, mol / dm^3;

V_1 is the volume of the solution of sodium thiosulfate which was used for idle determination, cm^3;

V_2 is the volume of the solution of sodium thiosulfate which was used for titration, cm^3;

m is the weight of the sample.

For the result of determining the iodine number, the arithmetic mean of two parallel measurements was taken which is rounded to decimal.

Determination of fatty acid composition of hemp oil by gas-liquid chromatography

In research process a method for determining the fatty acid composition of hemp oil, namely the gas-liquid chromatography method on a Shimadzu GC 2010 – Plus (Japan) chromatograph with a capillary Thermo TR – FAME column (Germany) has the characteristics given in Table 1.

Characteristics of the Zebron capillary column

№	Characteristic	Value
Column information:		
1	Column Dimensions	Thermo TR - FAME 30 m L × 0,25 mm ID × 0.25 μm df
2	Liquid Phase	Proprietary
3	Temperature Limits	-20 to 260 ºC (Isothermal)
4	Part Number	260M142P
5	Column Serial Number	1102181B20
Test conditions:		
6	Column Temperature	140 ºC / 5,0 min → 4,0 ºC / min to 220 ºC Hold l0 min
7	Instrument	Shimadzu GC 2010 – Plus
8	Injection Temperature	240 ºC
9	Injection Mode	Split @ 1:60
10	Carrier Gas	H_2UHP
11	Detector	F.I.D @ 240 ºC
12	Test Sample	0,75 μl of FAME-37

The analysis was carried out at a given temperature of 140 - 250 ° C (2 ° C / min). The injector temperature was 240 °C, the detector temperature was 240 °C.

Results and discussion

Sensory quality indicators

A sensory analysis of hemp oil samples was carried out, the results of which are given in Table 2.

Sensory indicators of quality of oil samples from organic and conversion hemp seeds

№ з/п	Indicator	Organic seed oil	Conversion seed oil
1	Transparency	Above the sediment is transparent	Above the sediment is transparent
2	Color	Light green	Light green
3	Smell and taste	Typical of hemp oil, without off-odors, tastes, and not bitter	Typical of hemp oil, without off-odors, tastes, and not bitter

From the table we can conclude that the sensory quality of all samples is inherent in hemp oil.

Acidity and iodine number of hemp oil

In order to assess the quality of hemp oil samples the following physical and chemical parameters such as acidity and iodine number are determined. Comparative characteristics of physico-chemical parameters of hemp oil are given in Table. 3

Table 3

Comparative characteristics of acidity values and iodine number of hemp oil

Indicator	Organic seeds oil	Conversion seeds oil	Control
Acidity, %	1,13	1,23	less than 1.5
Iodine number, g/100g	152	154	less than 145

These tables confirm the presence of sufficient amount of fatty acids in oil from hemp seeds which is an important factor in the production and storage of hemp products.

Fatty acid composition

According to the content of omega-3 and omega-6 – polyunsaturated fatty acids which are recommended for the prevention and treatment of diseases of the cardiovascular and nervous systems, obesity, hemp oil is the best (even for linen oil). Also hemp oil is rich in antioxidants, phytosterols, fat-soluble vitamins and minerals. Therefore it was important to study the content of saturated and unsaturated fats in hemp oil.

Determination of the fatty acid content of hemp oil was carried out by chromatographic method by analyzing the methyl esters of fatty acids contained therein based on the testing laboratory of "Cotecna Ukraine Limited" Ltd. The chromatogram results are shown in Fig. 1 and 2.

According to chromatogram data the percentage content of acids in hemp oil which is given in Table 4 was determined. Hemp oil contains the maximum amount of unsaturated fatty acids in comparison with known vegetable oils. Scientists have long confirmed the need for humans in polyunsaturated fatty acids Omega-3 and Omega-6, but the primary importance is not only the content of these acids in the product but the right combination [2]. According to literary data in hemp oil the ratio of essential fatty acids (EFA) is close to the ideal: Omega-3 and Omega-6 are 1:3, while in linseed oil is 4:1, in rape is 1:2, in soya is 1:7 [4].

As can be seen from the data given, the content of basic acids in hemp oil from seed variety "Hliana" corresponds to the data of literary sources of information. It was confirmed that the ratio of Omega-3 and Omega-6 in hemp oil is 1: 3.6 which is approximately ideal for human digestion, and the content of gamma-linolenic acid (Omega-6) is about 2%.

It is known that the human body needs about 2-3 grams of omega-3 and 4 grams of omega-6 each day. This amount of unsaturated fatty acids can provide 1 tablespoon of hemp oil per day.
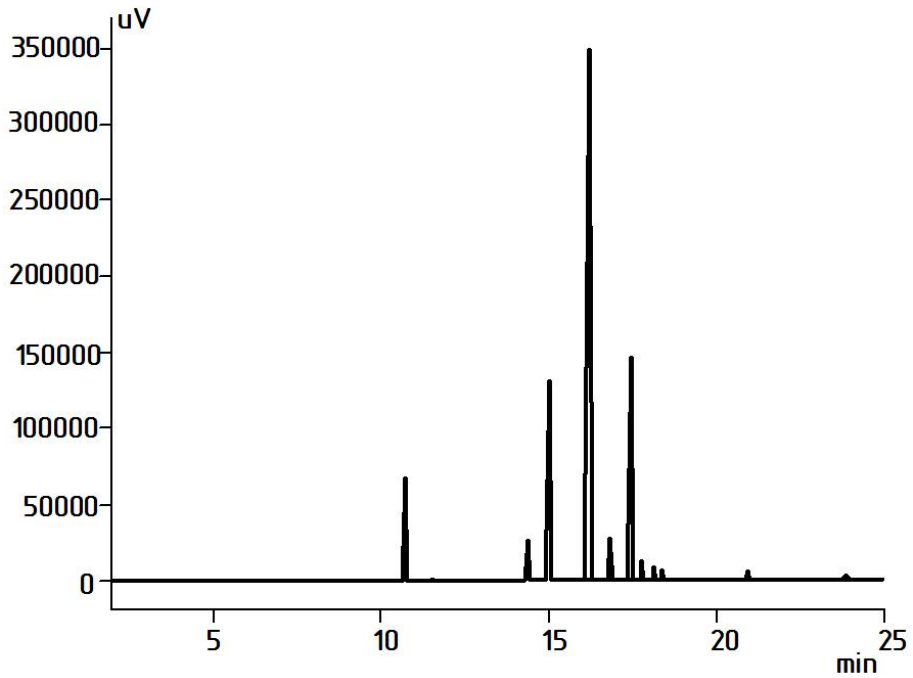
Figure 1. Chromatogram of oil fatty acids from organic seed of industrial hemp variety "Hliana"
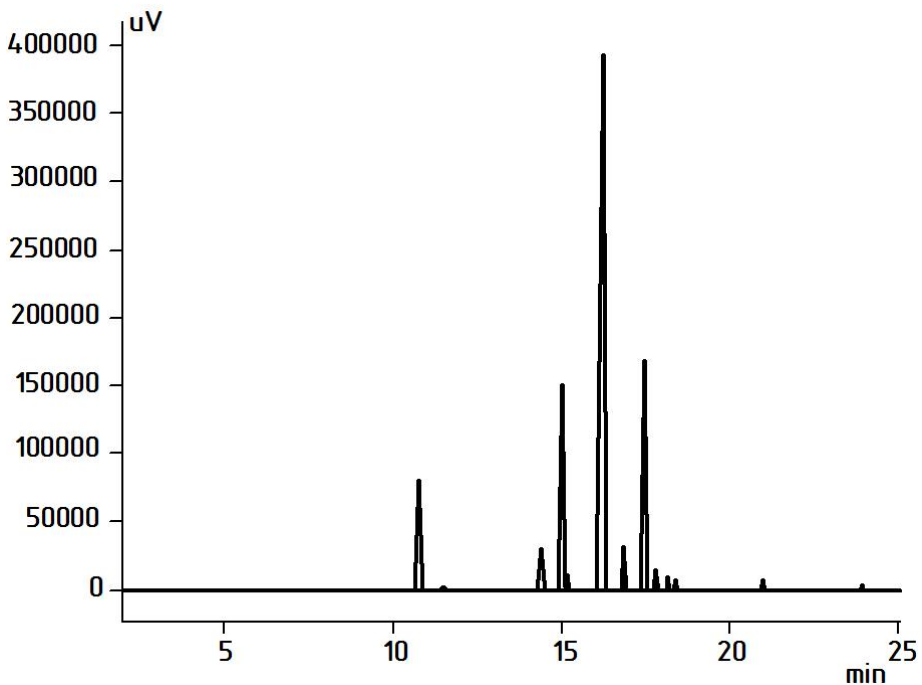

Figure 2. Chromatogram of oil fatty acids from conversion seed of industrial hemp variety "Hliana"

Comparative characteristics of the fatty acid composition of the test samples of hemp oil

Name of the acid	The content of acid % relative to total acids	
	Organic seed oil	Conversion seed oil
C 16:0 Palmitic	6,007	5,994
C 16:1 Palmitoleic	0,098	0,104
C 18:0 Stearic	3,033	3,070
C 18:1n9c Oleic	16,155	16,154
C 18:2n6c Linoleic	54,803	54,989
C 18:3n6 gamma-Linolenic	2,269	2,260
C 18:3n3 Linolenic	14,821	14,654
C 20:0 Arachidic	1,019	1,012
C 20:1 cis-11-Eicosenic	0,695	0,684
C 20:2 cis-11,14-Eicosadienoic	0,461	0,446
C 22:0 Behenic	0,443	0,434
C 24:0 Lignoceric	0,197	0,198

Conclusion

During the researches of physical and chemical indices of hemp oil from organic and conversion seeds it was established:
− the acidity of the test specimens of the hemp oil is within the range of 1.13 – 1.23%;
− the iodine number of prototype hemp oils is in the range of 152 – 154 g / 100 g;
− hemp seed variety "Hliana" contains approximately 55% of linoleic (Omega-6) acids, 16% oleic acid (Omega-9), 15% alpha-linolenic (Omega-3) and 2% gamma-linolenic (Omega-6) acid. It is confirmed that the ratio of Omega-3 and Omega-6 in hemp oil is 1 : 3.6 which is close to the ideal for human assimilation;
− indicators of composition and quality of oil from organic and conversion seeds of hemp are not nearly identical.

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Effect of gluten-free flour on sensory, physico-chemical, structural and mechanical properties of wafer batter and waffles

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Abstract

Introduction. The research was carried out to determine the impact of different varieties of gluten-free flour on semi-finished and finished wafer sheets.

Materials and methods. Materials: rice, corn, buckwheat flour, waffle batter and waffle sheets. Sedimentation of the dough was determined by measuring the column of the liquid; bound and free moisture – by the derivatization method, strength – by determining the force required for breaking the wafer sheet.

Results and discussion. Rational moisture content of dough with rice flour is 63, buckwheat – 80, corn – 65%.

The highest density has a dough with buckwheat flour – 1,113, corn – 1,083, rice – 1,065 g/cm^3, the least with wheat – 1,053 g/cm^3. This can be explained by different water absorption capacity of flour.

Sedimentation is maximal for dough with rice flour – 25.2, corn – 15.1, wheat – 10%. Dough with buckwheat flour is not subject to sedimentation. This is due to the presence of cellulose and pentosans.

The dough of buckwheat flour has a maximum viscosity (25.3 Pa·s), minimum – with rice (4.97 Pa·s). Viscosity of the dough with wheat flour-corn 7.97 Pa·s. It is substantiated by different chemical composition and different dispersion of wheat and gluten free types of flour, and is consistent with the content of free and bound moisture – for a test with buckwheat flour 56.04%, with rice – 35.97.

The highest strength – wafer sheets with corn and wheat flour (4.9 n and 4.1 respectively). The highest sedimentation – wheat and buckwheat flour (119.4 and 115.4% respectively), it is explained by different nutrient composition of all types of flour.

Calculations of the nutritional value showed that wafer sheet with buckwheat flour has bigger amount of proteins than the wafer sheets with rice and corn flour. Energy value of wafer sheets for different types of flour do not have much difference.

Conclusions. Gluten-free flour changes physico-chemical parameters of semi-finished and waffle sheets.

Introduction

Celiac disease (gluten enteropathy) – a disease characterized by chronic inflammation of a mucosa of small intestine, accompanied by malabsorption and arises as a result of intolerance to gluten. Approximately 1% of the population of America, Europe and the Eastern Mediterranean; and about 0.33% of the population in Asia, Africa and Australia suffer from celiac disease [3].

Patients with celiac disease should follow a gluten-free diet for lifetime. This leads to a reduction of symptoms and restoration of normal activity of the intestine. Therefore, people with celiac disease need gluten-free food, and it becomes a real challenge for manufacturers, especially in bread, pastry and pasta making. [5] Gluten (a protein found in most cereals) plays a key technological role in baking quality characteristics, being responsible for water absorption capacity, cohesivity, viscosity, and elasticity of dough. [6]

A range of gluten free products have been developed using rice and corn flours, which are often combined with corn, potato, or cassava starches as base flours because they are widely available, inexpensive ingredients that are bland in taste and flavor [7], [8]. However, the assortment of gluten-free products remains very small, while the needs of the modern consumers are constantly growing. [8], [9]. There are a lot of scientific works on the and research of quality indicators and development of gluten-free bread with different types of gluten free flour, starches and hydrocolloids published in modern scientific magazines [12], [13], [14] while the issue of the and research of quality indicators and development of gluten free pastry requires additional researches.

Most of the time nutritional status and demands of celiac patients are not satisfactorily covered when formulation and production of gluten-free products is carried out [11]. It is expedient to develop and implement technology in the production of gluten-free flour confectionery products for people with celiac disease based on gluten-free types of flour, such as rice, corn, buckwheat.

Nowadays there is no conducted research on the impact of gluten-free flour on quality parameters of the batter and waffles. In particular, viscosity, density, sedimentation, water absorption, strength, free and bound moisture content, require additional research and scientific justification. The complexity of the technology of gluten-free flour confectionery is that gluten-free flour and different kinds of starches have other properties than wheat flours. Scientists should improve technologies of gluten-free products to achieve similar structural, mechanical and physicochemical characteristics of gluten free and traditional in semi-finished products. Consequently, these gluten-free products can be produced on existing equipment.

Among the variety of pastry products, products based on waffles occupy a significant place. Due to this fact the research and scientific justification of quality indicators of the batter and waffles with using of the gluten-free flour are essential.

The main aim and tasks of research are: determination and scientific justification of the influence of gluten-free flour on Sensory, physical-chemical and structure-mechanical properties of the batter and waffles which patients with celiac disease can consume; calculation of nutritional and energy values.

Materials and methods

Materials

The technology of waffles based on gluten-free flour which patients with celiac disease can consume; rice, corn, buckwheat flour, waffle batter and waffle sheets based on different types of gluten-free flour. [1], [3], [17]

Methods

Determination of density of waffle batter

Picnometric method was used, which is based on measuring the mass of a certain volume of the product at a temperature from the following absolute and relative density [15].

Determination of viscosity

The rotational viscometer was used to determine the viscosity of the wafer batter [15].

Determination of sedimentation

Following method was used:50 cm^3 of the wafer batter was poured into a glass and measured the height. The height of the column of liquid that formed above the test was measured every 30 min for 120 min. The sedimentation rate is determined from the ratio of the height of the dough column to the height of the liquid column [17], [15].

Determination of bound and free moisture

The determination was performed by derivatograph Q-1500 [16]. The sample and the standard are loaded into the working volume and heated at a constant rate. The device measured the temperature of the sample and the difference between the temperature of the sample and the standard reference temperature difference, sample mass change, and the difference in masses of the reference and working samples. Samples are heated and at a rate of 1.25 °C/min at the temperature range from 20 to 250 °C. The recording device captures the graphs. Analysis of derivatograms was made [16]

Determination of strength

The strength was determined by method used for determination the strength of macaroni [18]. The wafer sheet was placed in the grooves of the walls of the device, which are attached to the pad of the dial scale. Pressed the "down" button, immediately after the sheet was broken clicked the "stop" and "up". The force by which the sheet was broken was determined by the arrow on the dial at the time of the break.

Determination of water absorption

To determine the absorption of water was used a bucket which consists of a bowl with a diameter of 90 mm, a height of 30 mm, cover and handle that can be removed. The bowl and cover have holes of 2 mm in size, the distance between them is 5-6 mm. Pieces of waffle sheet were placed in a bowl and weighed then the bowl was closed with a cover and lowered for 5 minutes into water with a temperature of 60 degrees Celsius. After that the cup was taken out of the water and weighed [15]. The coefficient of water absorption was determined from the ratio of the mass of wafer sheets before and after wetting [17].

Results and discussion

Sensory properties of the waffle dough

The consistency of the dough was evaluated in the first phase of research. Firstly, the dough was made with a moisture content 67%, which is rational to received quality wafer made of wheat flour under laboratory conditions. Established that there is a need to adjust the moisture content in the case of different types of gluten-free flour (Table 1).

Table 1

Sensory properties of waffle dough

Dough with the addition of flour	Moisture content, %	Characteristics of the dough
Wheat flour	67	The dough has needed consistency, which enables the formation of waffles
Rice flour	67	Very liquid consistency, which is not typical for waffle dough
	63	The dough has needed consistency
Corn flour	67	The consistency of the dough is more liquid than the dough from wheat flour. The dough separates quickly.
	65	The dough has more dense consistency, which is close to the wheat flour dough
Buckwheat flour	67	The dough is thick, elastic and has not fluidity. Formation waffles impossible by casting
	80	Consistency: sparse dough acquires some fluidity that makes it possible to form a wafer sheets

The research found that rational moisture for the dough with rice flour is 63% with buckwheat flour – 80%, with corn flour – 65%.

Important indicators for the dough for wafers are density and resistance to separation (sedimentation).

Density of the waffle dough

The research on the density of waffle dough with gluten-free flour (Figure 1) showed that it is different from the density of wheat flour dough.
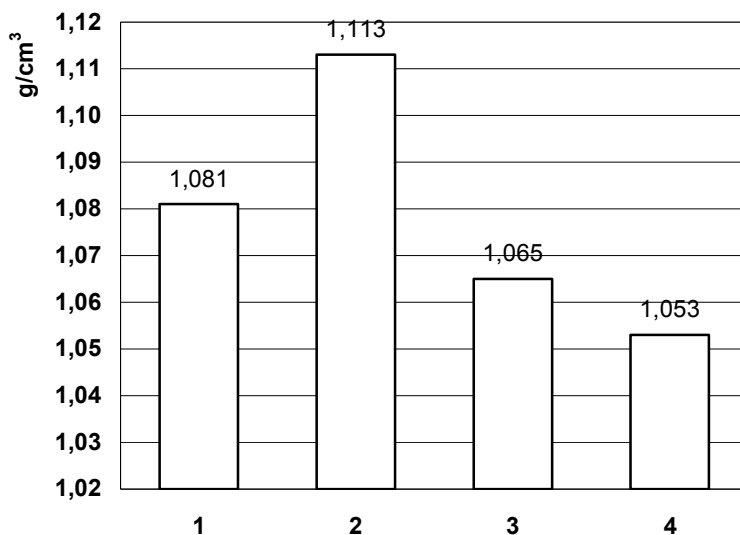
Figure 1. Density for waffle dough with using of different types of gluten-free flour for rational moisture content:
1 – Dough with corn flour;
2 – Dough with buckwheat flour;
3 – Dough with rice flour;
4 – Dough with wheat flour.

In the light of the results of the research on determination the density of waffle dough it can be concluded that the dough with buckwheat flour has the maximum density and the dough with rice flour has the minimum density. It can be associated with a water absorption capacity of flour: the dough with buckwheat flour has the maximum water absorption and the dough with rice flour has the minimum water absorption.

Sedimentation of the waffle dough

According to the technology of wafers production, after mixing in the dough mixer the dough does not fed to the formation simultaneously, and some time is in the intermediate tank. Therefore, an important technological aspect is the stability of the dough to the separation, i.e. sedimentation.

The research on the sedimentation of waffle dough with gluten-free flour (Figure 2) showed that it is different from sedimentation of dough with wheat flour.
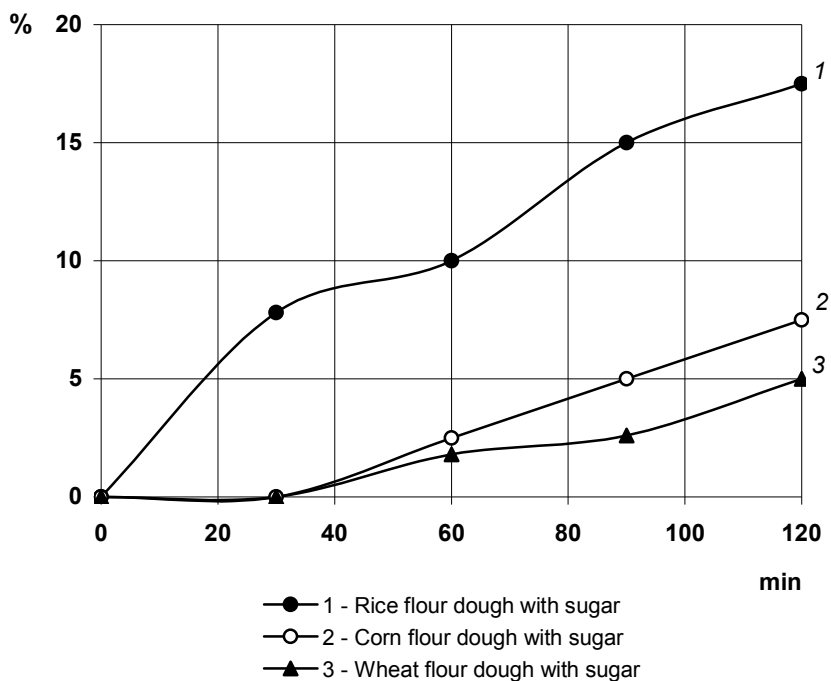
Figure 2. Sedimentation of waffle dough with gluten-free flour for the rational moisture content and with sugar

The dough with corn flour has the maximum sedimentation and the dough with buckwheat flour does not have sedimentation. This can be explained by large water absorption capacity of buckwheat flour, due to peculiarities of its chemical composition, including the presence of cellulose and pentosanes.

Viscosity of the waffle dough

The dough viscosity index is very important in the technology of waffles. It causes the accurate dosage of the dough during its filing in the form of wafer ovens and getting waffles with smooth edges.

The viscosity of the dough depends on the moisture content of the dough and the amount of free and bound water. Change of moisture content of the dough with wheat flour increases or decreases the thickness of the hydration shell around the particles of gluten. The thickness of the hydration shell around the particles of gluten increases with increasing of moisture content of the dough, aggregation decreases and consequently viscosity of the dough decreases. The thickness of hydration shell decreases with decreasing of moisture content of the dough, sustainability of the system with the formation of aggregates of particles of flour decreases. Accordingly, the viscosity of the dough increases.

There is need to create a rare mass with some viscosity indexes in the case making waffle dough. The research of viscosity of dough with gluten-free flours showed that the doughs with different types of flour and the dough with wheat flour have different viscosity indexes.

However, in the case of manufacturing it at a certain rational moisture which is different for different types of dough with different gluten-free flour, it is within the range that allow to form product (Figure 3).
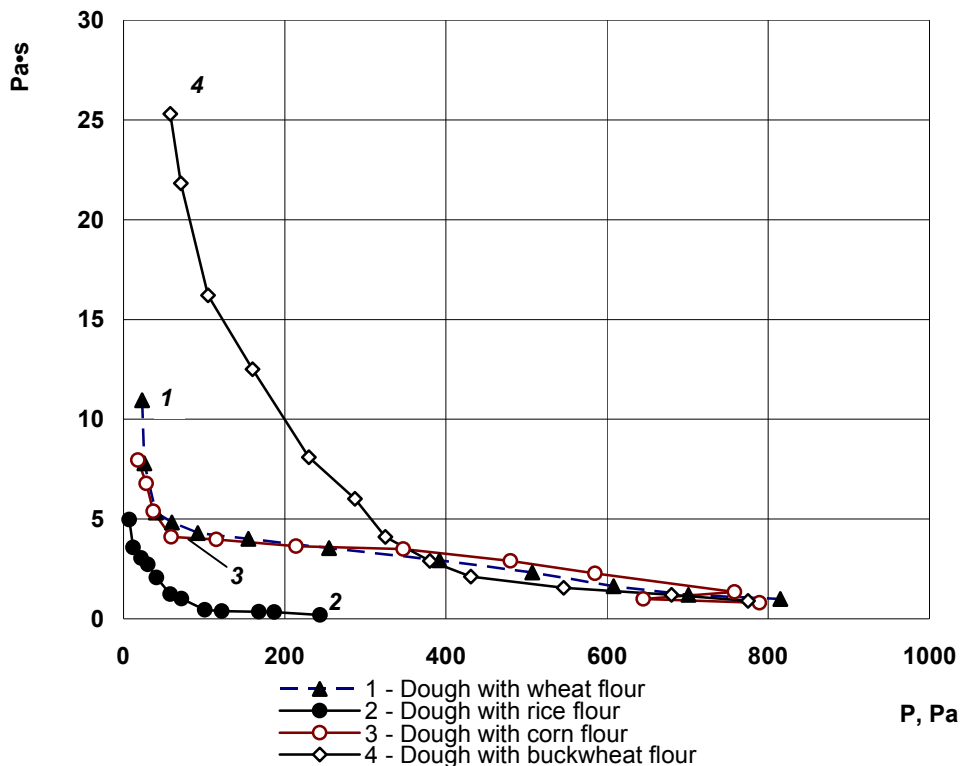

Figure 3. Viscosity of waffle dough with gluten-free flour for the rational moisture content

In the light of the results it can be conclude that the dough with buckwheat flour has the highest viscosity and the dough with rice flour has the lowest viscosity. Different viscosity of the doughs can be explained by the different moisture content of the doughs and different composition of wheat, rice, corn flour.

If we analyze the change of viscosity of the dough from one type of flour, depending on moisture content, it should be mentioned that the dough viscosity increases with decreasing of moisture content. The research that have been conducted found that the viscosity of waffle dough with rice flour on a 67% moisture content is 2.98 Pa·s, and with 63% moisture content – 4.97 Pa·s. At the same time moisture of dough with rice and corn flour are lower than with wheat flour; the viscosity indexes are also lower. Moisture content and viscosity of dough with buckwheat flour is higher than with wheat flour.

This is due to different chemical composition and dispersion of different types of gluten-free and wheat flour. So, buckwheat flour contains higher amounts of fiber, significant content of pentosane, which makes high ability to absorb water and causes an increase in viscosity. Rice flour contains less protein than corn, wheat and buckwheat flour.

The viscosity of intact structures (η_0), the viscosity of the destroyed structures (η_m) and the range of variation of viscosity with increasing shear stress ($\eta_{0\text{-}m}$) were calculated according to the viscosity curves (Table 2).

Table 2

Dependence of the of viscosity of waffle dough with gluten-free flour with sugar, Pa·s

The dough with the addition of flour	Viscosity, Pa·s		
	η_0	η_m	$\eta_{0\text{-}m}$
Wheat flour	10,95	0,36	10,59
Rice flour	4,97	0,18	4,79
Corn flour	7,96	0,6	7,36
Buckwheat flour	25,3	0,57	24,73

Free and bound moisture

As it has been noted before, the viscosity of dough also has affects the distribution of moisture in free and bound. Than smaller the amount of free moisture and more bound moisture, than higher the viscosity of the dough. The results of differential thermal studies found the number of free and bound moisture in the doughs with various kinds of gluten-free flour (Table 3).

Table 3

Calculation of free and bound moisture

Dough with the addition of flour	Moisture content					
	Total		Free		Bound	
	mg	%	Mg	%	mg	%
Wheat flour	130,40	100	79,20	60,73	51,20	39,26
Rice flour	125,30	100	80,00	63,84	45,30	36,15
Corn flour	131,20	100	84,00	64,02	47,20	35,97
Buckwheat flour	145,60	100	64,00	43,95	81,60	56,04

Calculation of percentage of free and bound water showed (tab. 3) that the buckwheat flour dough has a lot of bound moisture, the rice dough – the less content of bound moisture. This is consistent with the results of the research of viscosity (Fig. 3): the maximum in the buckwheat flour dough and the minimum in the rice dough.

Sensory and physico-chemical properties are important parameters of quality of final products.

Sensory characteristics of the waffles

Waffles with different types of flour showed their differences (Table 4) due to the peculiarities of taste, smell and color flour.

Sensory characteristics of waffles with different types of flour

Waffles with the addition of flour	Name of the index	Characteristics of the index
Wheat flour	Taste	Sweet, inherent for wafers, without foreign tastes
	Smell	Inherent for wafers, without foreign smell
	Color	From light yellow to cream
Rice flour	Taste	Sweet, inherent for wafers
	Smell	Inherent for wafers, without foreign smell
	Color	From white to light yellow
Corn flour	Taste	Sweet, inherent for wafers
	Smell	Inherent for wafers, without foreign smell
	Color	From white to light yellow, white on a break
Buckwheat flour	Taste	Sweet inherent for buckwheat flour
	Smell	Inherent for buckwheat flour
	Color	Brown

Strength and water absorption of the waffles

Strength and water absorption arethat physical and chemical properties, which in greatest degree characterize the final products. Research of these parameters for waffles which contain different types of gluten-free flour and waffles which contain wheat flour are different (Table 5).

Strength and water absorption of waffles with different types of flour

The waffles with the addition of flour	Strength, N	Water absorption %
Wheat flour	4,1	119,4
Rice flour	4,9	106,8
Corn flour	2,5	107,3
Buckwheat flour	2,7	115,4

The wafer sheets made with corn and wheat flour has the biggest strength. The wafer sheets made with wheat and buckwheat flour has higherwater absorption, this is due to different compositionof all types of flour.

Nutrition and energy value of the waffles

Food including pastry largely characterizes by their nutritional and energy value. This information must necessarily be indicated on the packaging.

It should be noted that there are strict requirements for foods for people who suffer from celiac disease. Gluten concentration should not exceed 20 mg per 1 kg in products that initially did not contain gluten and 200 mg / kg in the products of which gluten has been

removed in the production process [8]. So, it requires careful control of raw materials and finished products for the presence of gluten.

Results of calculation of nutrition and energy value of products are shown in Table 6.

<div align="right">Table 6</div>

Nutrition and energy value of waffles with different types of flour

Nutrients	Waffles with corn flour	Waffles with rice flour	Waffles with buckwheat flour
Proteins, %	12,26	9,37	12,53
Fats, %	7,17	7,22	7,09
Carbohydras,%	13,17	12,61	15,86
Energy value, kcal	339,25	319,22	338,06

Conclusions

The moisture content of a dough in case of use rice and corn flour should be reduced compared to moisture of dough with wheat flour, in the case of use buckwheat flour it should be increased to obtain high quality waffles.

The dough with buckwheat flour has the maximum density and viscosity, the dough with rice flour has minimum. Maximum separation occurs in the dough with corn flour, the dough with buckwheat flour does not separate. This is due to the peculiarities of the chemical composition of different types of flour and their ability to absorb water, different moisture of dough, different contents of free and bound water in the dough.

Wafer sheets, especially with buckwheat and corn flour have certain characteristics of flavor and color, but do not adversely effect on the Sensory characteristics.

Wafer sheet with buckwheat flour has bigger amount of proteins than wafer sheets with rice and corn flour. Energy value of wafer sheets for different types of flour do not have significant difference.

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Effects of storage of fresh cassava in moist sawdust on the proximate chemical and functional properties of gari

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Abstract

Introduction. The research was carried out to evaluate the utilisation qualities of cassava roots stored in sawdust for *gari* production.

Materials and methods. A completely randomised design was used to investigate the effect of storage time on the results of processing *gari*. Fresh cassava roots were stored in sawdust for 12 weeks and *gari* which is a cassava product was produced every two weeks. The proximate composition, chemical composition and functional properties of the *gari* were determined.

Results and Discussion. Cassava major food product in Africa is *gari,* the latter covers about 70% of cassava use in human consumption. Cassava *Manihot esculenta Crantz* is a starchy root which is a highly perishable crop, it starts to deteriorate within two or three days after harvest if not stored or processed. This study investigates the quality of *gari* produced from stored cassava roots.

The results show that there were significant differences in the proximate composition of *gari* samples in terms of the ash content, moisture content, fat content, fibre, protein and carbohydrate ($p<0.05$). The pH, TTA, HCN values of the *gari* ranged from 3.9 to 4.89, 0.77 to 0.9%, and 0.25 to 0.33mg/kg respectively. Also, there were significant differences ($p<0.05$) in the bulk density, water absorption capacity and swelling index, which ranged between 7.79 and 8.169g/cm^3, 199.18 and 311.11ml/g, and 3.13 and 3.96, respectively.

Conclusion. Cassava roots stored for about 12 weeks will still produce a good quality *gari*.

Introduction

Gari is the most popular of the cassava products in Africa (Oluwole *et al.,* 2004). *Gari* is a creamy-white, granular flour with a slightly fermented flavor and a slightly sour taste made from fermented, gelatinized fresh cassava tubers (Sanni *et al.,* 2008). It is consumed as processed or reconstituted with hot water to give a dough-like paste called *Eba*.

Cassava is different from other major root crops in that its roots are not organs of dormancy, making the pre-process storage a main problem of its utilisation (Karim *et al.,* 2009). NSPRI (1995) reported that the shelf life of cassava can be extended to about 8-10 weeks, based on high visual acceptability of stored cassava root in transverse section.

However, storage and utilisation quality of cassava has not been established for that length of time except for Akingbala *et al.,* (2005) and Karim *et al.,* (2009) who only investigated the samples after 3 and 2weeks of storage respectively.

However, there is need for more studies to establish other limits and benefits of the recommended methods in terms of the functional, chemical, and physical properties of the stored cassava and its products.

Hence, the aim of this work is to evaluate the utilisation quality of cassava roots stored in sawdust for *gari* production.

Materials and methods

Storage of Cassava roots

12-months-old (var. TME 7), was harvested from Lasuju farm settlement in Asa LGA of Kwara State, Nigeria. The storage was done using the storage method described by Babarinsa and Oluwalana (2018), the root were arranged in layers and surrounded with moist sawdust so that no two tubers touched one another.

Gari production

15Kg of stored cassava was processed into *gari* for analysis every two (2) weeks. *Gari* was produced by the process described by Onyekwere *et al.* (2004). All the *gari* samples were prepared by one commercial *gari* processor, this is to avoid variability in processing. The cassava root of was peeled manually using sharp stainless steel knife. The peeled roots were washed and grated in a diesel powered grater. The grated meal was dewatered and was allowed to ferment for 72 hours. The pressed cake was broken and sieved with a wire mesh screen. The sieved pulp was *gari*fied using a wide shallow cast iron pot and stirred continuously over a low fire until well dried. It was then cooled, packaged, labeled and sealed.

Laboratory Analysis

The proximate analysis (moisture content, ash content, fat content, fibre, protein and carbohydrate) was carried out according to AOAC (2005). Estimation of hydrogen cyanide was done using silver-nitrate volumetric analysis described by Oboh *et al.,* (2002), while the pH and Total titratable acidity (TTA) as lactic acid was determined according to AOAC, (2005). Bulk density swelling index, water absorption Capacity of the sample was determined using the method described by AOAC (2005), Ukpabi and Ndimele (1990) and Ogungbenle *et al.* (2002) respectively.

Statistical analysis

A Completely Randomised Design was used to investigate the effect of storage time on the analytical determinations. Results from the analysis were subjected to analysis of variance ($p<0.05$). The Duncan (1955) multiple range test was then used to separate means. All analysis were in triplicate and Statistical analysis was done using SPSS 17.

Results and discussion

Moisture content

The moisture content of the *gari* was significantly affected by the processing rather than storage time ($p<0.05$), the values was generally low and were between 8.11 and 8.59% (Table 1). The moisture content of all the *gari* samples were below the 10% stipulated standard of the revised regulation of the Standard Organization of Nigeria and the export range of 6–10% (Sanni *et al.,* 2005).

Moisture is a significant parameter in cassava flour storage, high moisture greater than 12% allow for microbial growth. This is because moisture content and water activity of foods affect the progress of their chemical and microbiological spoilage reactions and thus low levels are favourable and give relatively longer shelf life. All the *gari* will be able to store for 7 months because their moisture contents were below the levels reported by Ukpabi and Ndimele (1990, who found that *gari* samples with a moisture content of < 16% but > 13% could be stored for 2-7 months without mould infestation. All the samples had good moisture levels and hence have the potential for better shelf life.

Ash content

The *gari* samples were significantly different ($P<0.05$), with the *gari* produced after Week 8 having the lowest value of 1.28% and Week 6 having the highest value of 3.34%. The values obtained in weeks 0, 2, 8 and 10 were comparable to the range of 1% to 2.84% dry weight reported by Aryee *et al*. (2006) and the range of values reported by Okolie *et al*. (2012) in their comparative study of different *gari* samples in Nigeria.

Ash content, which is a measure of the mineral element contents in the plant, is said to depend on the mineral contents of the soil. The slight differences in the ash content must have been due to processing. During processing, the dewatering of the grated cassava mash by pressing with a screw press may have resulted in loss of some minerals via the expressed water thereby reducing the ash content. The reduction may also be due to degradation of naturally occurring chemicals and loss due to spoilage (Ajala *et al.* 2012).

Fat content

All the *gari* had low fat content with the highest being 0.42%. There were significant differences ($p<0.05$) in the fat content amongst the studied *gari* samples. The *gari* samples were in line with those of 0.1% to 0.4% reported by Charles *et al*. (2005) and 0.65% reported by Padonou *et al*. (2005).

Fibre content

Fibre content of the *gari* samples were in the range of 2.82-2.92% (Table 1), which were significantly different between each other ($p>0.05$). Week 0 had the lowest with

2.82%, and Week 12 had the highest with 2.92%. The *gari* samples were comparable in fibre content to the range of 1.61 and 3.63% reported by Franklin *et al.,* (2009) and close to the result of the studies by Oduro *et al.,* (2000) on quality of *gari* from some selected *gari* processing centres in Ghana.

Protein content

The protein content of the *gari* investigated ranged from 0.78% to 0.98% (Table 1). There were significant differences amongst the studied samples and this may be attributed to storage time. This is in line with the protein content of cassava ranging between 1% and 3% on a dry matter basis, reported by Buitrago (1990). The increase in the protein content may likely be due to the presence of organisms that had been processed along with the cassava (Ajala *et al.,* 2012).

Carbohydrate content

The carbohydrate content of the *gari* samples were significantly different (p<0.05), having values ranging between 84.19-86.48% (Table 1). The values compared favorably with the values reported by Akingbala *et al.* (2005) and Karim *et al.,* (2009) and about the same value reported by Rose-Monde *et al.,* (2009). The high carbohydrate values obtained in this study suggest that cassava could be utilized as a reliable food and energy security crop (FAO, 2002).

pH

The storage time had significant (p<0.05) effect on the pH of the samples. The *gari* from Week 0 cassava root was more acidic, having pH of 3.90 while that of Week 10 was the lowest acidity with 4.89 (Table 1). Generally, there was decrease in the acidity as the storage time increases in the *gari* sample. The values agree with those of Oduro *et al.,* (2000) for the normally fermented cassava *gari* (pH 3.6 to 4.0), and Bainbridge *et al.,* (1996) who reported pH of 3.5 – 4.5 for acid fermented product. The acidity of fermented cassava product has been found to be caused by the synthesis of lactates, acetates and some volatile organic acids (Oyewole and Odunfa, 1989) caused by microoganism such as C*ornebacterium manihot, Geotriucm candida, Lactobacillus spp*, which hydrolyze starch to this organic acids. The acid contributes to the desirable sourness of *gari* and is also an indication of the duration and effectiveness of the fermentation step in *gari* processing (Akingbala *et al.,* 2005).

Total titratable acidity

The titratable acidity of the *gari* was significantly affected by the storage time (p<0.05). The total titratable acidity expressed as percentage lactic acid of *gari* samples was between the range of 0.76-0.90% (Table 1). The total titratable acidity agrees with the Codex standard of total acidity for *gari* which is between 0.6 and 1.0%, expressed as percent lactic acid (Codex Alimentarius Commission, 1989) and the recommended standard of 0.6 – 1.2 for cassava-*gari* by Oduro *et al.,* (2000). Since changes in total titratable acidity is due to dissociation of the weak organic acids, mainly lactic and formic acids, Table 1 implies that the dissociation occurred and reached its optimum in the early week of storage, and subsequently there were poor or no dissociation. Fermentation is as a result of the lactic acid bacteria conversion of sugar content to organic acid (lactic acid) which consequently cause the increase in the total titratable acidity of the cassava mash (Akingbala *et al,.* 2005). The value ranged between 0.01- 0.16% with Week 0 having the

highest and was significantly different from the rest of the weeks. The total titratable acidity which ranged from of 0.01-0.16 compares favourably with the report of Akingbala *et al.*, (2005) and Karim *et al.,* (2009).

HCN

There were significant differences ($p<0.05$) among the *gari* samples, with Week 4 having the lowest value and Week 12 having the highest value with a range value of 0.25-0.33 (Table 1). The *gari* samples range of 0.25-.33 and is far below the estimated lethal dose of 0.4-0.6 mg/kg reported for *gari* by Bokanga (1994).

Bulk density

Gari samples exhibited a decrease in bulk density value throughout the storage period and they differ significantly ($p<0.05$). The bulk density of *gari* produced from cassava roots ranged from 7.79 – 8.16 (Table 1).   The bulk density conforms favourably with the findings of Olaleye *et al.* (2014) which values ranges from 0.70- 0.81 g/cm^3 and 0.61 - 0.77 g/cm^3 for *gari* produced from bitter and sweet cassava varieties respectively but higher than those reported by Achinewhu *et al.* (1998) for six different cassava cultivars whose relative bulk densities ranged between 0.15 and 0.30 g/cm^3. The bulk density is a reflection of the load the samples can carry if allowed to rest directly on one another. Bulk density is affected by moisture and reflects particle size distribution of the *gari* products (Olaleye *et al.,* 2014). Bulk density may also be attributed to high starch content in cassava which affect the mass and hence relative bulk density. According to Ukpabi and Ndimele (1990), good *gari* should have bulk density between 0.56 to 0.908 g/cm^3. High bulk density increases the rate of dispersion which is essential in the reconstitution of flours in hot water to produce dough.

Water Absorption Capacity

The Water absorption capacity of the *gari* was significantly affected by the storage time ($p<0.05$). Generally, the water absorption capacity reduces from 3.13 to 3.96ml/g as the storage time increases though Week 8 was the lowest (Table 1). Water absorption capacity is a very important property of all flours or starches used in food preparations. The observed differences in water absorption capacity of the *gari* products as suggested by Olaleye *et al.,* (2014) might be due to various factors such as particle size, amylose/amylopectin ratio and molecular structure. The larger the granular size, the greater the water absorption capacity while the higher the amylose levels, the lower the water binding capacity of starches (Akalu *et al.*, 1998). Processing factors such as fermentation have also been found to increase water absorption capacity. Since polar groups of carbohydrates (for starchy foods like *gari*) are chiefly responsible for the binding of water, it therefore follows that the *gari* starch contains polar (hydroxyl) groups which are able to interact with water through hydrogen bonding (Obadina *et al.*, 2008). It follows, therefore, that the higher the value of water absorption capacity, the greater the number of hydroxyl groups available to form hydrogen bonds with water (Obadina *et al.*, 2008).

Swelling Index

Generally, the swelling index increased with increasing storage time ranging from 3.13-3.96. The values compare favourably with the Codex Alimentarius standard of 3, while a range of 2.7 to 3.3 was reported by Oduro and Clarke, (1999) and 2.84±0.26 by Ajibola *et al.*, (1987) in the Nigerian market Swelling index is the ability of *gari* to swell

and this is influenced by the quantity and type of amylose and amylopectin present (Bainbridge *et al.,* 1996) in the *gari*. Swelling index is very important because it indicates the degree of gelatinization of the *gari* sample and the rehydration characteristic. Swelling index reflects the extent of associative forces within the granules, thus, the higher the swelling index the lower the associative force (Sanni *et al*., 2001). According to Babarinsa (2011) a good quality *gari* should swell when soaked in water, to at least three times its dry volume because consumers demand *gari* with good swelling capability.

Table 1

Proximate, chemical and functional properties of the *gari* samples

Period of storage	MC (%)	ASH (%)	FAT (%)	CF (%)	CP (%)	CHO (%)
WEEK 0	8.41±.09[bc]	1.63±.05[e]	0.42±.12[a]	2.82±.06[b]	0.78±.02[d]	85.94±.33[b]
WEEK 2	8.44±.03[b]	2.38±.04[c]	0.33±.02[bc]	2.86±.01[ab]	0.85±.05[c]	85.13±.14[c]
WEEK 4	8.37±.02[c]	3.24±.02[a]	0.23±.01[d]	2.85±.05[ab]	0.91±.01[b]	84.41±.04[e]
WEEK 6	8.39±.00[bc]	3.34±.02[a]	0.27±.01[cd]	2.85±.01[ab]	0.97±.02[a]	84.19±.06[e]
WEEK 8	8.19±.02[d]	1.28±.05[d]	0.39±.01[ab]	2.82±.03[b]	0.83±.02[c]	86.48±.02[a]
WEEK 10	8.59±.03[a]	2.53±.02[b]	0.29±.01[cd]	2.86±.01[ab]	0.98±.01[a]	84.76±.03[d]
WEEK 12	8.11±.01[d]	3.24±.01[a]	0.21±.01[d]	2.92±.08[a]	0.87±.01[bc]	84.65±.05[de]

Period of storage	pH (%)	TTA (%)	HCN (mg/kg)	BD (g/cm³)	WAC (ml/g)	SI
WEEK 0	3.90±.02[f]	0.77±.01[a]	0.30±.01[b]	8.16±.05[a]	311.11±5.13[a]	3.14±.02[a]
WEEK 2	4.32±.01[b]	0.77±.01[a]	0.30±.01[b]	8.02±.01[b]	214.44±1.76[c]	3.27±.01[b]
WEEK 4	4.27±.01[c]	0.80±.00[a]	0.25±.00[a]	8.03±.00[b]	220.81±2.27[b]	3.21±.01[b]
WEEK 6	4.26±.01[c]	0.83±.01[b]	0.26±.00[a]	8.05±.01[b]	212.65±.89[cd]	3.15±.01[a]
WEEK 8	4.19±.01[d]	0.83±.03[b]	0.32±.01[ab]	7.79±.00[d]	199.18±.17[f]	3.13±.01[a]
WEEK 10	4.89±.01[a]	0.76±.01[c]	0.26±.01[a]	7.89±.00[c]	204.97±.27[e]	3.86±.05[c]
WEEK 12	4.11±.01[e]	0.90±.01[a]	0.33±.00[a]	7.90±.00[c]	210.10±.01[d]	3.96±.01[c]

Values are means of triplicates and standard deviation. Mean values having different superscripts within the same column are significantly different ($p < 0.05$).

KEY
MC = Moisture content ASH = Ash content
FAT = Fat contentCF = fibre
CP = Protein content CHO = Carbohydrate
TTA = Total Titratable Acidity   HCN = Hydrogen Cyanide
BD = Bulk density   WAC = Water absorption capacity
SI = Swelling Index

Conclusion

The study has shown that stored cassava root can produce good quality of *Gari*. The chemical values obtained in terms of the total titratable acidity and pH of *gari* produced compared effectively with the *gari* of published recommended values. HCN content were reduced during storage. The proximate composition was also comparable to the Week 0 sample and published recommended values. The functional properties in term of the swelling index, water absorption capacity and bulk density of the stored cassava also compared favourable with that of Week 0 and published recommendations.

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Energy transformations in processes of anaerobic fermentation

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Abstract

Introduction. The course of energy transformations in the processes of anaerobic fermentation refers to the indices of chemical energy as a result of biochemical reactions. This part of transformations is deeply studied and recognized, however, the synthesis of carbon dioxide in culture media is accompanied by the creation of energetic potentials in gas and liquid phases, is seriously understudied as of today.

Materials and methods. The object of this research is the gas-liquid medium in the processes of anaerobic fermentation. Evaluation has been carried out for their energy potentials created on the basis of carbon dioxide synthesis. The theoretical study was carried out on the basis of the Henry's, Pascal and Archimedes laws.

Results and discussion. Synthesized in anaerobic processes, carbon dioxide passes two stages of transformation. On the first stage, during the mass transfer between yeast cells and the medium, the concentration of CO_2 increases to the saturation index in accordance with Henry's law, and on the second stage the formation of the dispersed gas phase is carried out. The endogenous process of carbon dioxide synthesis, the processes of saturation of the liquid phase and the formation of the dispersed phase are self-loading and those in which the corresponding energetic potentials are created, resulting in a circulating mixing of the media. In cases of using sealed fermentation vehicles, the gas phase is characterized by an appropriate energy potential due to the increased pressure. The levels of energy potentials of the compressed gas medium and dissolved CO_2 are thermodynamically determinable and their ratios are interconnected due to the geometric volumes of the liquid and gas phases.

The possibility of creating local zones of desaturation and saturation of the liquid phase in the total volume of the gas-liquid medium is shown. The presence of such zones means the possibility of regulatory influences on osmotic pressure and the removal of media from saturated and supersaturated states.

Conclusions. The energy potential, associated with the saturation gradient of the media on CO_2, provides a fast and continuous implementation of restoration in the saturation possibilities of the liquid phase and the activation of fermentation in the case of the saturation circuit restoration.

Introduction

Processes of anaerobic fermentation of the wine-making, alcohol and brewing branches are similar in their essence and finish with the transformations of sugars of input materials into alcohol and carbon dioxide as a result of the life of the yeast- saccharomycetes. The course of these processes corresponds to the Gay-Lussac equation in accordance with the laws of conservation of mass and energy in the form:

$$C_6H_{12}O_6 = 2C_2H_5OH + 2CO_2 + 169 \text{ kJ} \tag{1}$$
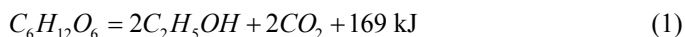
The chemical energy of glucose which is 2870 kJ transforms into 2640 kJ of alcohol and 230 kJ of free energy. The latter consists of energies of two molecules of ATP in the amount of 61 kJ and 169 kJ of thermal energy, and two molecules of synthesized CO_2 have no chemical energy potential. However, for the explicit awareness of the energy balance relative to condition (1), the analysis of the situation can not be considered to be complete, since the excited cultural medium has features of a system with an increased hydrodynamic state [1, 9, 10]. The latter is characterized by active upward and downstream streams of the circular circuits of gas-liquid mixtures and relatively independent upstream streams of the dispersed gas phase etc. These circumstances have at least two reasons. The first one concerns the process of generation and removal of heat stream generated during the fermentation process. It is obvious that there is a prerequisite to consider the process of generation of heat energy to be distributed sufficiently even in the full volume of the medium. However, the necessity to stabilize the temperature requires the presence of cooling surfaces, often in the form of external shirts of fermentation devices. This means the presence of volumetric temperature fields in the media, which results in the creation of circulating circuits [4, 5]. For cases of fermentation vehicles of cylindrical or cylindrical-conical geometry, the central part of the volume of media that are the most equidistant from the cooling surfaces correspond to relatively higher temperatures. Due to this, the conditions for the ascending flows of circulation circuits are created in the central zone and, conversely, the downstream flows adjacent to the surfaces of the occupation.

The intensity of such circulation circuits is proportional to the generated heat energy flow and depends on both the geometry of the fermentation apparatus and the total volume of the medium [6, 7].

The second reason for the creation of circulating circuits in fermentable media is the response of the system to the presence of dissolved CO_2 and its dispersed gas phase. The formation of these two forms is connected, firstly, with the gravitational field of the Earth and, secondly, with the manifestation of the gravitational field in the form of hydrostatic pressure, which is reflected by the Henry's law of solubility of gases. Transient processes of solubility of CO_2 are completed by the state of saturation, and they transit to the regime of creating the dispersed gas phase [8]. Under the action of the motive factor in the form of the Archimedes law, the dispersed gas phase fades from the formation of the gas phase in the ingenious volumes. In cases of sealed volumes of fermentation vehicles, the pressure in the ingenious volumes increases, creating the energy potential. At the feedback level, this increase of pressure leads to an increase of the solubility of CO_2 in the liquid phase and to the creation of additional energy potential of the dissolved gas. The latter can be transformed into the mechanical energy of the circulating circuit in case of a sharp decrease of pressure in the gas phase. The energy potential of circulating circuits is gaining due to
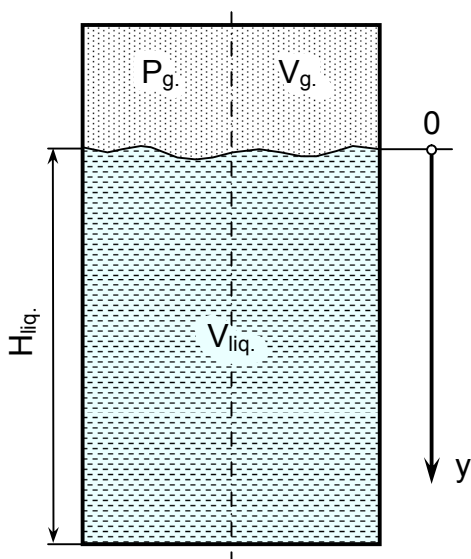
Figure 1. Scheme to determine the parameters

the presence of a gradient of saturation of the liquid phase on CO_2 due to hydrostatic pressures. It is obvious that the presence of circulation circuits leads to the creation of zones of desaturation of media in ascending streams by reducing hydrostatic pressures and saturation zones in downstream streams. In connection with the latter it is possible to conclude that the depth of desaturation and saturation processes, and even the manifestations of energy impulses, depends on the geometry of apparatus in the form of hydrostatic pressures [10].

The given analysis of energy potentials of systems of anaerobic digestion of sugar-containing media is executed on the basis of phenomenological generalizations, which it is expedient to supply by quantitative ratios of energy parameters.

The purpose of the study is to create mathematical formalizations for the establishment of energy potentials in anaerobic fermentation systems.

Materials and methods

The object of the study is the gas-liquid medium [1, 4] in the processes of anaerobic fermentation in the direction of evaluation of their energy potential.

The theoretical basis of the study relates to the laws of Henry [2], Pascal [11, 12], Archimedes [11], the laws and the provisions of thermodynamics.

Results and discussion

To establish quantitative estimates of the relations of energy parameters let's turn to the calculation scheme on Figure 1, which corresponds to the case of fermentation of the medium in a sealed apparatus. The pressure in the gas phase increases in the process of fermentation. The list of parameters for the calculation scheme includes: $V_{g.}$ - the volume of the gas phase in the ingenious volume, m³; $P_{g.}$ - pressure of the gas phase, Pa; $\rho_{g.}$ - specific mass of the initial gas phase, kg/(m³*Pa); $V_{liq.}$ - liquid phase volume, m³; ρ - specific mass of the liquid phase, kg/m³; g - acceleration of free fall, m/s²; H - height of the liquid phase, m; R - gas constant, J/(kg*K); T - absolute temperature of the medium, K.

The following relationships are established for these parameters:

$$P_{g.} = \frac{\left(\rho_g V_g + 0,489 M_{s.} - k V_{liq.} \rho g \frac{H}{2} \right) RT}{V_g + k V_{liq.} RT} ; \qquad (2)$$

$$grad\left(CO_2\right)=\frac{c_s\left(y=H\right)-c_s\left(y=0\right)}{H}, \tag{3}$$

where $c_s\left(y\right)$ - the saturation constant of the medium on CO_2.

$$c_s=kP_{g.}, \tag{4}$$

The results of calculations are given in the table 1 for the parameter values and on the Figure 2-6:

$$R=189\,J/\left(kg\cdot K\right);\quad V_{g.}=0,1;1,0\,m^3;$$
$$M_{s.}=10...130\,kg\quad R=189\,J/\left(kg\cdot K\right);$$
$$V_{g.}=0,1;1,0\,m^3;\quad M_{s.}=10...130\,kg$$

Table 1

Estimated parameter values

Parameters	Weight of fermented sugar, kg						
	10	30	50	70	90	110	130
When							
$P_g P_g$, MPa	0,303	0,894	1,473	2,076	2,26	3,2	3,75
c_s, kg/m^3	4,48	13,22	21,8	30,72	39	47,8	62,2
$E_{(0,1)}$, kJ	30,3	89,4	147,3	207,6	260	325,5	401
$E'_{(0,1)}$, kJ	256,6	757,1	1248,4	1759,2	2213	2736,5	3255
$E_{equal(0,1)}$, kJ	286,9	846,5	1395,7	1966,8	2500,6	3062	3720,2
When							
$P_g P_g$, MPa	0,21	0,513	0,81	1,12	1,4	1,73	2,05
c_s, kg/m^3	3,11	7,59	11,91	16,56	21,01	25,5	32,3
$E_{(0,1)}$, kJ	210	513	810	1119	1422	1725	2040
$E'_{(0,1)}$, kJ	178	434,7	682	948,3	1203,2	1465,5	1745
$E_{equal(0,1)}$, kJ	388	947,7	1492	2067,3	2625,2	3185	3890

The potential energy of the gas medium was estimated by dependencies:

$$E_{(0,1)}=P_{g.}V_{g.(0,1)}, J; \tag{5}$$
$$E_{(1,0)}=P_{g.}V_{g.(1,0)}, J; \tag{6}$$

Comparison of values $E_{(0,10)}$ and $E_{(1,0)}$ shows an advantage $E_{(1,0)}>E_{(0,1)}$ with multiplicity of more than 5, which is the result of increased solubility of carbon dioxide in connection with pressures. The potential of dissolved CO_2 is determined by referring to the Mendeleyev-Clapeyron equation with the assumption that it is transferred to the gas state and, under the condition $V_{liq.}=1,0\,m^3$, we have:

$$E'_{(0,1)} = c_{s(0,1)}RT; \quad E'_{(1,0)} = c_{s(1,0)}RT . \tag{7}$$

In these dependencies, the saturation constants $c_{s(0,1)}$ and $c_{s(1,0)}$ reflect the mass of carbon dioxide M_{CO_2} in the liquid phase.

As examples we will make calculations for cases with masses of fermented sugars 10 and 120 kg.

When $V_{g.} = 0,1 \, \text{m}^3$ we have:

for the gas phase:

$E_{(0,1)} = 0,303 \cdot 10^6 \cdot 0,1 = 30300 \, J = 30,3 \, \text{kJ};$

$E_{(0,1)} = 3,55 \cdot 10^6 \cdot 0,1 = 355000 \, J = 355 \, \text{kJ};$

for dissolved gas:

$E'_{(0,1)} = 4,48 \cdot 189 \cdot 303 = 256556 \, J = 256,556 \, \text{kJ};$

$E'_{(0,1)} = 52,6 \cdot 189 \cdot 303 = 3012244 \, J = 3012,244 \, \text{kJ};$

total energy values are:

$E_{equal(0,1)} = 30,3 + 256,556 = 286,856 \, \text{kJ};$

$E_{equal(0,1)} = 355 + 3012,244 = 3367,2 \, \text{kJ}.$

For the case $V_{g.} = 1,0 \, \text{m}^3$, we obtain respectively:

for the gas phase:

$E_{(1,0)} = 0,21 \cdot 10^6 \cdot 1,0 = 210000 \, J = 210 \, \text{kJ};$

$E_{(1,0)} = 1,88 \cdot 10^6 \cdot 1,0 = 1880000 \, J = 1880 \, \text{kJ};$

for dissolved gas:

$E'_{(1,0)} = 3,108 \cdot 189 \cdot 303 = 177985,8 \, J = 177,99 \, \text{kJ};$

$E'_{(1,0)} = 27,78 \cdot 189 \cdot 303 = 1590877 \, J = 1590,88 \, \text{kJ};$

total energy values are:

$E_{equal(1,0)} = 210 + 177,99 = 387,99 \, \text{kJ};$

$E_{equal(1,0)} = 180 + 1590,88 = 3470,88 \, \text{kJ}.$

From the calculation data and their geometric interpretation, the importance of influencing on the pressure system in the gas phase, which is created in self-propelled processes such as fermentation, takes place. The technical implementation of the pressure parameters is provided by sealing the fermentation apparatus with the corresponding ratio of the regulator of the boundary pressure.

The presence of energy potentials in the gas and liquid phases is subject to an assessment of the possibilities of their use in the directions of fermentation intensity and its efficiency. Phenomenological analysis leads to the conclusion about the special possibilities of using the potential of compressed CO_2 in the volume of the gas phase, since the regulatory pressure changes allow the liquid phase to be removed from the state of saturation in the desaturation mode or to return it to the saturation regime, including in the form of collapse (cavitation) of the dispersed gas phase.
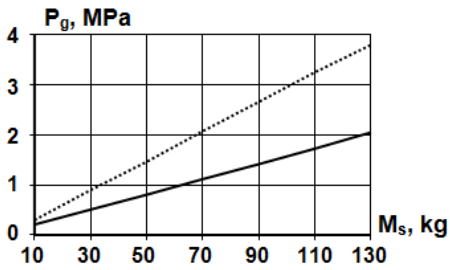
Figure 2. Graphs of dependence of pressure in gas ingenious volume on the amount of fermented sugar
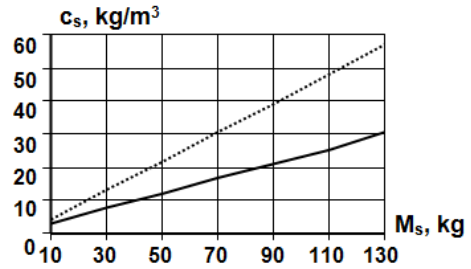
Figure 3. Graphs of the concentration of dissolved carbon dioxide in the liquid phase on the amount of fermented sugar
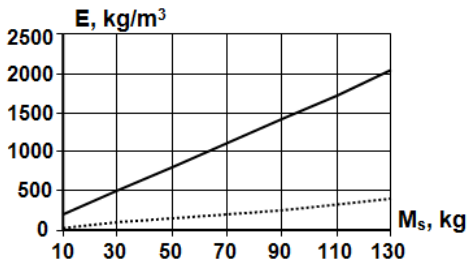
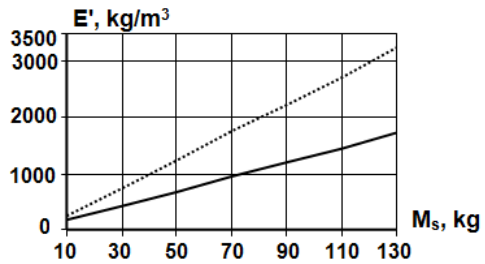Figure 4. Graph of the dependence of the gas phase energy on the amount of fermented sugar

Figure 5. Graph of the dependence of dissolved CO_2 in the liquid phase on the amount of fermented sugar
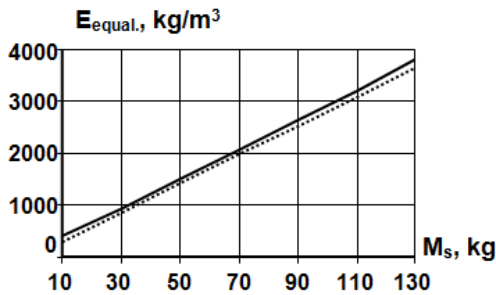
Figure 6. Graph of the dependence of the total amount of CO_2 energy in the liquid and gas phases on the amount of fermented sugar

It is obvious that the expansion of the range of energy influences, including impulse, on the gas-liquid medium is determined by its potential E'. From this point of view, limiting the volume of the gas phase in the ingenious volume is accompanied by extremely high efficiency when such conditions are reached:

$$E'_{0,1} \gg E'_{1,0}$$

In our case, the multiplicity of the ratio when $V_{g.} = 0,1\,\mathrm{m^3}$ was

$$E'_{0,1}/E_{0,1} \approx 8,5\,,$$

Whereas in the case $V_{g.} = V_{liq} = 1\,\mathrm{m^3}$ this ratio is:

$$E'_{1,0}/E_{1,0} \approx 0,85$$

The dependences shown on Figure 2–6, indicate the expediency of limiting the volumes of the gas phase due to the increased rate of saturation of the medium with the redistribution of energy potentials. It is important in the anaerobic technologies of digestion of secondary wine materials, beer, cider, etc., that is, in cases where saturation of the media with carbon dioxide is a composition of the technological task.

It is important to note that the indicated volume ratios do not almost affect the values of total potentials.

At the same time, in the technologies of alcohol fermentation, the transition to the limited volumes of the gas phase remains promising both for the intensification of mass-exchange processes, and for the creation desaturation and saturation periods and zones in gas-liquid media. The sharp reduction of pressure in the gas phase simultaneously and rapidly converts the full volume of the liquid phase into a supersaturated state, which is accompanied by an additional formation of the dispersed gas phase and increase of the volume of that part of the dispersed phase, which existed before the moment of decrease of pressure. The consequence of these two phenomena is an increase of the volume of the gas-liquid medium, which reflects its energy impulse, the intensification of mass-exchange processes and the level of desaturation. Complex of transition processes, associated with the reduction of pressure in the gas phase, is characterized by their self-determination until the new state of equilibrium. Saturation of the liquid phase on CO_2 corresponds to the latter but at a lower level with a corresponding decrease of the osmotic pressure.

The forced increase of pressure in the gas phase of the fermentation apparatus means the presence of a new transitional process of another direction, which transfers the liquid phase to the unsaturated state and to a new mode of saturation with the activation of yeast in the process of fermentation.

Conclusions

The energy potentials of synthesized in the processes of anaerobic fermentation carbon dioxide are divided into two parts. One of them relates to the gas phase, which transits into the ingenious volume, while the second is the potential of dissolved CO_2. An influential parameter for this redistribution is the ratio of volumes of liquid and gas phases. The convergence of these volumes in other existing conditions converges energy potentials, and the restriction of volumes of the gas phase is accompanied by a noticeable redistribution of energy potentials at the edge of the liquid phase.

The energy potentials of gas volumes do not find practical application in processes of fermentation, but the reduction of pressures in them provides the modes of desaturation of liquid volumes, the use of energy potentials of soluble gases, the intensification of mass-

exchange processes.

The energy potential associated with the saturation gradient of the media on CO_2, provides fast and continuous implementation of the restoration of the saturation possibilities of the liquid phase and the activation of fermentation due to the condition of realization the deterministic circulatory circuit.

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Modeling of extrusion-blown molding process of polymeric package

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Abstract

Introduction. For achievement of uniform minimum thickness of a wall of the created container and definition of the corresponding technological modes numerical researches of process of hollow polymeric products formation are conducted. Researches are conducted depending on a form of preparation and a finished product

Material and methods. In this work formation process by blowing of an axisymmetric bottle is modeled. Initial workpiece represents a cylindrical sleeve with an external radius of 10 mm. After creation of internal pressure workpiece is blown, the contact between polymer and a blown form will not be provided yet. The research is conducted on the case of formation of products from a polyethylene with low density (LDPE).

Results and discussion. When the process of blowing the internal pressure is being modeled, initial thickness and outer diameter of preparation are set as constants. With an increase in the radius of a bottom corner of a bottom a wall thickness increases, however at the same time the product becomes unstable. For ensuring the minimum necessary thickness in this place it is necessary to spend excess material in other sections. Extent of thinning of a wall of a product increases with an increase in extent of blowing on a certain local site. As it follows from the results of modeling, for achievement of the minimum necessary uniform thickness of a product it is necessary to change workpiece thickness on height (in this case - to reduce it in the lower and average parts). This method of calculation of a necessary profile of thickness of preparation allows to reach uniformity of thickness of walls of the product. For this purpose workpiece on height breaks into conditional nodes, in each of which the necessary thickness of workpiece depending on the calculated product wall thickness in the corresponding point is defined by iteration.

Conclusion. The interrelation between the workpiece, a finished product and the distribution of thickness in its walls is defined.

Introduction

Polymeric materials use as raw materials for production of packing materials, such as bottles, flasks, containers, canisters for packing of the wide range of foodstuff and other consumer goods, in particular soft drinks, alcoholic beverages, detergents, cosmetics, pharmaceutical products and food oils.

In the course of extrusion-blown molding process of a polymeric container at first polymeric workpiece forms by extrusion method. Then workpiece moves in a molding tool in which it is blowed by compressed air and takes the form of a final product [1]. Production of various container and canisters from polymeric materials is carried out by method of blowing on extrusion-blown units. All extrusion-blown units include three main components: an extruder, a die and a receiving device which basis is the molding tool for blowing.

Unlike the majority of methods of receiving products of plastic in which formation is carried out from melt in this technology polymer when blowing is exposed to mainly highly elastic deformation [2]. Workpiece which comes out an extruder die in a molding tool is affected by a body weight therefore it is extended. Degree of a blowing of workpiece is non-uniform on height therefore the container turns out with various thickness on height. In modern machines for controlling of thickness of walls of workpiece dies with program regulation which allow to form workpiece with the necessary distribution of thickness of a wall on its height are used. A problem of regulation is achievement of the necessary distribution of thickness of a wall of a finished product. Mathematical solution of the problem it is limited only by separate cases, the trial and error method demands considerable expenses of time. Therefore it is more expedient to use methods of computer modeling.

Within the last decades computer models promoted significant improvement of the analysis of formation processes therefore now they are widely used for process optimization [3-6]. Computer models can minimize undesirable variations of thickness of a wall of a finished product and reduce the weight of a finished product at ensuring of its durability. In spite of the fact that blown formation was used for many years, producers still meet difficulties in optimization and control of process [7]. Nevertheless, there are successful examples of similar glass blow molding process simulation [8].

The purpose of researches is determination of uniform minimum thickness of the wall of the created hollow polymeric products depending on the form of workpiece and a finished product, and also definition of the corresponding technological modes. The specified objectives are achieved by numerical modeling.

Material and methods

Material

The dependences received as a result of the analysis of numerical researches of extrusion-blown molding process of a polymeric container are given in the article. Distribution of thickness of a wall of hollow polymeric products depending on physical and technological parameters is investigated. On the basis of the executed researches the problem of receiving the hollow polymeric products received by extrusion-blown molding process with more uniform thickness of a wall is solved. Researches are executed for formation of products from polyethylene of the low density (LDPE).

In this work blowing process formation of simple 2-D axial-symmetric bottles is modeled. We assume that process single-stage, i.e. formation of workpiece with its subsequent blowing. At the same time the internal pressure as a result of which action workpiece is blown is set, contact between polymer and a molding tool will not be provided yet.

For material necessary following conditions:

– viscosity: $\eta = 2 \cdot 10^5$ Pa·s;
– density: $\rho = 820$ kg·m^{-3}.

Methods

From the geometrical point of view, initial workpiece represents a cylindrical sleeve with an external radius of 10 mm. The general height of a bottle is 150 mm (Figure 1).
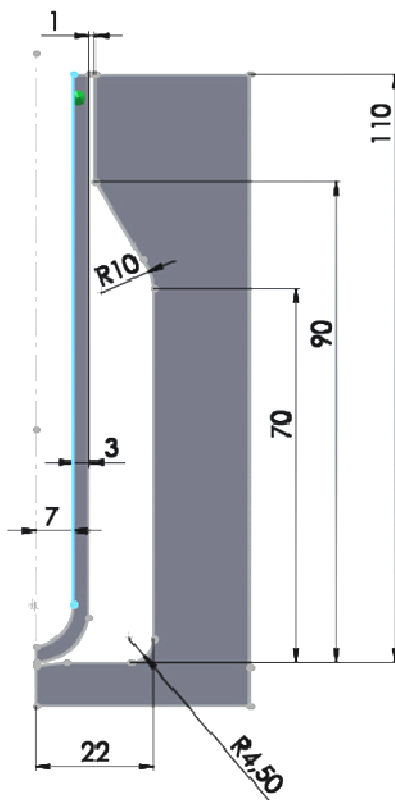
Figure 1. Initial configuration of workpiece and molding tool

The technique of numerical experiment is realized according to recommendations of the developer of an Ansys Polyflow software [9]. The design engineers have used this software to minimize physical prototyping when manufacturing extrusion dies or to reduce thickness variation to improve the quality of thermoformed or blown products [10].

The only working parameter is pressure of blowing P which equals $6 \cdot 10^5$ Pa·s. This pressure is set by normal force. In the given example pressure of blowing does not depend on time. Gravity and inertia is considered. As in the course of blowing the initial form of

workpiece is considerably deformed, on each step on time it is necessary to reconstruct net area. Therefore the most expedient is the calculation method on the basis of the "Thin Shell Method + Lagrangian master" method along the main line. The surface which will come under the greatest influence, that is a surface of contact with a form was chosen as the main line.

Control of temporary iterative parameters in accordance with the recommendations [11]:

Initial value of time: 0 s;
Top value of time: 2 s;
Initial value of time for one step: 0.01 s;
Minimum value of time for one step: 0.001 s;
Maximum value of time for one step: 0.05 s;
Maximum quantity of successful steps: 200;
Value of an error on time: 0.01 s.
Control of geometrical iterative parameters:
Correctional coefficient: 10^9;
The admission on penetration: 0.001;
Expansion of an element: 0.001;
Sliding coefficient: 10^9.

Results and discussion

Mathematical model

To formulate a mathematical problem for blown formation, it is necessary to consider various zones of a forming machine, namely zone of air, zone of a form and zone of melt [12–14].

In figure 2 it is shown breakdown of area of a forming machine for axial-symmetric formation.

Area borders: Γ_m is internal border of a form; Γ_o is external border; Γ_f is border melt – air (Γ_1 is internal surface of melt; Γ_2 is external surface of melt); Γ_s is symmetry axis; Ω_a is border of air area; Ω_1 is border of material area.

For the simplified modeling it is possible to assume that the equipment has constant temperature [15].

The mathematical model is based on conservation laws of mass and an impulse both for the formed material,
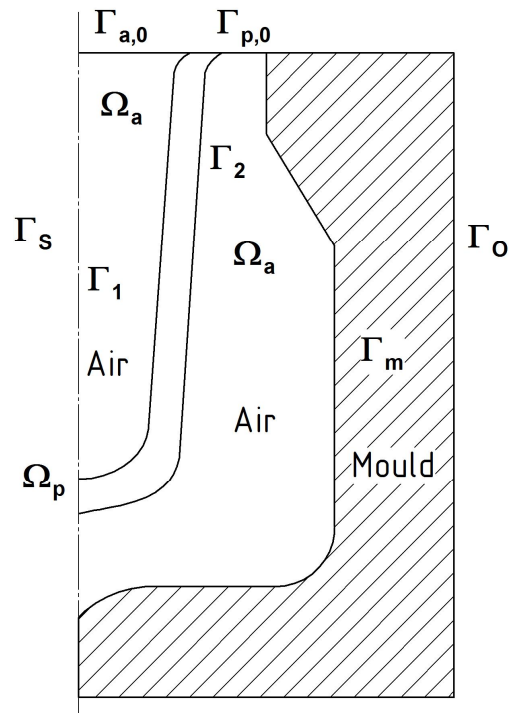
Figure 2. Axial-symmetric area and subareas of a forming machine

and for air:

$$\frac{D\rho}{Dt} + \rho\nabla\cdot u \;=\; 0, \qquad in\ \Omega\setminus\Gamma_f\times\mathrm{T},$$

$$\rho\frac{Du}{Dt} = \nabla\cdot\tau + \rho g, \qquad in\ \Omega\setminus\Gamma_f\times\mathrm{T},$$

where T is formation process duration, s; u - stream speed, m·s^{-1}; ρ is density, kg·m^{-3}.

    The limit of the section melt–air is defined from the usual differential equation

$$\frac{dx}{dt} = u \qquad in\ T,$$

for all $x(t) \in \Gamma(t)$ and any mobile border $\Gamma(t)$.

    In the equation of a state (Navier-Stokes) for viscous liquids [16] the tensor of tension is defined as

$$\tau = 2\mu\dot{\varepsilon} - pI,$$

where μ is viscosity, Pa·s; p is external pressure, Pa; I is single tensor of the second rank; the tensor of deformation speed is defined by derivative of a stream speeds vector

$$\dot{\varepsilon} = \frac{1}{2}\left(\nabla u + u\nabla\right)^{\cdot}$$

    Initial conditions include distribution a component of speed and pressure in an initial timepoint in settlement areas.

    Boundary conditions for a stream can be defined as follows:

– on Γ_s symmetry conditions are set;

– on $\Gamma_{1,o}$ and $\Gamma_{a,o}$ normal tension has to be to equally external pressure;

– the boundary condition for the description of a stream of liquid on an impenetrable wall is reduced to a sticking condition [17, 18]

$$u \;=\; 0, \qquad on\ \Gamma_{1,o}\times T.$$

    When modeling blown formation of a bottle from tubular workpiece several variations of process are carried out. At a blowing internal pressure P = 0.6 MPa·s was considered, the initial thickness of workpiece was set by uniform and made 3 mm, the external diameter of workpiece is 10 mm.

Results of modeling

In Figure 3 it is represented wall thickness in various characteristic points of a finished product. Follows from results of modeling that for achievement of minimum necessary uniform thickness of a product it is necessary to change workpiece thickness: in this case to reduce it in the lower and average parts.

When modeling process of blowing of a product with various values of a lower corner of a bottom dependence of thickness of a wall on the product height of which the schedule represented in Figure 4 is result is found.
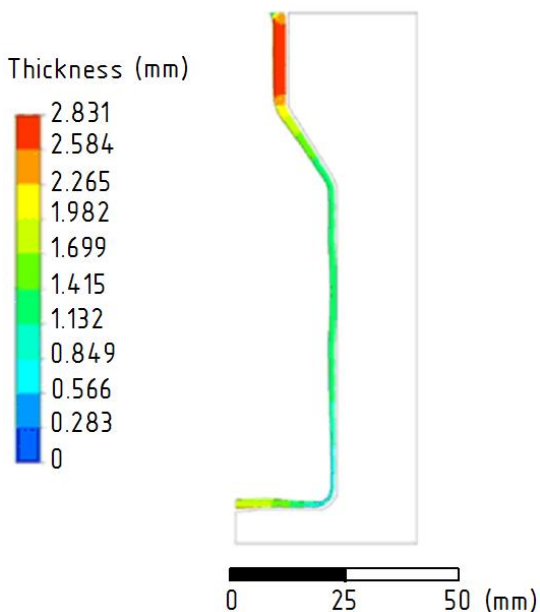
Figure 3. Distribution of thickness of the product wall at the radius of the lower corner of a bottom of 4.5 mm
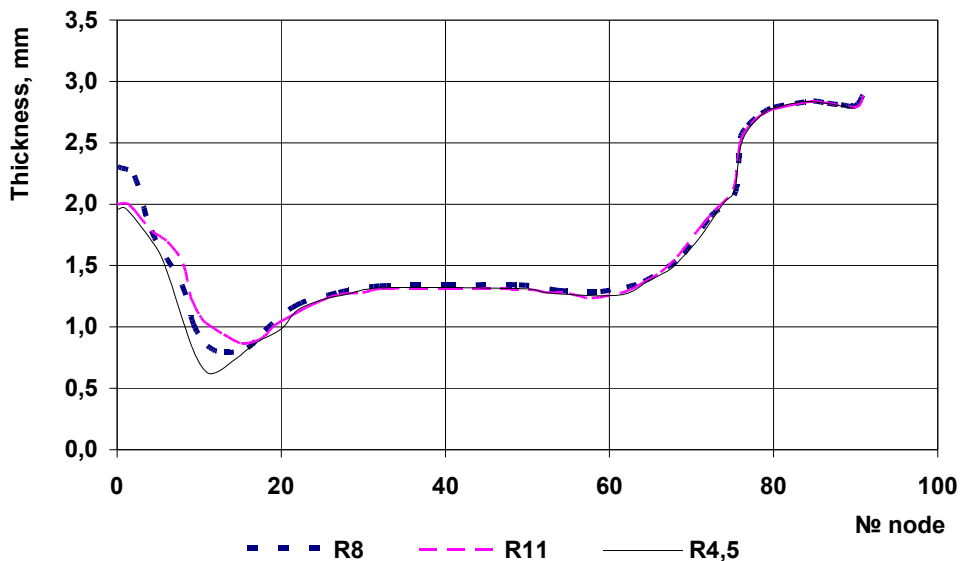
Figure 4. The schedule of dependence of thickness of a product at various values of radius of a bottom

It is obvious that at radiuses of 4.5 and 8 mm thickness of a product is not optimum relatively the product height, and at the radius of 11 mm the product becomes unstable that is caused by rather big radius of a bottom.

For more detailed analysis of blown formation process calculations for various products blowing degree are carried out. In this case degree of blowing depends on diameter of a cavity of a blown form therefore for calculations its various values are chosen. Dependence of the relation of thickness of workpiece to the minimum thickness of a wall of a finished product from extent of blowing it is shown in fig. 5.
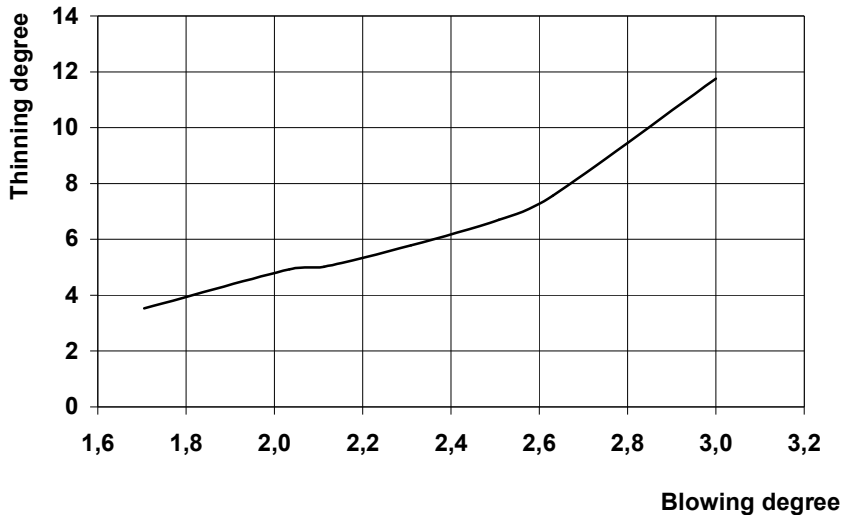
Figure 5. Dependence of thinning degree of a product wall on blowing degree

It is established that distribution of thickness of the container wall at a uniform thickness of workpiece is not optimum as for ensuring minimum necessary thickness in the most weak spot (as a rule, upon transition of a bottom to a wall) in other sections it is necessary to use excess material Therefore we will use the technique given in [9], which can provide the necessary thickness of walls on all height of a product. For this calculation it is used a tool with a radius of a lower corner of a bottom of 4,5 mm.

For each knot of workpiece we will calculate thickness H_i:

$$H_i = H_{i-1} + \alpha \left(\frac{h_c}{h_f} - 1 \right) H_{i-1},$$

where $\alpha \approx 0,9$ is a relaxation factor; h_c=1 is the set product thickness; h_f is current thickness of a product; H_0=3 is initial thickness.

Having calculated values, we receive distribution of thickness of a product which is represented in fig. 6.
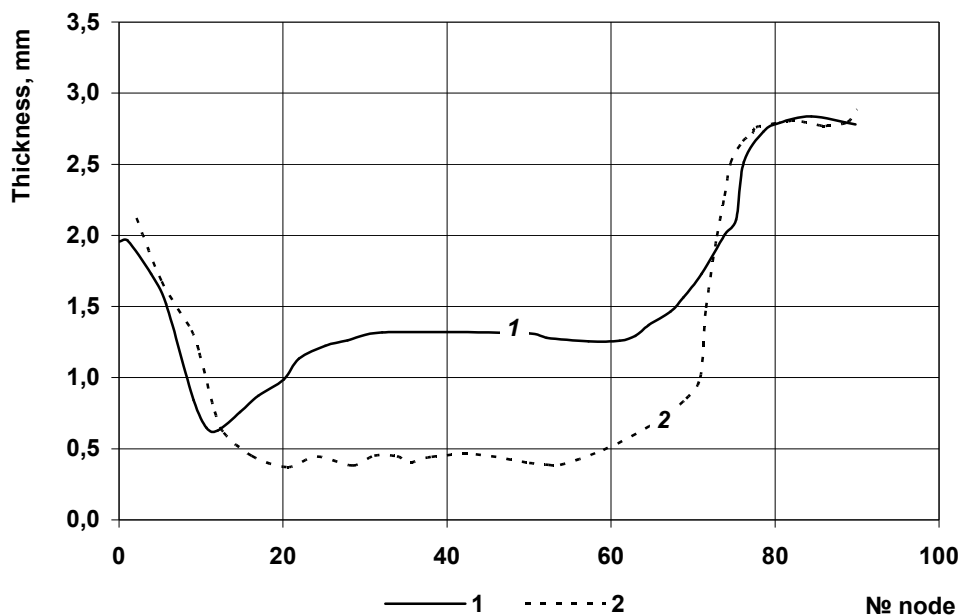
Figure 6. Dependence of thickness on product height:
1 – preliminary; 2 – after application of the techniques

From Figure 6 it is visible that in this example on the most part of height of a product it was succeeded to reach almost identical thickness of the wall.

For check of reliability of the received results comparison of theoretical distribution of thickness of the wall with the valid thickness of the wall of private enterprise "Crystal Glass" bottle with a capacity of 100 ml was carried out.

For comparison of calculated values of thickness of a product to the measured values the schedule which is represented in Figure 7 is constructed.

Thickness of the wall of a real product without a neck and a bottom fluctuates from 0.51 mm to 0.73 mm, and the dispersion of calculated values fluctuates from 0.64 mm to 0.87 mm. Comparison of schedules shows that thanks to a technique of optimization more uniform thickness of the product wall is reached. In the considered case uniformity of thickness of the wall increased to 25 %, and at the subsequent iterations it is possible to reach the best values. The profile of thickness received by calculations is realized at workpiece extrusion by program regulation of size of section of the forming die.
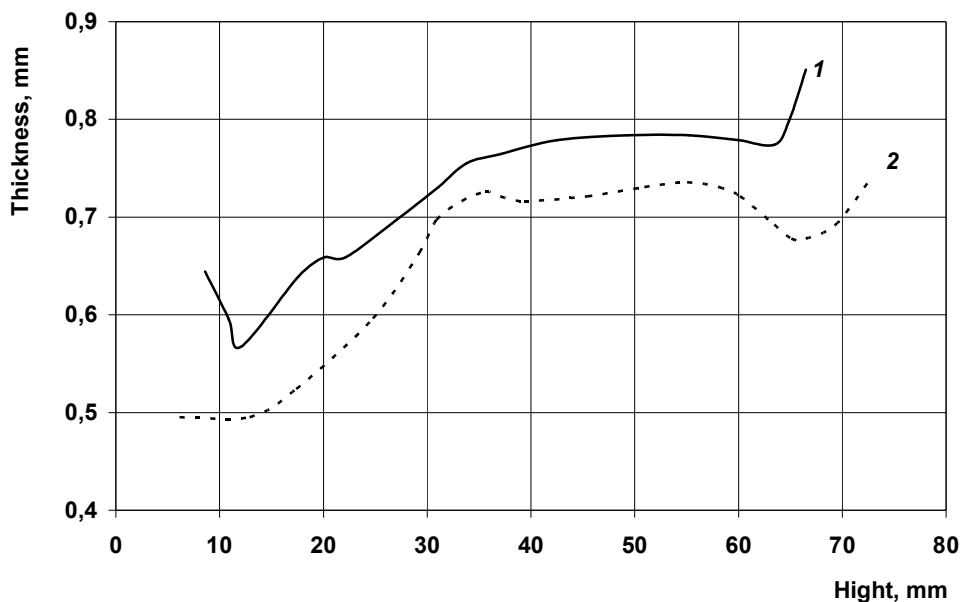
Figure 7. Distribution of thickness of the bottle walls
1 – calculated values; 2 – measured values.

Conclusion

Research of workpiece walls thickness at various initial parameters of extrusion-blown molding process of polymeric package is conducted.

The given technique of calculation of necessary of workpiece walls thickness wall allows to reach uniformity of product walls thickness. It is expedient to use this technique for production of hollow products by extrusion-blown molding method.

Further authors similarly assume to improve various hollow polymeric products and to introduce a technique of program calculation of workpiece thickness at the enterprises of the packing industry.

The interrelation between the workpiece, a finished product and distribution of thickness of its walls is defined.

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Effect of treatment modes on quality and antioxidant properties of tomato and beet processing products

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Abstract

Introduction. The research was conducted to substantiate the rational drying conditions of tomato seeds. The ratio and drying conditions of the composition from tomato waste with the addition of red beet were substantiated.

Materials and methods. The tomato seeds were prepared according to the traditional methodology used in the industry. From red beet and tomato waste compositions with the ratios of components 4:1, 3:1, 2:1, 1:1 were created. Tomato seeds have been dried using the convective method at the air temperature t = 50–80°C, as well as the composition from red beets and pulp of tomatoes – at t = 60–100 ºC. The quality of dried seeds was estimated on the basis of its germinability, dried mixtures – on the content of betanin in them.

Results and discussion. When the temperature of the air increases, the intensity of tomato seeds drying increases too. Thus, the drying time reduces by 2.5 times when the air temperature is raised from 50 to 80 °C. However, qualitative seed material, which gives the germinability of 98%, has been attained at the drying temperature of 50 ºC.

Non-waste processing of tomatoes involves the creation of compositions of pulp tomatoes and sliced red beets, their drying, grinding and packing. In industrial conditions, red beets need to be cut into chips, which intensifies the drying process of the composition. The slicing of tomatoes in compositions does not affect the process speed.

When the air temperature increases from 60 to 100 °C, the intensity of compositions drying is raised by 1,8 times. Maximum preservation of the useful substances in the finished product results from the choice of a soft drying condition and an air temperature of 60°C.

pH = 3.9 is characteristic for the ratio of red beet-tomato components 3:1 in composition, which ensures the maximum preservation of betanin (94.7%) at drying.

Conclusions. The heat carrier temperature substantially affects the tomato seeds germinability and antioxidant properties of tomato and beet processing products.

Introduction

Nowadays, the need to substantiate the optimal conditions of energy-efficient non-waste technological processes of seeds drying for sowing and complete processing of vegetables requires complex theoretical and experimental research.

There is a risk of shelf life reduction if the moisture content in the seeds is either too high or too low at storage [1]. At high moisture content in the seeds, the processes of metabolism and its breathing are sharply increased [2].

There is a low germinability in freshly collected seeds of many vegetables and flowers, they need a post-harvest maturation. Tomatoes at high humidity have the ability to sprout immediately after harvesting. Therefore, determining the modes of tomato seeds drying, which provide the required quality of seed material over a given time, is an urgent task.

There are not so many scientific works on the drying of tomato seeds. Most thoroughly this problem was examined by Sogi D.S., Shivhare U.S., Garg S.K., Bawa A.S. [3] who investigated the drying of tomato seeds in cabinet/fluidised bed driers, but the effect of drying conditions on the quality of the seeds was not mentioned.

The problem of processing of tomato pulp, which remains after removing the seed material is important too.

Tomato products have a promising potential as functional food for liver health. Tomato extracts and pure compounds are able to decrease the reactive oxygen species (ROS) generation of HepG2 cells, the phenolic compounds being more effective than lycopene [4]. Consumption of tomatoes has oncoprophylaxis and antioxidant effects, the condition of the cardiovascular system improves.

Another very useful vegetable is a red beet. Anthocyanin colorants, catechins, flavonol glycosides, vitamins, minerals contained in beets help cleanse the body, lower cholesterol levels in the blood, improve a fat metabolism, strengthen capillaries and blood vessels, promote hematopoiesis, increase hemoglobin content and increase the amount of erythrocytes, prevent oncological diseases, reduce blood pressure [5].

Betalains contained in red beet in vacuoles of cells are water soluble pigments that were previously referred to as anthocyanins. However, betalains are structurally and chemically different from the anthocyanins and have never been detected in the same plant simultaneously with them [6]. It is now known that betalains are aromatic indole compounds that are synthesized from tyrosine. They are not chemically similar to anthocyanins, as well as flavonoids [7]. Each betalain is a glycoside containing sugar and a dye component [8]. Important among betalains is betanin, which is glycoside. In the industry betanin, made from red beet, is used as a food colorant [9].

Vegetables contain a large amount of moisture (in some cases up to 95%), they are unstable when stored and their losses can reach up to 50%. So, it is important to create the proper conditions for their storage. According to statistics in the world about 20% of fruits and vegetables are dried [10]. At that different methods are used [11]: convective [12], vacuum [13], infrared [14], microwave drying [15], osmotic dehydration, freeze-drying, closed loop heat pump dryer [16], combined drying methods.

The production of dry fruits and vegetables and their powders is a promising direction [17]. As a result of industrial processing of tomatoes, in particular drying, it is necessary to preserve maximum useful substances and antioxidant potential [18 – 22], so many studies are aimed at determining the rational conditions of dehydration [23; 24] that can provide the quality of the finished product.The content of ascorbic acid in tomatoes after drying, which is the least stable component to the thermal effect [24], the moisture diffusivity and activation energy, color parameters, chemical composition [25], including the content of

lycopene [26], taste were considered as quality indices in previous studies. For beet it is, first of all, the betanine content [27].

In addition to the temperature, the size of the particles of the drying material should also has been included to the drying conditions. This is relevant both for the drying of tomatoes [28], beets [29], and mixtures thereof. There is also a requirement for drying in a thin layer [30].

The purpose of the research is to substantiate the drying conditions of tomato seeds and compositions based on red beet and tomato waste, as well as content of composition, in which, after thermal treatment, the maximum content of betanin and antioxidant properties are preserved.

Materials and methods

Preparation of tomato seeds for drying

To obtain high quality seeds, ripe and intact plum tomatoes were harvested in the middle of bearing of shrubs. The pulp of tomato prevents seeds from germination, and in damaged vegetables the seeds may germinate prematurely even during the drying process at low temperatures. The selected tomatoes were washed, cut and seeds were separated from the main pulp. The seeds fermented in tomato juice at an ambient temperature of 25 °C throughout the two days. After that, the liquid was drained and the seeds remaining on the bottom of the container were washed several times with water and supplied for drying [2].

Creation of beet-tomato composition [31]

After removal of tomato seeds a large quantity of pulp remains, therefore the technology of their use was offered for the purpose of creating beet-tomato composition, which has therapeutic and prophylactic, in particular antioxidant, properties.

To obtain an antioxidant powder, a composition of tomatoes and beets was created in appropriate ratios, dried below equilibrium humidity, cooled to ambient temperature, crushed, sifted and packed in kraft bags.

The size and shape of the material substantially affect the kinetics of the drying process. To create the composition, tomatoes was cut into slices 5×5×5 mm and red beet – into chips 2×5×2 mm and plates 5×5×2 mm. The size of tomatoes was kept constant. The effect of the size of the crushed beet on the drying process was studied because its content in the composition is greater.

Research of drying kinetics

Studies on determining the drying kinetics of tomato seeds, as well as vegetable compositions of beet-tomato, were carried out on a test bench of convective drying equipped with an automatic system for processing and collecting information that allows more accurately characterize the drying process with the construction of graphic dependences [32].

The tomato seeds were dried in a layer of thickness $\delta = 10$ mm at a velocity of the air V = 1.5 m/s (the speed was chosen from the condition of more effective drying of the same material in existing modern dryers [33]) at a temperature t = 50–80 ºC to equilibrium moisture content 8%, and compositions of beets and tomatoes pulp – at the air speed V =

3,5 m/s and in the temperature range of the air from 60 C to 100 °C to a residual moisture content of 3,0%. The drying processes lasted 12–100 min.

Determination of the germinability of tomato seeds

The germinability of tomato seeds after different drying conditions was analyzed at 20 °C for 7 days, determining the percentage of sprouted seeds [2].

Evaluation of the quality of dried beet-tomato compositions

The quality of the dried compositions was evaluated according to the content of betanin, which should be preserved as much as possible as compared to the raw material. The content of betanin in beet-tomato composition depends on its acidity. The method for determining the betanin content in the compositions is given in detail in [31].

Results and discussion

As the air temperature increases, the intensity of the drying process of the tomato seeds increases (Figure 1). Thus, drying at 50 ° C is a long process and takes 30 minutes, which is 2.5 times more than the drying time at a temperature of 80 °C.
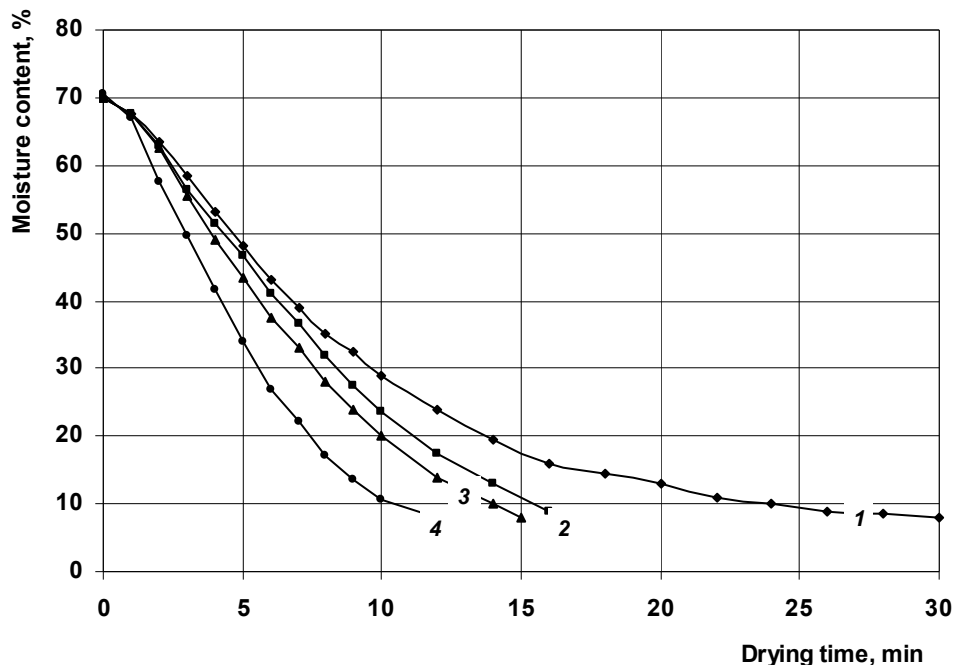
Figure 1. Effect of the air temperature on the drying kinetics of tomato seeds,
$V = 1,5$ м/с, $\delta = 10$ мм:
1 – 50°C; 2 – 60°C; 3 – 70°C; 4 – 80°C

However, it is the quality of the seed material rather than the duration of drying that determines the choice of rational temperature of the air. The quality of the seeds is determined by its ability to sprout.

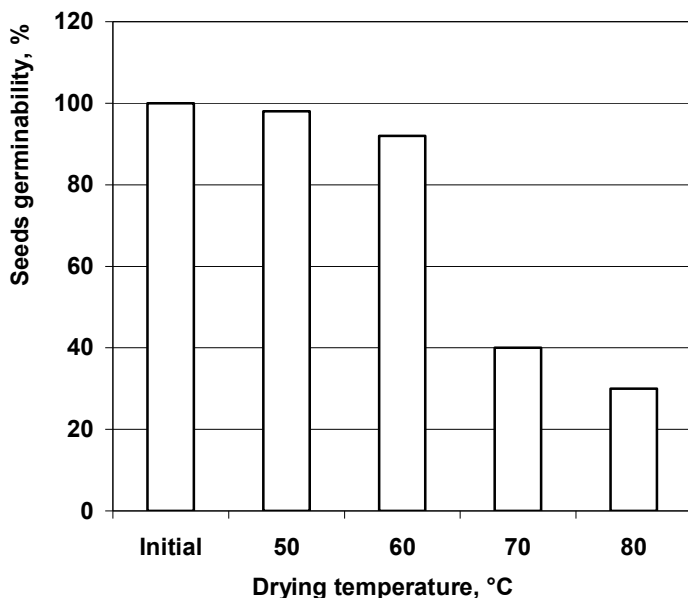The air temperature significantly affects this index (Figure 2).

Figure 2. Germination of tomato seeds from the drying condition

The temperature of 60 °C gives the seed germinability at the level of 92% of the initial seed germinability. The rational condition of tomato seeds drying is the air temperature of 50 °C, the germinability at which is 98%.

Five samples with different contents of the components were investigated to determine the required ratio of components of beet-tomato composition with optimum pH, which results in a high percentage of betanine preservation. At pH 3–4 maximum betanin is preserved during heat treatment. As can be seen from Figure 3, the required pH level is characteristic for the ratio of three parts of red beet and one part of tomato. It was this composition that was used in further research.

The drying kinetics of beet-tomato composition with the change in the size of the cut beet into the chips 2×5×0.2 mm and into the plate 5×5×2 mm (figure 4) was studied.

As can be seen from Figure 3, the duration of drying the composition with red beets, cut into chips, is 78 minutes, and into the plate is 100 minutes.

The curves of drying the beet-tomato composition (Figure 5) show that the drying process occurs in falling-rate period, no constant-rate period of drying was observed. This is due to the peculiarities of composite raw materials.
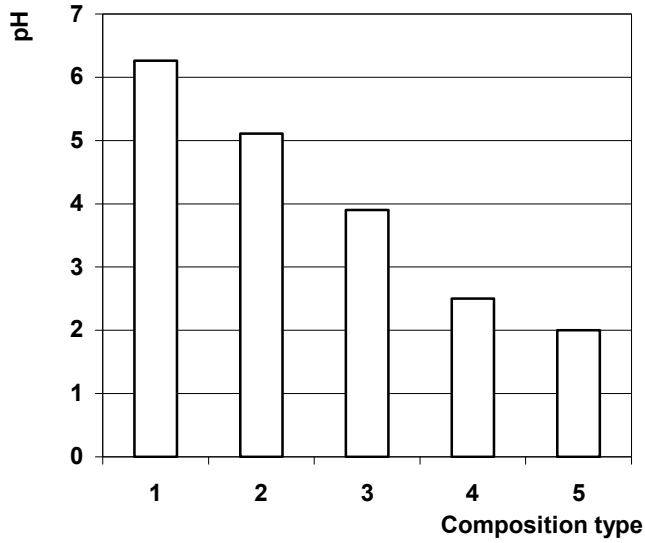
Figure 3. The pH of the composition depending on the ratio of components:
1 – red beet; 2 – beet-tomato (4: 1); 3 – beet-tomato (3:1);
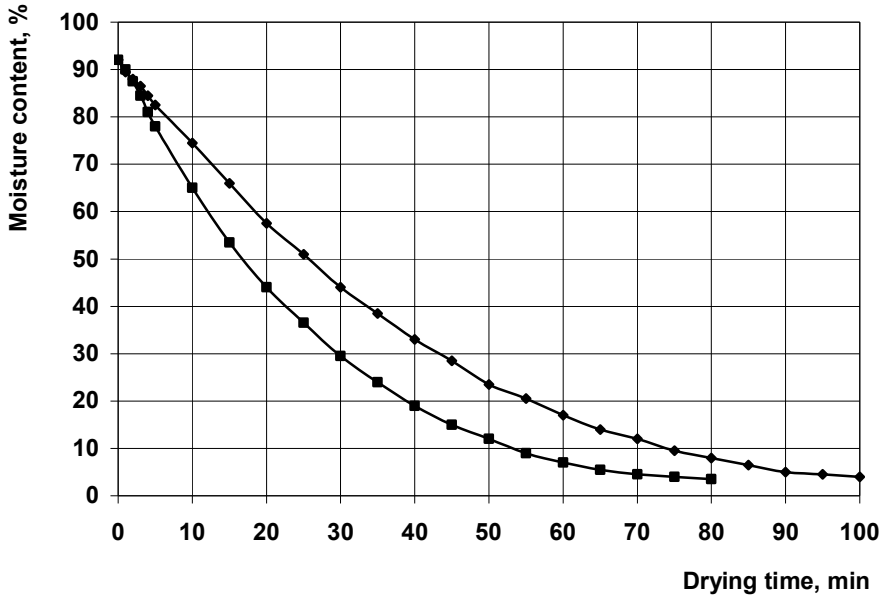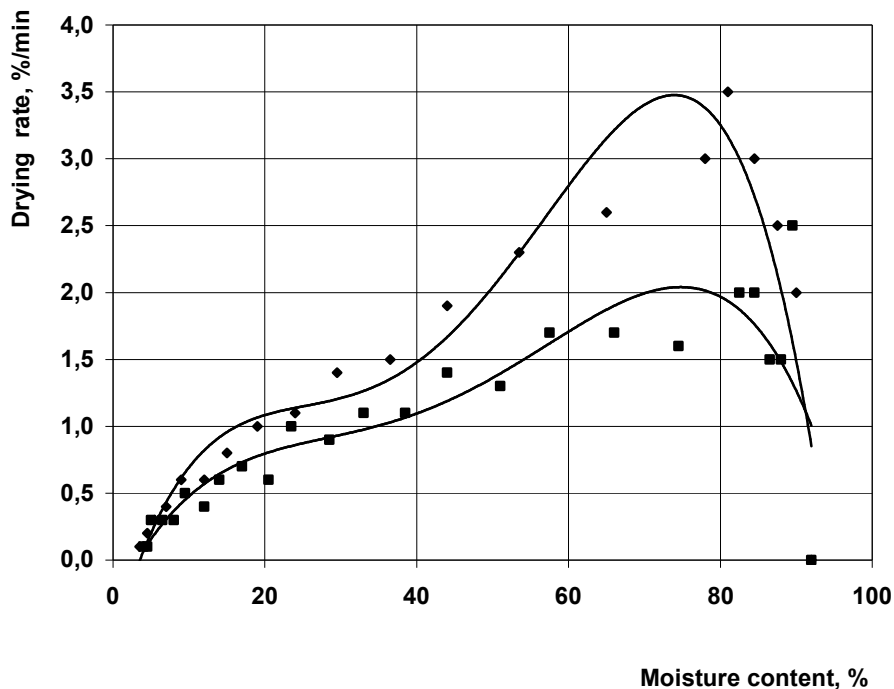**4 – beet-tomato (2:1); 5 – beet-tomato (1:1)**

Figure 4. Effect of cutting beets on the drying kinetics
of the composition red beet-tomato (3: 1) t = 60 ° C, V = 3.5 m/s, δ = 10 mm:
1 - plate; 2 – chips.

**Figure 5. Effect of beets cutting on the drying speed of the composition
red beet - tomato (3: 1) t = 60 ° C, V = 3,5 m/s, δ = 10 mm:
1 – plate; 2 – chips.**

As the results show, the drying process of the composition with beets, cut into chips, is more intense than with those cut into plate, and the kind of slicing of tomato in the composition does not affect the speed of the process. Therefore, to intensify the drying process in industrial conditions, the red beet in the composition must be cut into chips.

The air temperature changes the drying kinetics of the beet-tomato composition (Figure 6) and the drying rate (Figure 7).

The curves have the appearance typical of colloidal capillary-porous materials. With the increase in the air temperature, the intensity of the drying process of the composition increases. The duration of the process reduces by 1.8 times when the air temperature is raised from 60 to 100 °C. At an air temperature 60 ° C, the drying time is 100 minutes. However, the need to preserve as much as possible the useful substances in the finished product causes the choice of a soft drying condition and the air temperature 60 °.

As the temperature rises, the material is heated more rapidly and the free moisture is removed faster, as a result of which the first critical drying point is shifted to the left.
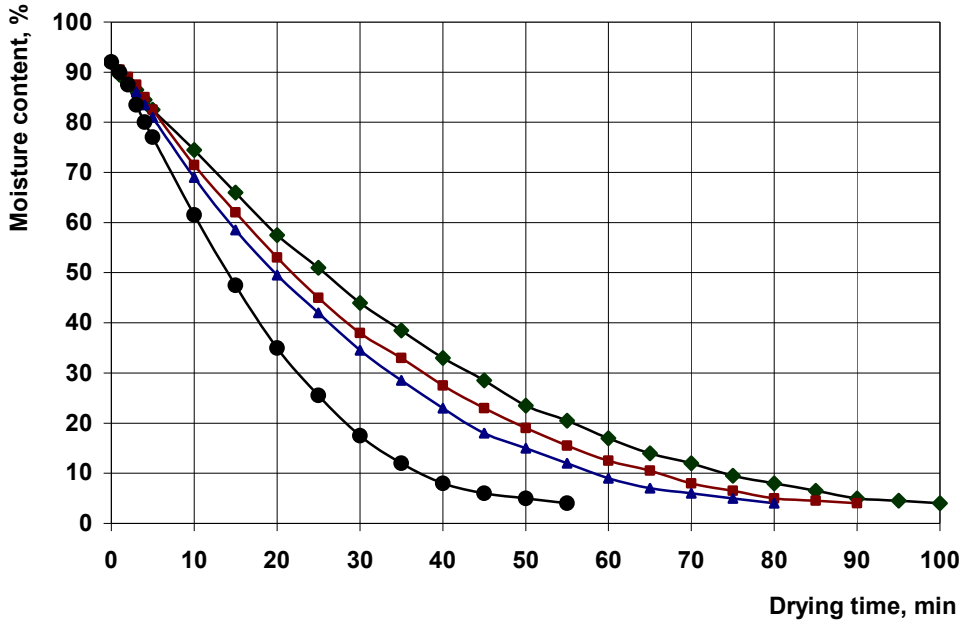
.

Figure 6. Effect of the air temperature on the drying kinetics of the red beet-tomato composition (3: 1) V = 3.5 m / s, δ = 10 mm: 1 – 60 °C; 2 – 70 °C; 3 – 80 °C; 4 – 100 °C.

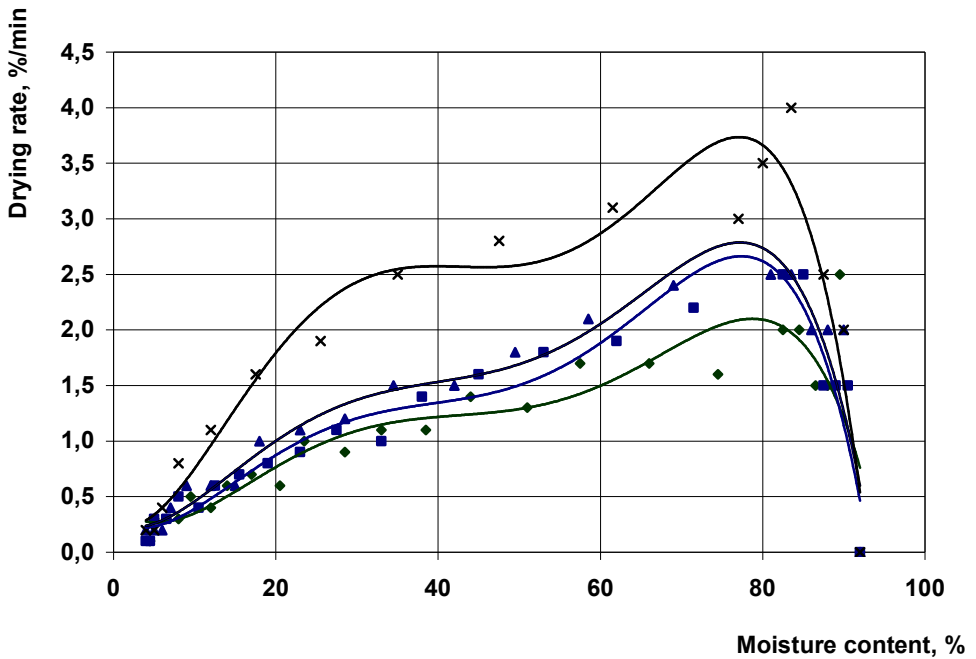**Figure 7. Effect of the air temperature on the drying rate of the composition red beet-tomato (3:1), *V* = 3,5 m/s, *δ* = 10 mm: 1 – 60 °C; 2 – 70 °C; 3 – 80 °C; 4 – 100 °C.**

The effect of the composition components on the drying kinetics is shown in Figure 8.

The initial humidity of the components is different, it is the largest in tomato, the drying time of which is respectively 130 minutes, the duration of drying of beet is 85 minutes, and of the composition is 100 minutes.
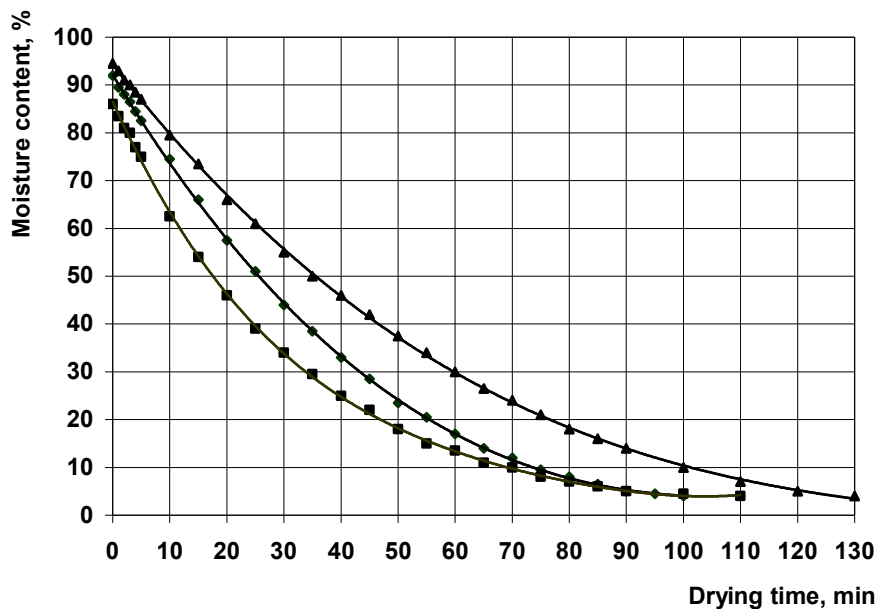

Figure 8. Influence of composition components on drying kinetics
t = 60 ° C, V = 3,5 m / s, δ = 10 mm:
1 – beet-tomato (3: 1), 2 – tomato; 3 – red beet

From the curves of the drying speed of the composition components and the composition itself (Figure 9) it is evident that at the beginning of the drying process, the highest drying rate in beet is 2.8% / min, the lowest in tomatoes – 1.6% / min, for the composition its value is equal to 2.2% / min.The second period of drying is characterized by slowing down the drying rate of beet, and for a composition after reaching a moisture content of 35%, the process is quickened and the moisture evaporates intensively.This is due to the influence of organic acids of tomato on the cellular shell of red beet.

The main requirement for beet-tomato composition is the conservation of betanin during the processing of raw materials. The drying of red beet itself destroys betanin by almost 62% (Figure 10), while the combination of red beet with tomato waste after the removal of seeds retains a high content of betanine after drying. Its maximum content is 94.7% at an air temperature 60 °C and at a ratio of components 3: 1, which is due to the optimum pH value of the composition (see Figure 3).
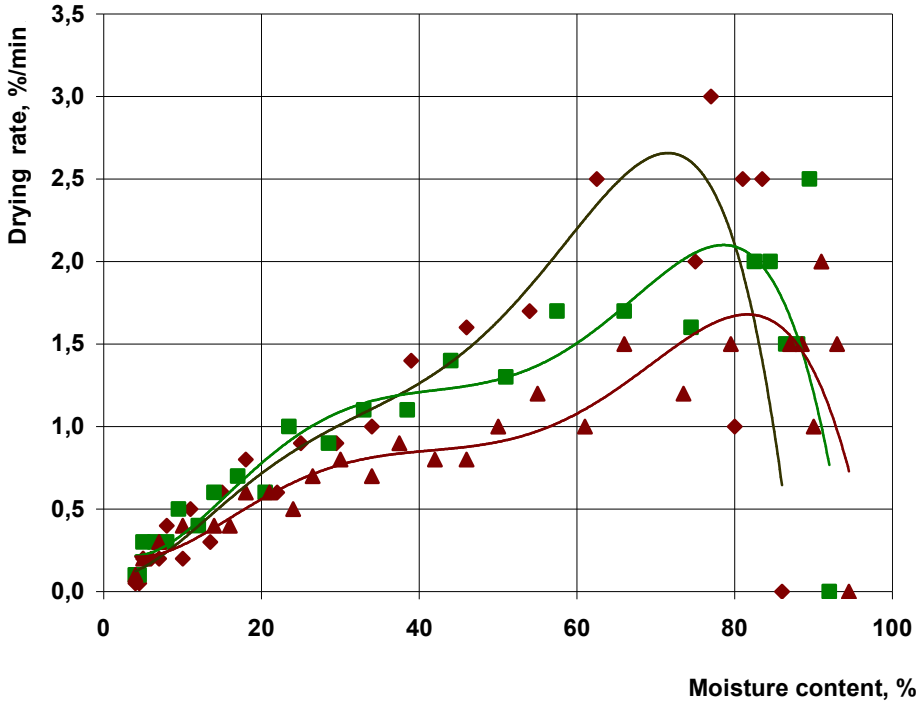
Figure 9. Influence of the composition components on the drying rate
t = 60 ° C, V = 3,5 m/s, δ = 10 mm:
1 – red beet; 2 – beet-tomato (3: 1); 3 – tomato

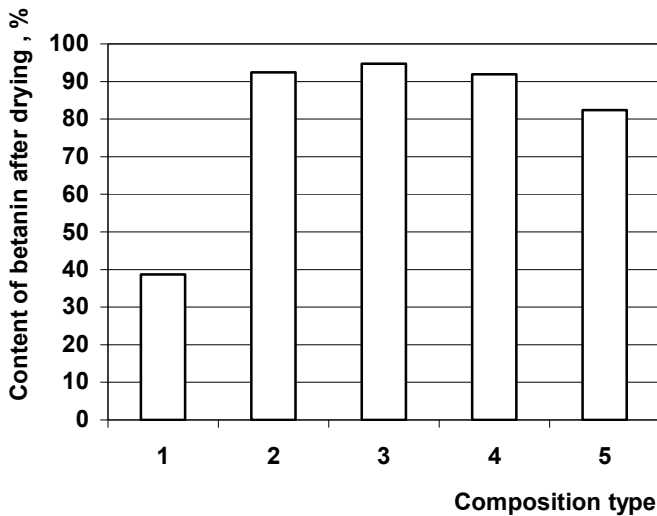**Figure 10. Influence of compositions type on the content of betanin after drying at t = 60 °C:**
1 – red beet; 2 – beet-tomato (4: 1); 3 – beet-tomato (3:1)
4 – beet-tomato (2: 1); 5 – beet-tomato (1:1)

Conclusions

The waste-free technology of tomatoes processing involves the production of seeds and the use of tomato pulp to produce antioxidant powder based on beets and tomatoes. When using the convection method of drying 10-mm-thick layer:

1. The greatest germinability of tomato seeds (98% in comparison with untreated) is provided at air temperature of 50 °C.

2. Maximum preservation of the useful substances and antioxidant properties of the composition based on the waste of tomato and beet is achieved at a soft drying at air temperature of 60 °C.

3. For the composition with the ratio of red beet and tomato components 3:1, the pH is 3.9, which results in a high level of betanin content preservation (94.7%) at heat treatment.

The novelty of the scientific research consists in obtaining new experimental data on the influence of drying conditions on the quality indices of tomato seed and the quality and antioxidant properties of tomato and red beet products.

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Mathematical modeling of mass transfer in baromembrane processes

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Abstract

Introduction. To determine the optimal modes of rational exploitation of membranes the phenomena of concentration polarization was studied here.

Materials and methods. Distribution of the concentration of the dissolved substance in solvent by height of the channel of the baromembrane apparatus was obtained by the method of mathematical modeling. Membrane channels were represented as a rectangular grid with a predetermined step. The stability condition of the solutions was verified using the Courant criterion.

Results and discussion. Applying the corresponding boundary conditions characterizing the physical essence of the baromembrane processes, as well as numerical methods for solving differential equations, we obtain a system of algebraic kinetic equations that allow us determine the distribution of concentration of the dissolved substance by the height of the pressure channels, which is practically impossible to do experimentally. To simulate the real processes of separation, we used geometric, physical and mass-exchange characteristics of the real membrane systems. It is established that due to the semi-permeable properties of membranes, the amount of the dissolved substance at its surface over time increases, that is, the phenomenon of concentration polarization appears. Depending on the pressure, membrane characteristics and flow turbulence, the value of the concentration polarization may exceed the value of 10, which must be taken into account in order to prevent the formation of sediment on the surface of the membrane.

The character of the obtained dependencies is in good agreement with the theoretical foundations of the membrane processes and allows us apply the proposed algorithm for the preliminary analysis of the phenomena occurring in the pressure channels in the division of complex multicomponent liquid systems.

Conclusions. The level of concentration polarization in the membrane channels of barometric apparatuses at separations processes of food industry liquids may exceed 10 and depends upon the parameters of the process.

Introduction

The problem of the use of membrane technology lies in the increased level of membrane contamination due to the use of wrong operating modes. As a result, the concentration of solutes at the membrane surface increases significantly (the phenomenon of concentration polarization). At high concentrations, some components may form insoluble compounds, gel-form sediment and other. When the concentration in the layer near surface of membrane becomes higher than the concentration of the feeding solution, then there are diffusion streams directed in the opposite direction relative to the flow of the filtering solution. Such effects significantly reduce the membrane productivity, in the process of separation processes [1, 2].

Therefore, it is advisable to investigate the phenomenon of concentration polarization, studying the distribution of concentrations and its change over time, in the channel, to determine the optimal modes of rational operation of membranes. Since experimentally, determining the distribution of concentrations during the filtration process is very difficult, methods of mathematical modeling are used. Unfortunately, there is now no single theory capable of fully describing the processes that take place near the surface of the membrane for the processes of separation (concentration) of multicomponent solutions [3], so this task remains relevant. Among modern works, there are stochastic approaches [4], various semi-empirical models [3, 5], but in most cases the theoretical study of mass transfer processes is carried out by methods of continuum mechanics using methods of finite-difference approximation [3, 5, 6, 7].

For filtration, mass transfer occurs by two mechanisms: convective transfer and diffusion [8]. Differential equations that can describe the behavior of such systems, in general, have no precise analytical solutions due to their complexity and effect nonlinearity [3, 9, 10]. Therefore, numerical methods such as finite-difference approximation methods are used to obtain approximate solutions [5, 7].

This method allows solving the differential equation under given boundary and initial conditions and requires a minimum of information [5, 6]. Relative simplicity and visibility of the method allows it to be applied very quickly to solve various technological and research problems [3].

The purpose of this work was to determine level of the concentration polarization in the membrane channels of barometric apparatus by methods of mathematical modeling in the separation processes of food industry liquids.

Materials and methods

The phenomenon of concentration polarization related to mass transfer processes, namely, the distribution of the concentration of C (x, t) of the dissolved substance in solvent by height of the channel of baromembrane apparatuses is studied.

Concentration, kg/m^3, is defined as the mass of the target component per unit volume:

$$C = \frac{dM}{dV} \tag{1}$$

For one-dimensional models, the concept of linear concentration, kg/m, is introduced, that is, the mass of the dissolved substance per unit length of the segment of the coordinate x:

$$C_{line} = \frac{dM}{dx} \tag{2}$$

Then $C_{line}=C_{volume} \cdot S$, where S is the area, C_{volume} is the volumetric concentration. The mass flow q_m, kg/s, is the mass of the dissolved substance passing through the surface S per unit time.

The investigated medium is considered in generalized (dimensionless) coordinates (grid nodes are applied) [3, 5]. By using the boundary and initial conditions and the first principle of differentiation, the function of concentration can be determined for each point of the space. As a result, the differential equation is approximated by a system of algebraic and at known values of the concentration function at certain points (or at a certain point in time) we can obtain the value of a function at any point of the system under study [5, 6, 7].

For explicit schemes of finite-difference approximation the stability conditions formulated by the Courant's criterion [6]. The physical essence of this criterion is that the speed of movement along the grid should be less than the transmission rate of perturbations in the system. For this case, the Courant's criterion is determined by the relation:

$$\Delta t < \frac{\Delta x^2}{2D},$$ (3)

where D is the diffusion coefficient, Δx, Δt is the spatial and temporal step according to the scheme, respectively.

Results and discussion

The density of the mass flow q_{Sm}, kg/s·m^2, is the mass of the target component passing a unit of the surface over time in a given direction. Although q_{Sm} is a vector value, but in one-dimensional models it becomes essentially a scalar: $q_m = q_{Sm} \cdot S$. The main empirical diffusion law is Fica's law:

$$q_{Sm} = -D \frac{dC}{dx},$$ (4)

where D is the diffusion coefficient, m^2/s. Moreover, he represents the characteristic of the system «dissolved substance – carrier (solvent) ». If the solution moves at a velocity v, then the mass flow (i.e., convective flow) is defined as:

$$q_m^{conv} = C_{volume} \cdot S \cdot v = C_{line} \cdot v = C \cdot v,$$ (5)

And formally coincides with the density of the flow. In the study of one-dimensional models, it should be borne in mind that C·v is the flow, not its density. Similarly, for a diffusion stream of mass (at S = const):

$$q_m^{diff} = q_{Sm}^{diff} \cdot S = -D \frac{\partial C_{volume}}{\partial x} \cdot S = -D \frac{\partial C}{\partial x},$$ (6)
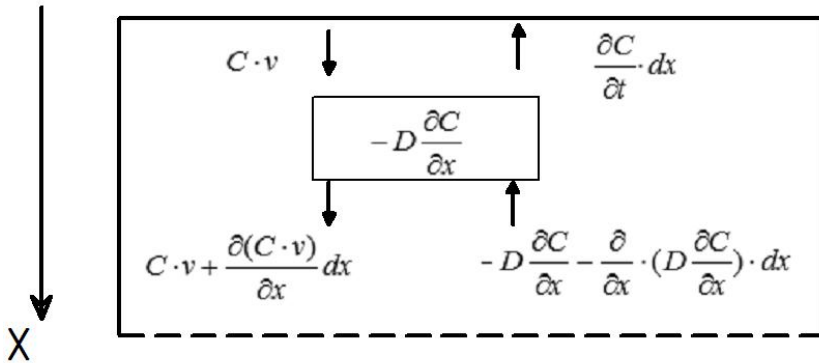
Figure 1. Scheme of flows in the membrane channel:
X – spatial coordinate.

$C = C(x,t)$ - concentration of the dissolved substance at the point x, at time t, kg/m. Change of its mass in volume S·dx for time dt equals $\dfrac{\partial C}{\partial t} \cdot dx$. As a result of the movement of convective and diffusion streams, the concentration of the target component in the considered elemental volume also changes (Figure 1).

Diffusive flows:

$$q_1^{diff} = -D\frac{\partial C}{\partial x}, \tag{7}$$

$$q_2^{diff} = -D\frac{\partial C}{\partial x} - \frac{\partial}{\partial x}\left(D\frac{\partial C}{\partial x}\right)dx, \tag{8}$$

Convective flows:

$$q_1^{conv} = C\cdot v, \tag{9}$$

$$q_2^{conv} = C\cdot v + \frac{\partial(C\cdot v)}{\partial x}dx, \tag{10}$$

q_e·dx - mass flow from external sources, kg/s, q_e - flow density, kg/m s.
Taking into account the balance of masses in the allocated volume we obtain the equation of convective diffusion with an external source:

$$\frac{\partial C}{\partial t} = -\frac{\partial(C\cdot v)}{\partial x} + \frac{\partial}{\partial x}\left(\frac{D\cdot\partial C}{\partial x}\right) + q_e, \tag{11}$$

where v, D, q_e are known functions and parameters. In the general case, this is a nonlinear equation in partial derivatives with variable coefficients. But the classical form of the equation has v = const, D = const, q_e = 0:

$$\frac{\partial C}{\partial t} = -V\frac{\partial C}{\partial x} + D\frac{\partial^2 C}{\partial x^2}, \tag{12}$$

The solution C=C(x,t) must satisfy the initial and boundary conditions set at the boundaries of the interval [0, h] at the points x=0, x=h and set the upper boundary of the channel and the surface of the membrane. $C(x,0)=C_0(x)$ - initial conditions, concentration of feeding solution [7, 11, 12].

Consider the boundary conditions and their physical interpretation. Target component completely passes the boundary:

$$C(0,t) = 0 , \tag{13}$$

Target component does not cross the boundary:

$$\frac{\partial C(0,t)}{\partial x} = 0 , \tag{14}$$

The flow of the target component through the membrane surface is proportional to the concentration on it:

$$-D\frac{\partial C(0,t)}{\partial x} = \alpha_{0,1} \cdot C_{0,1} , \tag{15}$$

Applying the boundary conditions (13-15) in this way, the simulation of the phenomenon of concentration polarization (the formation of sediment on the membrane surface) is achieved, and the concentration C acts as a key parameter of the process [13, 14].
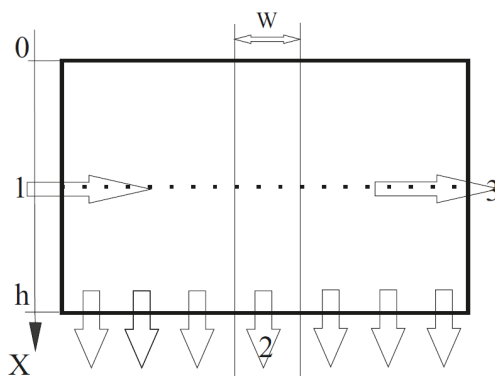

Figure 2. Scheme of the pressure channel:
1 – the flow of feeding solution; 2 – flow of permeate (filtrate); 3 – the flow of concentrate.

Consider a one-dimensional system simulating a portion of space (vertical line, with width $w \to 0$) of the channel of length l, height h, with a membrane, whose area S is completely filled with a flow of solution (carrier) in which the target component is present. From the bottom there is a membrane that completely passes the carrier (solvent), but does not pass the target component (Figure 2).

For a numerical solution of equation (12), we apply the finite difference method. It is necessary to switch from continuous variables to discrete ones:

$$x \to x_j, j = 0,1,...,n , \tag{16}$$

$$t \to t_i, i = 0,1,...,m , \tag{17}$$

$$\Delta x = \frac{h}{n} , \tag{18}$$

$$\Delta t = \frac{t_{\max}}{m} , \tag{19}$$

Similarly for concentration:

$$C(x,t) \to C(x_j,t_i) = C_{i,j} , \tag{20}$$

We apply marginal and initial conditions. At the initial moment of time (at $t = 0$) the concentration is equal to the concentration of feeding solution:

$$C(x, 0) = C_0, \qquad (21)$$

The key component doesn't pass through the membrane and the upper boundary of the channel:

$$C(0, t) = C(h, t) = 0, \qquad (22)$$

We approximate derivatives by difference schemes:

$$\frac{\partial C}{\partial t} \approx \frac{C_{i+1,j} - C_{i,j}}{\Delta t}, \qquad (23)$$

$$D \frac{\partial^2 C}{\partial t^2} \approx D \frac{C_{i,j+1} - 2C_{i,j} + C_{i,j-1}}{\Delta x^2}; \qquad (24)$$

Consequently, by substituting expressions (22, 23) into equation (11), we obtain a one-dimensional equation in discrete variables with initial and boundary conditions:

$$C_{i+1,j} = C_{i,j} + D \frac{\Delta t \cdot (C_{i,j+1} - 2C_{i,j} + C_{i,j-1})}{\Delta x^2}, \qquad (25)$$

$$C_{0,j} = C_0, \qquad (26)$$

$$C_{i,0} = C_{i,n} = 0, \qquad (27)$$

With the help of an explicit finite-difference scheme, with a given concentration value $C_{i,j}$ at a given point, for fixed i,j we can calculate $C_{i+1,j}$ and thus obtain the distribution of concentrations along the entire height of the pressure channel, and its change over time.

The resulting design scheme is stable, provided that the condition of the Courant (3) [3, 5] is fulfilled. Based on this ratio, to ensure the stability and convergence of the circuit, the step in the direction of the axis X will be 0.05mm, respectively, the time increment is 0.01s [6].

Using the calculation procedure described above (16-27), the concentration distributions by the height of the channel obtained for different values of time t (Figure 3). The following initial data was accepted:
1. The height of the channel h=1mm;
2. The area of the membrane surface S=1m^2;
3. Convective transfer rate (velocity) V=const=0.28 m/s;
4. Diffusion coefficient D=const=0.05 m^2/s;
5. Initial concentration (feeding solution) C_0=2 g/l.

Estimated parameters:
1. Step by spatial coordinate Δt=0.05 mm;
2. Time increment Δt=0.01 s.

On Figure 3 shows how the concentration distribution by the height of channel changes over time. At the initial time (Figure 3), the target component is evenly distributed in a solution that fills the channel space (ideal mixing), but for a fairly short period of time Δt = 512 sec, the concentration of the target component gradually increases in the region near the surface of the membrane. Distribution of concentration by the height of the channel takes an exponential character (the curve "1").

This is due to the fact that the particles of the target component are delayed on the surface of the membrane, due to which there is an increase in concentration in the membrane layer of the channel. With certain critical values of concentration, the gel sediment may be formed [12, 13, 15]. For values of dimensionless heights of the channel in the range from 0.7 to 0.9, the concentration values coincide within 10% with the results

presented in the works of other authors [3, 5, 15]. However, in the interval from 0.9 to 1, the estimated concentrations are much higher than expected [5], due to assumptions and limitations of a one-dimensional model.

This is explained by the fact that in real systems, the convective flow, having a turbulent flow pattern, makes the distribution of concentrations more uniform, diverting the mass flow of the target component into the channel volume from the membrane surface. As a result, the effect of concentration polarization decreases and the sediment is formed less intensively. Consequently, the concentration at the surface of the membrane will grow at a lower intensity than the proposed model shows.

In the presented work, the convective transfer rate is assumed to be unchanged, both modulo and direction, which prevents the effects mentioned above from being taken into account. Therefore, in further work, to study the phenomena of concentration polarization, it is planned to construct a 2-dimension model based on this algorithm, taking into account the velocity distributions and effects associated with turbulence of the flow.
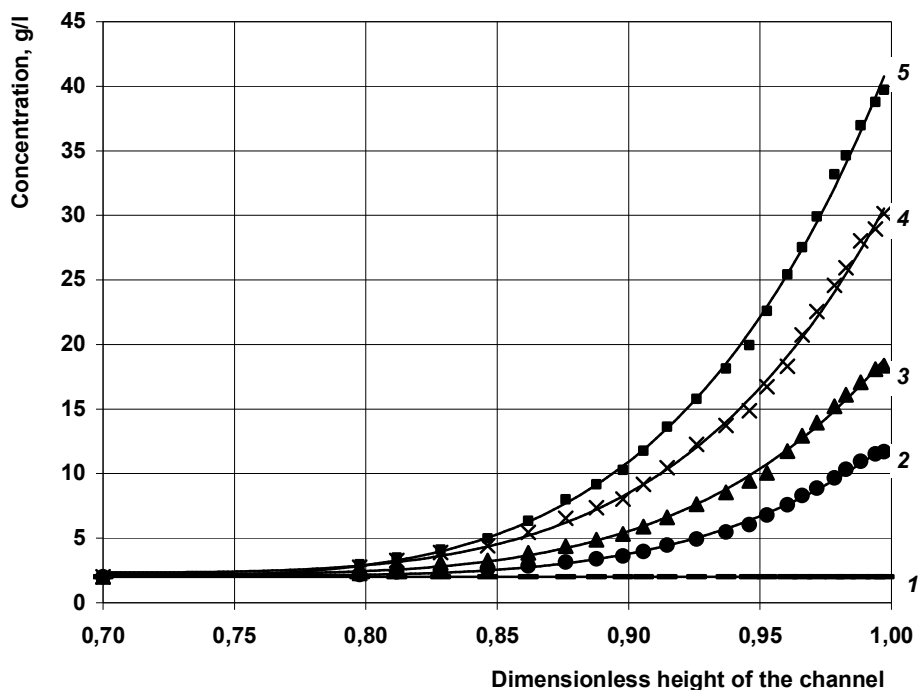

Figure 3. Distribution of concentrations by the height of the channel:
1 – 0 sec, 2 – 32 sec, 3 – 384 sec, 4 – 448 sec, 5 – 512 sec.

Conclusions

1. The distributions of concentrations of the target component by height of the membrane channel were obtained and analyzed. The character of the curves coincides with the physical representations of the process, with the exception of the region located near the surface of the membrane. This is explained by the fact that in real systems, the convective flow, having a turbulent flow pattern, makes the distribution of concentrations more uniform, diverting the mass flows of the target component into the

volume of the channel from membrane surface. As a result, the effect of concentration polarization decreases and the sediment is formed less intensively.

2. The one-dimensional model presented does not allow for the effects associated with turbulence, but can be applied to a dead-end separation scheme.

3. The scientific novelty consists in determination of the kinetic changes in the level of concentration polarization in the membrane channels of barometric apparatus in the separation of food industry liquids.

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Kinetics of drying the titanium dioxide paste in the vortex dryer

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Abstract

Introduction. The purpose of the work is mathematical modeling of the process of drying the titanium dioxide TiO_2 paste, which takes place under the conditions of hydrodynamics of vortex fluxes of heat carrier and continuous dispersion, which will increase the efficiency of heat and mass transfer processes and reduce energy costs.

Materials and methods. The process of drying the finely divided paste of TiO_2 in the vortex fluxes of the coolant with the use of continuous dispersion of the starting material was carried out in a conical drying chamber of the drying apparatus equipped with a special device for dispersing the material in the lower part and the zone of drying in the upper part.

Results and discussion. The process of drying the titanium dioxide paste in the vortex flow of the heat carrier during the application of the original design of the drying apparatus with the dispersant and the zone of drying of the material to a high residual dryness of 99.7% is implemented. Enriched intensive grinding of conglomerates of the material and their mixing with an already dried fine powder with an equivalent diameter $D_e = 100–200$ μm and a density $\rho_{TiO2} = 4,23$ g/cm^3 has been carried out here. The presence of separation zone of particles of the already dried powder from conglomerates of the paste provides effective grinding of the latter and an increase in the contact surface of the wet material with the coolant. Specific load of the surface of the layer of conglomerates of the paste TiO2 in the vortex flow for moisture has the value af = 138–155 kg$_{vol}$/(m^2·h). A physical model of paste drying was selected. On the basis of the physical model, a mathematical model of the process, consisting of differential equations of the first order, describing the dependence of change in the temperature of the heat carrier and the material particles from the drying time, as well as the dependence of change in the moisture content of the material from the drying time, was developed. Given the continuous grinding of wet material, this model allowed determining: the conditions of the process, namely, the temperature at the entrance to the drying chamber should be 95-120°C, the flow of the coolant 60–80 m^3/s, the moisture content of the paste TiO_2 not more than 50.

Conclusions. The kinetics of the process of drying the titanium dioxide paste was studied and a physical, based on the modified mathematical, model was obtained that allowed determining the drying time of the wet material and the main kinetic parameters of the drying process.

Introduction

The process of drying finely divided paste is a technological process that consists of a combination of heat transfer processes of heat and mass. When choosing the optimal drying and rational design of the dryer, it is necessary to provide the conditions necessary for obtaining the technological properties of the material, which require industry standards. The rational method of heat treatment and the most suitable design of drying apparatus are established only for a particular material or group of materials having similar physical and chemical properties. In this paper, as a material, a finely divided titanium dioxide titanium dioxide TiO_2 is considered.

An important scientific challenge is to reduce the cost of heat energy in the drying process, which consumes up to 25% of world energy production [1]. An insufficiently solved problem is the reduction of energy costs and the intensification of drying in the production of finely divided powders, in particular titanium dioxide. The market demand for titanium dioxide is increasing. Major consumers of TiO_2 titanium dioxide are paint and varnish, metallurgy, paper, pharmaceuticals and other industries where it is used as filler. Titanium dioxide is also used as filler for the manufacture of various plastic masses and products, and for the production of high-quality paper.

In the technology of producing titanium dioxide, the process of drying paste of TiO_2 is the most energy-intensive and limiting process [2]. One of the main indicators of finished products is the low residual moisture of fine powder. It should be no more than 0.3% [3]. To obtain such a value of residual moisture in conventional drying machines, the temperature of the waste heat carrier at the exit of the dryer increases, this leads to significant costs of thermal energy. In the process of drying it is necessary to destroy agglomerates, with stand a narrow range of moisture content, to separate the particles in geometric sizes (remove dust particles), to clean the coolant.

The purpose of experimental research is to determine the conditions under which the process of drying the titanium dioxide paste in the vortex flow of the heat carrier occurs, and the resulting dried product meets the technical requirements.

Choice of dryer type

The choice of the most appropriate type of apparatus for drying the fine titanium dioxide paste is based on the analysis of a significant number of various factors affecting the drying process, such as [1, 4]:
- characteristics of paste as an object of drying;
- productivity of the device;
- technological requirements for drying, taking into account all the processes necessary for obtaining high-quality products;
- requirements of environmental and industrial sanitation;
- energy and economic requirements.

The analysis of literature [5, 6] showed that at present the choice of optimal and expedient type of drying apparatus for fine disperse paste is a complex task of the system analysis of processes and apparatuses of chemical technology. Almost such a choice is made on the basis of a quantitative or qualitative assessment of the conformity of known types of apparatus to the properties of the paste. Important such properties are [7]:
- the value of the specific surface, the size and volume of the pores, which determine together the diffusion resistance of the internal mass transfer;
- thermal properties that determine the thermal resistance during drying;

− the forms of moisture communication with the material, which determine the energy that needs to be spent on drying and affect the heat transfer mechanism;

− hydraulic properties.

Determining the full set of these properties is a complex and bulky task that requires a lot of experimental work. Therefore, in order to expedite the choice of the most appropriate type of dryer, in this work it was decided to assess the existing modern drying equipment for the conformity of the dried product.

After a preliminary assessment of existing drying equipment, many of the presented vehicles preferred a group of dry-cleaners such as "fluidized bed" (FB). This is the most promising group of devices for fine-grained materials [14, 15], since only they can provide heat and mass transfer to each individual aggregate unit. This group includes aggregates:

− boiling bed (BB) and passage boiling bed (PBB);

− type "Flash";

− fountain bed (FB) and air fountain bed (AFB);

− vibro boiling bed (VBB);

− vortex bed (VB);

− pneumatic transport (PT);

− with twisted streams (TS);

− with counterclockwise twisted streams (CTS).

The selected list of drying appliances should be supplemented with devices with an organized fluidized bed (OFB) and pneumatic helix driers (PHD) [15], as well as combined plants of various types.

Problems of intensification of heat and mass transfer in drying apparatuses for dispersed materials, as well as elimination of the removal of non-material material or reduction of the retour and some other problems characterizing the quality of the chosen drying method and design of the dryer, are determined by the hydrodynamic regime. Hydrodynamics of vortex flows, as well as physical and mathematical modeling of the fine-grained drying process, are studied in detail and widely represented in the literature [2, 3].

It is known equations that determine the range of the fluidized bed, namely, expressions for $K = \dfrac{v_{fl}}{v_{cr}}$ Re_{cr} Re_{fl} K_{max} [9], where Re_{cr} Re_{fl} the value of the Reynolds criteria corresponding to the beginning of the fluidization and removal of the material, v_{cr} v_{fl} speeds that determine the relevant criteria Re [8, 9].

The distribution of thermal energy and moisture, for a single particle, along the length of the drying apparatus, is always a complex problem of external and internal heat and mass transfer, which is rather complex and requires considerable computational effort [5]. A simpler approach to finding a change in system parameters is based on the use of a boundary task. The system of equations of internal heat and mass transfer recorded in the framework of the boundary problem in its most general form is represented by formula 1:

$$\begin{cases} \dfrac{\partial U}{\partial \tau} = a_m\left(\dfrac{\partial^2 U}{\partial r^2} + \dfrac{\Gamma}{r}\dfrac{\partial U}{\partial r}\right) + \dfrac{\partial a_m}{\partial r}\dfrac{\partial U}{\partial r} + a_m\delta\left(\dfrac{\partial^2 T}{\partial r^2} + \dfrac{\Gamma}{r}\dfrac{\partial T}{\partial r}\right) + \left(\delta\dfrac{\partial a_m}{\partial r} + a\dfrac{\partial \delta}{\partial r}\right)\dfrac{\partial T}{\partial r} \\[4mm] \dfrac{\partial T}{\partial \tau} = \dfrac{\lambda}{c_T\rho_T}\left(\dfrac{\partial^2 T}{\partial r^2} + \dfrac{\Gamma}{r}\dfrac{\partial T}{\partial r}\right) + \dfrac{1}{c_T\rho_T}\dfrac{\partial \lambda}{\partial T}\dfrac{\partial T}{\partial r} + \dfrac{\varepsilon r}{c_T}\dfrac{\partial U}{\partial T} \end{cases}, (1)$$

where a, a_m in accordance, thermal conductivity and conductivity.

Materials and methods

Materials

As a drying material, a thyrotrophic fine TiO_2 titanium dioxide paste with an initial moisture content of w = 55% and a density of ρ = 2173 kg/m^3 was used which, when applied mechanically, reduced its viscosity and increased fluidity. This feature of the paste allows you to feed it into the drying chamber with an increased dryness of up to 80% and, at the same time, will not clog the feeder-dispenser installation.

Experimental installation

In order to achieve the prescribed requirements for a dried titanium dioxide powder, a specially designed technique for conducting experiment.

Investigation of the drying process of fine titanium dioxide paste in vortex fluxes of a heat carrier was carried out on a pilot plant with the dimensions of a vortex conical drying chamber $A{\times}B{\times}H$ = 0,1×0,4×0,7 m. The vortex chamber of the drying apparatus in the lower part is equipped with a dispersant for grinding agglomerates of paste [Patent of Ukraine № 108688 IPC F26B 17/10 (2006.01)]. Also, the authors of the article developed a method for drying paste-like materials, on which the design of the dryer [Patent of Ukraine № 107089 IPC F26B 17/10 (2006.01)].

Measuring complex

The pressure difference in the dispersion zone and the pre-drying zone was continuously measured by two difemometers D_2 and D_3, the power of the dispersant drive was measured by a measuring complex of the K50 type No. 1654, the temperature of the coolant – the diffusion meter D_1, the temperature and humidity of the vortex fluxes of the heat carrier and the particles of titanium dioxide by the computerized system at application humidity and temperature sensors MLX90614 with a frequency of 63 measurements per second (63 Hz) connected to a computer through the Arduino Pro Mini controller. The diagram of the arrangement of devices and sensors for data storage, differential meters and main elements is shown in Fig. 1.
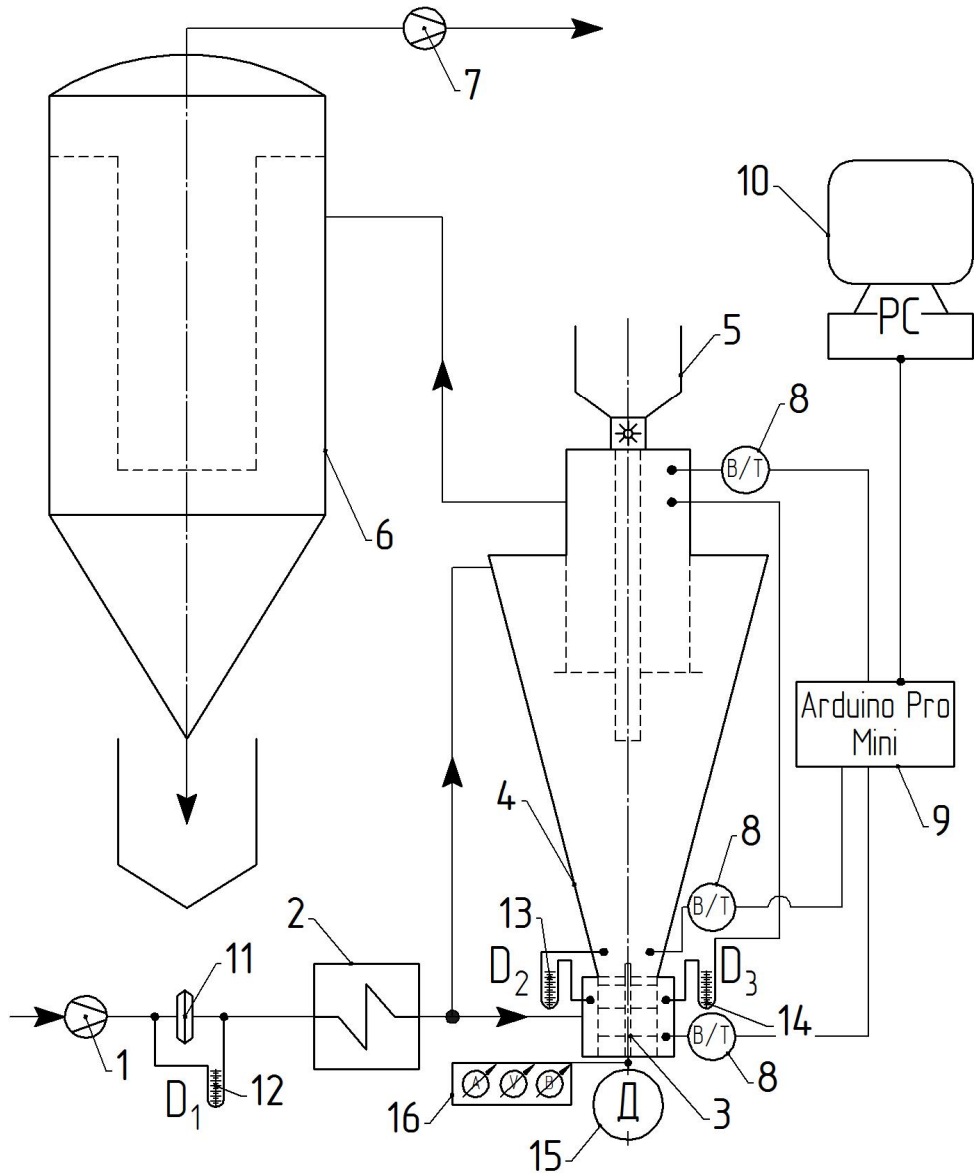
Figure 1. Scheme of a computerized system for measuring pressure drop, power, temperature and humidity in an experimental drying plant:
1, 7 – booster and exhaust fans; 2 – heater; 3 – dispersant; 4 – drying chamber;
5 – feeder–dispenser; 6 – a sleeve filter; 8 – temperature and humidity sensor MLX90614;
9 – Microcontroller Arduino Pro Mini; 10 – computer for visualization and data storage;
11 – diaphragm; 12, 13, 14 – difemometer; 15 – electric drive;
16 – measuring complex type K50 №1654

Results and discussion

Theoretical studies of trajectories and hydrodynamics of vortex flows of a drying agent in a developed drying chamber

In this paper, the original design of a drying apparatus (Figure 2) is considered for the production of a fine powder of titanium dioxide.
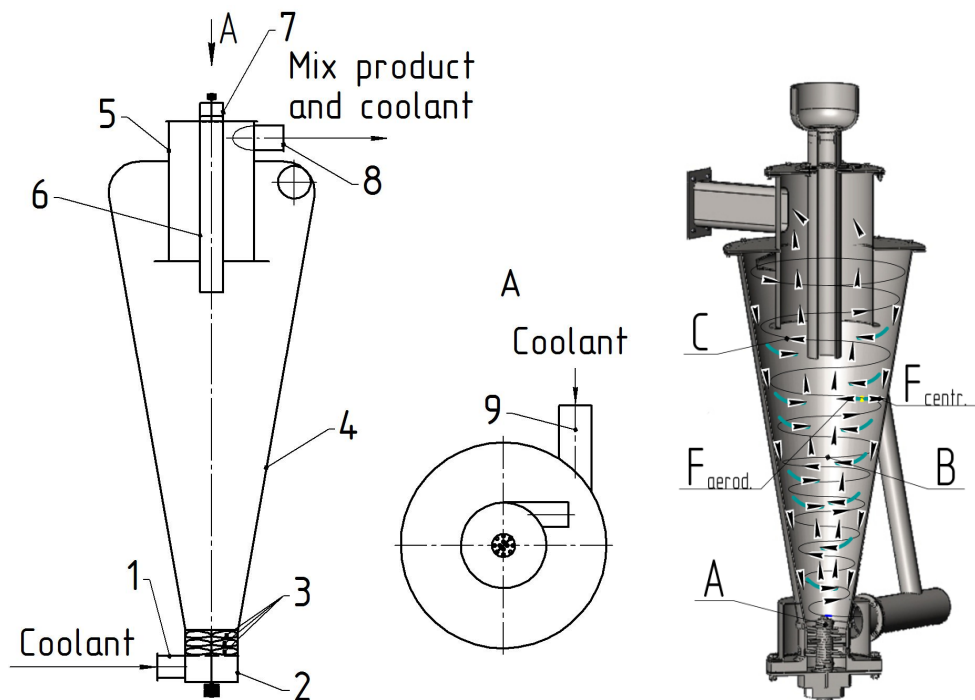

Figure 2. Scheme of the original drying apparatus for obtaining fine dispersions:
1 – the main supply pipe coolant; 2 – diffuser; 3 – dispersant; 4 – Cone-shaped drying chamber; 5 – nozzle for supplying the drying agent to drying; 6 – separation cylinder; 7 – the system of supply of moist dispersions; 8 – outlet pipe; A – dispersion zone; B – fractional separation zone; C – zone of intensive drying

First of all, it is necessary to know the distribution of gas flow between continuous gas and fine material for the development of methods for calculating heat and mass transfer processes when drying fine-grained pastes and the creation of appropriate equipment with two–phase media. These tasks form the basis for describing the behavior of two–phase environments, namely vortex flows, and therefore cause great interest in these problems. However, satisfactory quantitative patterns that adequately reflect the aerodynamic and hydrodynamic characteristics of vortex flows are still rare in the literature.

Two–phase vortical streams arise in the drying chamber, in which a process of drying of a wet product – a finely divided paste of TiO_2 – occurs. As a coolant the heated dry air is used at a temperature of 90–120 ° C. These flows at each stage play an important role in

addition to the heat and mass transfer processes, as well as the displacement of solid dispersion over the respective zones of the drying chamber A, B, C (Figure 2).

A 3D model of the drying machine was designed using the Solid Works SolidWorks program and the Flow Simulation simulation, and the velocity and pressure velocity fields of the vortex fluxes of the coolant were studied (Fig. 3). By setting different combinations of charges of the drying agent at the inlet of branch pipes 1 and 5, one can determine the nature of the movements of the drying agent in the cell of the apparatus.
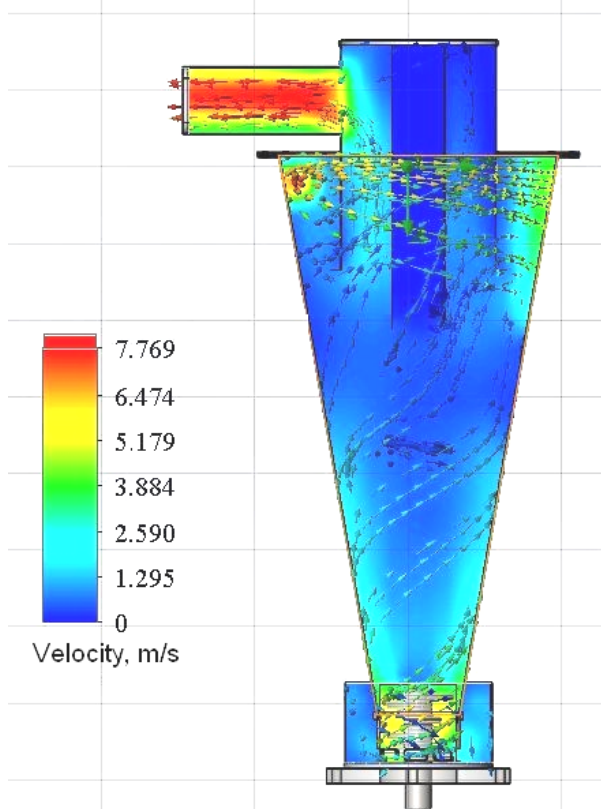

Figure 3. Study of vortex flows for expenses 20 m³/s for the bottom of the chamber and 80 m³/s for the upper part of the chamber

As can be seen from the diagram of the distribution of flows, the speed of the drying agent is divided into two components: axial and tangential. The axial speed is centered around the drying chamber, and which transports the finely divided particles of the material from the grinding zone to the drying zone and removes from the chamber. The tangential velocity of the gas phase is concentrated on the periphery of the drying chamber and separates the particles of the material and increases the heat transfer efficiency between the particles and the coolant due to the turbulence of the common two–phase flow and the increase of the Re number. The tangential velocity of the vortex stream decreases as a result of decreasing the radius of the drying chamber. The swirling coefficient of the vortex flows is the ratio of the tangential velocity to the axial and is 5.5–7.0 for this configuration of the drying chamber, which is almost the same as in the similar constructions that were considered in the works [7, 9].

Physical modeling of TiO₂ paste drying process in a vortex dryer

Fine particles of titanium dioxide powder are presented in the form of crystals (Fig. 4). The sizes of crystals depend on the technological conditions of crystallization of the product. Fine particles should have a size of 0.22 – 0.25 microns [11]. When mixed with water, particles of TiO_2 form a thyrotrophic paste that, when applied mechanically, reduces its viscosity and increases its fluidity.
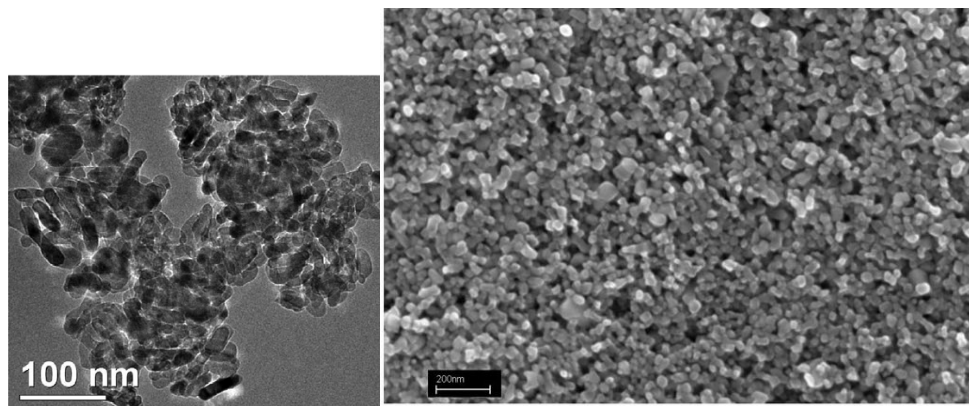

Figure 4. Crystal origin of finely divided particles of titanium dioxide [12]

As can be seen from Figure 4, crystals are chaotic, so thin channels, educations; cavities are formed between them, which fill up with water, forming a heterogeneous substance – a paste. Within the paste crystals are held by the forces of surface tension of water. In addition to the surface tension of additional forces, the interaction between the crystals is not present. When drying paste of TiO_2 in vortex streams after removing all moisture, the paste turns into a fine pigment.

Moisture in the paste of TiO_2 exists in such species:
- capillary moisture on the surface of agglomerates (Figure 5);
- micro capillary moisture;
- adsorption–bound moisture, moisture on the surface of the crystals;
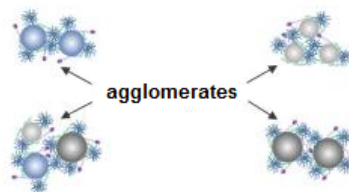- nanocapillary moisture.

Figure 5. Titanium dioxide paste agglomerates [12]

In this work, the drying of the fine paste occurs in the vortex flow of the coolant, which has many significant advantages over conductive, spray drying or drying on inert bodies.

The speed of the drying process depends on the internal structure of the disperse material, its thermo physical properties, the size, shape and condition of the outer surface,

the degree of grinding agglomerates of the paste, as well as the parameters of the drying agent (Figure 6). Parameters of the drying agent are: temperature, relative humidity, amount of heat and its consumption. When drying, the process of submerging the localized front of moisture evaporation into the middle of the agglomerates of the paste TiO2 passes, and the heat is supplied by the heat conductivity of the dry material and is spent on the conversion of moisture into the vapor.
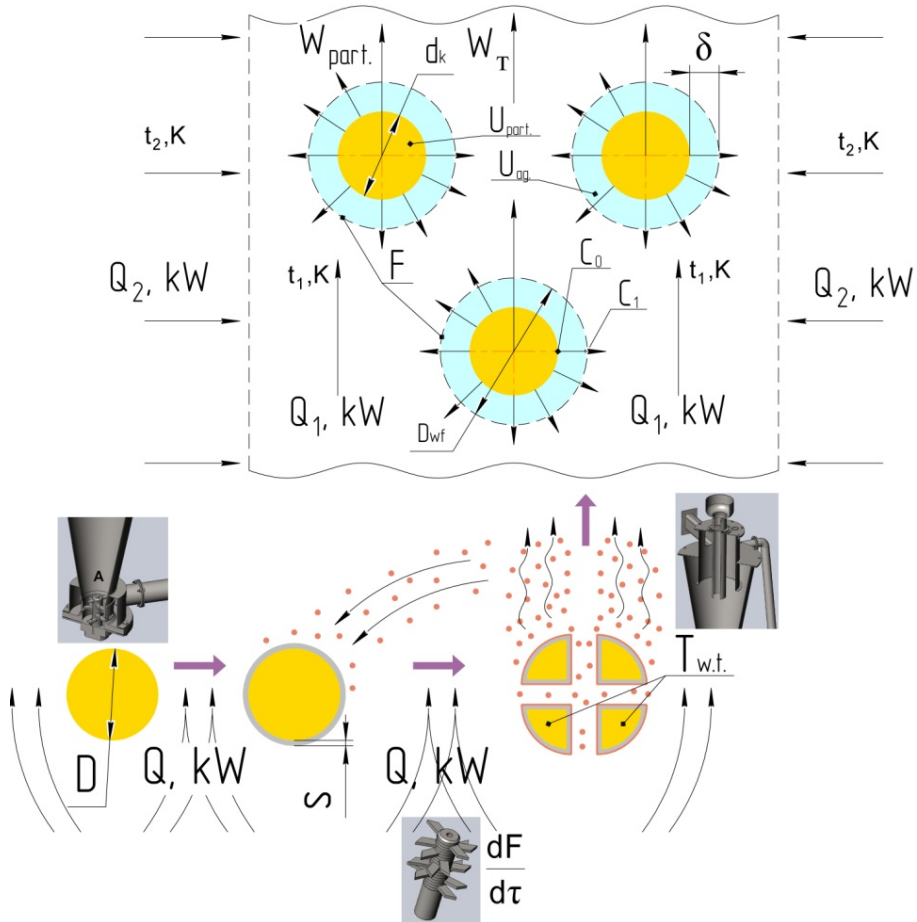

Figure 6. Physical model of drying of TiO$_2$ paste conglomerates

Due to the evaporation of moisture inside the material, an excess pressure is formed through which the steam formed is filtered from the evaporation front to the outer surface of the wet body.

Mathematical description of the process of drying of finely divided paste of titanium dioxide

Thermal balance of the drying process:

$$dQ = dQ_1 - dQ_2 \quad (1)$$

where dQ heat flow to heat paste, kJ; dQ_1 convective heat flow from the drying agent, kJ; dQ_2 heat flux on the evaporation of water from the paste of titanium dioxide, kJ.

By drawing the constituents of the equation (1), we obtain:

$$G_{mat.} \cdot (c_{mat.} + c_w \cdot U) \cdot dt_{part.} = \alpha \cdot F_{part.} \cdot (t_{ag.} - t_{part.}) \cdot d\tau - G_{mat.} \cdot \frac{dU}{d\tau} \cdot r \cdot d\tau \quad (2)$$

where $G_{mat.}$ the mass flow of a completely dry powder of titanium dioxide, $\frac{kg}{s}$ w speed of the drying agent (air), $\frac{m}{s}$ l the equivalent diameter of the particle of titanium dioxide paste, m; $v_{ag.}$ kinematic viscosity of the drying agent, $\frac{m^2}{s}$ $c_{mat.}$ specific heat of a titanium dioxide powder, $\frac{J}{kg \cdot K}$ c_w specific heat of water, $\frac{J}{kg \cdot K}$

U moisture content of titanium dioxide, $\frac{kg}{kg}$ α coefficient of heat transfer from the coolant to the surface of the particle, $\frac{W}{m^2 \cdot K}$ $F_{part.}$ outer surface of the particle, m^2; temperature of the drying agent, $℃$; particle temperature, $℃$; drying speed, $\frac{1}{s}$ r specific heat of steam generation, $\frac{J}{kg}$ $d\tau$ drying time, s;

Drying rate in the first period is limited by the rate of heat transfer from the coolant to the lumps of paste [2]:

$$\frac{dU}{d\tau} = \frac{\alpha \cdot (t_{ag.} - t_{w.t.})}{r} \quad (3),$$

in the second period, the water evaporates, bound by the adsorption forces [2]:

$$\frac{dU}{d\tau} = -K \cdot (U_{1k} - U) \quad (4),$$

де $t_{w.t.}$ temperature of the wet thermometer, $℃$ K drying rate, $\frac{1}{s}$ U_{1k} critical moisture content, $\frac{kg}{kg}$ U equilibrium moisture content, $\frac{kg}{kg}$ On the basis of the thermal energy equation (2), the mathematical description of the drying process can be represented by the following system of equations:

$$\begin{cases} \dfrac{dt_{part.}}{d\tau} = \dfrac{\alpha \cdot F_{part.} \cdot \left(t_{ag.} - t_{part.}\right)}{G_{mat.} \cdot \left(c_{mat.} + c_w \cdot U\right)} - \dfrac{\dfrac{dU}{d\tau} \cdot r}{c_{mat.} + c_w \cdot U} \\ \dfrac{dU}{d\tau} = \dfrac{\alpha \cdot \left(t_{ag.} - t_{w.t.}\right)}{r} - K \cdot \left(U_{1k} - U\right) \end{cases} \qquad (5)$$

We accept the initial conditions for this system of equations (5):

$$u\,|_{\tau=0} = u_0, u_2 = u_{1cr}, \tau_0 = 0, t_0 = t_1, d_0 = 1\,mm, \qquad (6)$$

$$\alpha = \frac{Nu \cdot \lambda_{ag.}}{D}\,1],\ Nu = 0,021 \cdot Re^{0,8} \cdot Pr^{0,43} \cdot \left(\frac{Pr}{Pr_{pl.}}\right)^{0,25} \cdot \varepsilon\,1,\,2],$$

The mathematical description of the process of drying the titanium dioxide paste is solved by direct integration of the system of equations (5) using the initial conditions (6). The results of calculations are shown in Figures 2 and 3.
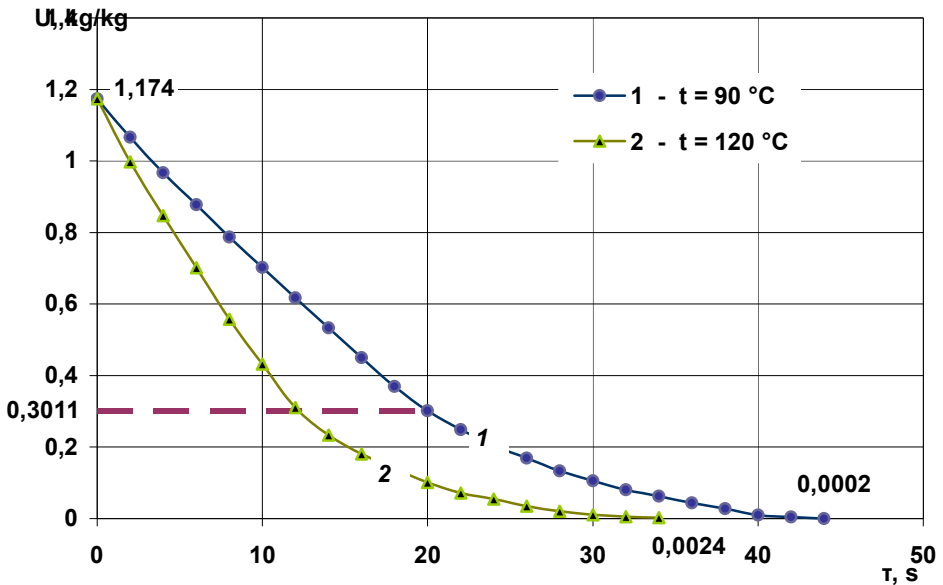

Figure 7. The dependence of the moisture content of the particle of titanium dioxide from the time of drying
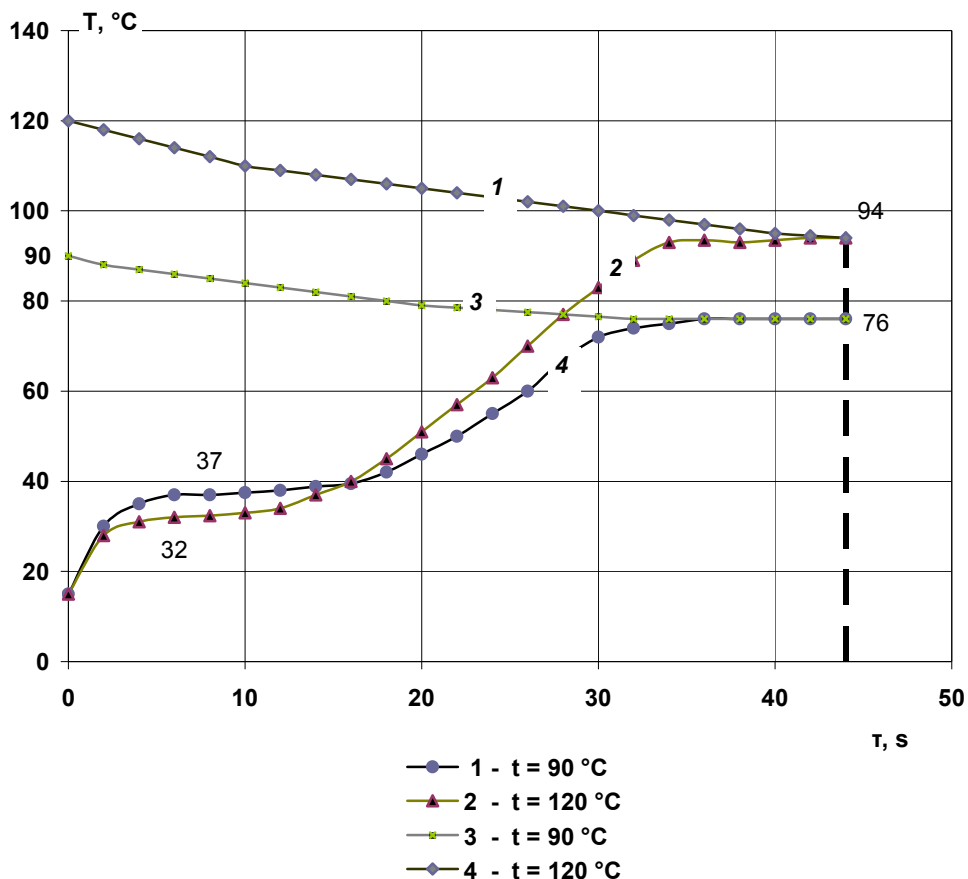
Figure 8. Dependence of the temperature of the particle of titanium dioxide from the time of drying

The dependence of the moisture content on time indicates that the drying process of the paste includes the period of heating to the temperature of the wet thermometer, the period of constant drying rate flowing in the range from $U_1 = 1{,}174 \frac{kg}{kg}$ to $U_{1cr} = 0{,}3011 \frac{kg}{kg}$ and the period of the falling rate of drying, proceeding from $U_{1cr} = 0{,}3011 \frac{kg}{kg}$ to $U_2 = 0{,}002 \frac{kg}{kg}$.

Figure 2 shows that the limiting stage of the drying process is a period of falling velocity in which the adsorbed moisture is dried.

Figure 3 shows that the temperature mode of drying in the period of constant drying rate is stable. The temperature of the layer at the end of this period sharply rises to equilibrium with the temperature of the coolant.

Conclusions

The mathematical process of drying fine titanium dioxide paste has been developed, which allows us to obtain the kinetic parameters of the process that are necessary for the design of an industrial drying apparatus. With the help of the developed design of the laboratory drying apparatus, the ability to dry the paste of TiO_2 to a high residual dryness of 99.7% and the production of fine pigment was experimentally confirmed.

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Peculiar features of business incubators functioning: Ukrainian and world experience

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Abstract

Introduction. It was analyzed the modern approaches to the functioning of business incubators in Ukraine with the purpose of ensuring the initiation of effective structural changes in the national economy.

Materials and methods. The experience of creating and operating business incubators in the United States, Italy, Britain, Portugal, Brazil, China has become a material for research.

Results and discussion. Business incubators play an important role in the development of national economies. The creation of business incubators will provide conditions for the development of entrepreneurship in the agri-food sector, the creation of new jobs, the effective use of innovative capacity and resources.

The largest number of start-up projects is in the following areas: service – 17%, trade – 13%, industry – 9%, IT – 8%, hotel and restaurant business – 7%, transport and agriculture – 6%.

Implementation of the main functions of business incubators, namely: business expertise for new enterprises and financing contribute both to the economic development of regions and increasing their investment attractiveness, and to the development of entrepreneurship, ensures the implementation of innovative ideas, creating additional jobs, and improving the welfare of the population.

In Ukraine the prospects of business incubators are determined by the following factors: increasing demand of business structures for new training technologies, consulting and information support; increasing demand of potential investors that not only should firms prove their steady material and financial position but also show an ability to dispose of investments provided to them; credit policy of banks forbidding companies to take up loans to purchase fixed assets, especially buildings, office and other equipment which results in an increase of their costs and reduction of current assets; pre-final stage of market formation which increases competition and makes business spend more time on sales of goods (services), diverting their attention from issues of functional management and strategic marketing; time needed for start-ups to develop and adapt to the market under terms of the current fiscal policy.

Conclusion. The study of the history of the creation of business incubators in the world made it possible to identify the main directions of innovative entrepreneurship and the prospects for its development in Ukraine.

Introduction

Entrepreneurial activity represents a mechanism of society's socio-economic life, which forces companies to introduce new technologies and creates competition promoting application of innovative technical equipment that can accelerate the product development process resulting in improvement of efficiency of production and economy as a whole. Thus, it is safe to say that development of enterprises depends on the functioning of country as a whole. Therefore, the development of business incubators in Ukraine is a certain impetus for development of the entire country's economy.

The problems of business incubators functioning were researched in the works by the following scholars, namely: J. Bone, O. Allen, C. Haley. (2017), J. Bruneel, T. Ratinho, B. Clarysse, A. Groen (2012), L. M. Vasiliev (2010), R. Grimald, A. Grandi (2005), S. Mian, W. Lamine, A. Fayolle (2016), J. M. Shepard (2013), R. I. Zavadiak, Ya. F. Kopusiak 92014), T. V. Kysil (2013), A. B. Nemchenko, T. B. Nemchenko (2010), V. Yu. Frolova, H. I. Frolova (2010), L. T. Shevchuk, A. V. Kolodiichuk (2013), Wenqing Wu, Qing Han (2017). However, we consider it necessary to carry out generalization and systematization of the theoretical grounds of business incubators development, given the existing world and domestic experience. The development of entrepreneurship in agriculture and the food sector is important for the economies of different countries.

The agri-food sector plays a leading role in the economic development of Ukraine.

The creation of business incubators will provide conditions for the development of entrepreneurship in the food industry, the creation of new jobs, the effective use of innovative capacity and resources.

Aim of the research is deepening of the theoretical foundations for development of business incubators, revealing the peculiar features of business incubators functioning under modern conditions, identifying the measures for business incubators successful development, given the international and domestic experience.

Materials and methods

Business incubators, which are innovative structures, are examined in the article. Business incubators contribute to the development of innovative entrepreneurship and help in the implementation of start-ups. The main task of business incubators is to ensure effective conditions for the creation and development of start-ups. Innovative ideas are the basis of start-ups. Innovative ideas are one of the main factors of competition in the modern world. Innovations provide competitive advantages to start-ups. The effectiveness of introducing innovations provides start-ups with a stable market position.

The role of business incubators is to provide the necessary support when preparing and presenting the project to the investor. The business incubator avoids the typical mistakes by providing consulting services in the derivation of projects. It helps in finding investors. World experience of organization of business incubators and trends of development of business incubators in Ukraine have been studied to ensure the reliability of the results during the research.

The method of statistical analysis was used in the study of data from the State Statistics Service of Ukraine and business associations.

Theoretical and methodological approaches, which were highlighted in the works of scientists [1–6], were used in research.

The study of the main characteristics and functions of business incubators from different countries of the world make it possible to forecast trends in the development of innovative entrepreneurship in Ukraine.

The results of the studies are obtained through the use of grouping methods, generalizations and comparisons. The graphical method is used to provide visibility of the obtained results.

Results and discussion

Business incubators are the object of research by scientists in many countries. Ukraine is passing the period of the formation of business incubators. Business incubators serve as a role for the development and support of small and medium-sized businesses in the economies of developed countries. There are many varieties of business incubators. They differ in size, forms of interaction with start-ups, venture capitalists.

Studying the experience of the formation of business incubators of other countries will allow to build an effective model of business incubators in Ukraine. The material for writing the article was the experience of business incubators in the USA, Italy, UK, Portugal, Brazil, China.

Business incubators are effective instruments for the development of new firms. The authors studied the mechanisms of cooperation between business incubators and venture capitalists and proposed three mechanisms for interaction between business incubators and venture capitalists: revenue sharing mechanism, cost sharing mechanism and knowledge sharing mechanism. Wenqing Wu, Qing Han (2017) consider the effect of the business nonprofit incubators and compare the three cooperation mechanisms in the profit incubators. The results indicate that the mechanism of revenue sharing leads to the highest incubator's revenue sharing proportion. Additionally, the incubator's revenue sharing proportion decreases even though its final profit increases when considering altruism. Therefore, the nonprofit incubator can be better for cooperating with the venture capitalist than the profit incubator [1].

Luisa Margarida Cagica Carvalho, Simone Vasconcelos Ribeiro Galina (2015) presented a comparative study on the specifics of business incubators to promote the development of new companies in Portugal and Brazil [2].

Rosa Grimald, Alessandro Grandi (2005) argue that the variety of incubating organizations is driven by the evolution of companies' requirements and needs. These needs requirements contribute to the differentiation of the range of services by incubators. The authors identify four types of incubators and a list of variables incubator characteristics that help to describe the incubation models. The authors obtained empirical data on two incubating models based on the studies of eight Italian incubators [3].

Johan Bruneel,Tiago Ratinho, Bart Clarysse, Aard Groen (2012) show the accelerator as a new generation incubation model. Accelerators have become an umbrella term for any program providing a service structure of mentorship, networking opportunities and access to funding [4].

Sarfraz Mian, Wadid Lamine, Alain Fayolle (2016) describe the features of incubators, accelerators and scientific parks as tools for business development. Science parks, incubators and accelerators are Technology Business Incubation mechanisms considered to be important policy tools for supporting innovation and technology-oriented entrepreneurial growth. Their popularity is premised on the belief that these mechanisms provide critical

value-added inputs essential for the creation and development of innovative Technology-Based Firms [5].

Jeffrey M Shepard, (2013) to discuss the historical evolution of business incubators from 1959 to the present. Three cohort periods were defined: 1959-1979, 1980-1999 and 2000-2012. The business characteristics of corporate mission, plans and strategies, leadership/management, staff competence and expertise, facilities and resources and technology were described for each cohort period [6].

Nowadays survival in fairly harsh conditions is crucial for companies without a sustainable economic and financial support. Power and invincibility are not determined by country's size but knowledge and ability to generate new ideas for sustainable economic mechanisms in competition. Small and medium-sized business is a locomotive of economic reforms as its stable and successful performance is a step into future. Today, application of modern approaches, the effectiveness of which is proved by global practice, is of significance to business and entrepreneurship development [7].

Ukraine is currently experiencing fundamental reform of its law system and its adaptation to new socio-economic conditions. Against this background, there arise many problems associated with entrepreneurial activities. In order to ease the situation, based on the amended and altered law of Ukraine "On state support of small business" No. 2063-III dated October 19, 2000, which provides for the legal framework for state support of small business irrespective of ownership form with a view to early recovery from the economic recession, the conditions for introduction and extension of market reforms in Ukraine are created.

Today, of urgency is the problem of effective use of business incubators as a form of institutional support for implementation and innovation, which will enhance entrepreneurship development. New economic conditions require active work and increased attention to forms of institutional support for innovative projects implementation.

The interest in business incubators is growing thus attracting the attention of the government, local authorities, academia, economists, etc. This interest is based on assisting small and medium-sized enterprises, and acts as a tool of ensuring economic growth, poverty reduction and elimination of territorial disparity through decentralization of development at the local or regional levels.

Business incubator is a structure that creates favourable conditions for functioning of start-ups by providing financial, informational and consulting services. Incubation provides necessary assistance to newly established businesses in acquiring necessary professionalism in the selected production area and rapid overcoming of problems arising in the process of their development and activities.

For the purposes of this study, we consider an incubator as being defined by the following characteristics: open-ended duration (exit usually based on the stage of the company, rather than a specific time frame); typically rent/fee-based; focus on physical space over services; admissions on ad-hoc basis (not cohort-based); provision of services including mentorship, entrepreneurial training; often provide technical facilities such as laboratory equipment; selective admission (but typically less so than accelerators) [8].

The main emphasis in the activities of business incubators is on encouragement of local and regional economies' development and creation of jobs.

In our opinion, business incubators are quite profitable and successful projects for improving the country's economic level. At present in Ukraine there are about 70 business incubators working in various fields. According to the data of 01.01.2014 provided by the State Committee of Ukraine on Entrepreneurship, in Ukraine there are 480 business centres, 79 business incubators, 50 technology parks, 538 leasing centres, 4 148 non-banking

financial institutions, 226 funds for support of entrepreneurship (among them 23 established with participation of the Ukrainian Fund for Entrepreneurship Support), 3034 investment and innovation funds and companies, 4238 information and consultation institutions [9, 10]. For Ukraine these figures are not too high, neither they are low, however, that means we are approaching the current level of development in world countries. Our state has a great potential to enter the lists of the leaders in the production of individual product or service groups, but it is still very "immature" and therefore, we are faced with some problems, especially in the economic field.

The country's economy development depends on development of enterprises in its territory, as they determine the GDP rate, economy structure and living standards of the population. We constantly observe some progress: something is being modernized, new technologies and new management techniques are being introduced, everything is being done to improve the comfort of living, and, consequently, it results in gradual development of business incubators, a new for Ukraine form of assistance provided to small business.

The main objectives of business incubator are to provide small businesses with comprehensive services: legal and consulting services, information support, training for small enterprises, search for investors, lease of equipped office spaces, etc. The incubator is a specialized organization (or a large company division), whose main objective is creation of a local business environment favourable for small venture enterprises. The scale of incubator activities can be various: from a small incubator to incubator centres for small business development.

According to R. I. Zavadiak and Ya. F. Kopusiak [11], creation of first business incubators in Ukraine was stimulated by international financial assistance. Thus, at the end of the 1990-ies the Agency for International Development (USAID) funded the implementation of the Program on Business Incubation Development in Ukraine (BID). In the framework of this program the following business incubators were established: Kharkiv Technologies technological business incubator, business incubator of the Kherson Chamber of Industry and Commerce, business incubator of the Joint Trade Union of the Chernobyl Nuclear Power Station, etc.

The first business incubator in Ukraine was Happy Farm. It is located in the village of Shchaslyve, the Kyiv oblast. Per year Happy Farm holds 2 full cycles: from selection of teams to launch. Every start-up is supervised by experienced venture businessmen of the Happy Farm Supervisory Board.

The creation of business incubators in the agri-food sphere will help to resolve problems such as:
− research of niches in the agri-food sector to generate innovative products and services.
− ensuring interaction at different stages in the chain of production of agricultural products and food products.
− development of models for innovative management of subjects agricultural production and food production, processing, logistics and marketing.
− strengthening collaboration among academia and businesses to create innovation and share results.
− ensuring economic and environmental sustainability in agriculture and the food industry.

The development of entrepreneurship in agriculture and the food sector is important for the economies of different countries.

In 2016, the European Commission services (including Directorate General (DG) REGIO, DG JRC, DG AGRI and DG RTD) established the Thematic Smart specialisation Platform on Agri-food (S3P Agri-food) with the goal of accelerating the development

of joint investment projects at the EU level in the smart specialisation areas linked to agriculture and food. With this initiative, the European Commission encourages the regions and member states to implement their Research and Innovation Strategies for Smart Specialisation (RIS3) strategies more efficiently. Regional stakeholders benefit from the new cooperation opportunities with partners from other regions [12].

Ukraine has great potential for development of the agrarian sector of national economy. The agricultural sector forms almost 19% of the Gross value added.

The business incubators ensure the development of entrepreneurship in the food industry, promote the creation of new jobs and the effective use of innovative capacities and resources.

Business incubator areas of activity are provided for by a business plan. It defines the amount and time of firms' participation in the incubator, the amount of financial and material resources needed for its work, principles and conditions of cooperation of the business incubator with launched start-ups.

There are many types of business incubators: non-profit, commercial, University research parks or science parks.

Non-profit business incubators are provided with funds by local authorities.

Commercial business incubators work on a commercial basis and demand partial refund of charges from their clients.

University research parks are branches of higher educational institutions established with support of enterprises, commercial banks, investment funds, which provide funding for development of a new generation of students. Such branches use educational services of professors, research and laboratory facilities of universities, their premises, technological equipment, library, etc.

Thus, in order to support innovative activities, the Kyiv Council initiated creation of an innovative business incubator, which includes the business incubator as a supervising body, coordination bodies to ensure cooperation with local authorities; independent centres to provide services to incubated firms and client firms. Innovative incubators work at Lviv, Dnipro and Kyiv technical universities. In 1996, in Ivano-Frankivsk the Ukrainian-Canadian Business Centre performing basic functions of a business incubator was created.

Let us consider the largest business incubators in Ukraine. GrowthUP was one of the first business incubators in Ukraine established in 2008 with the consulting company BayView Innovations. The cost of admission to a training session is 1200 UAH for each project. GrowthUP receives 5% of the project authorized capital. The company intends to invest $ 25000-50000 in best launched start-ups.

Polyteco Youth Business Incubator was established on the basis of the Kyiv Polytechnic Institute (KPI). It closely cooperates with Ukraine's first science park Kyivska Polytechnika, whose activities are aimed at commercialization of the Institute and start-ups' developments. Kyivska Polytechnika receives from 5% to 20% of the start-up authorized capital. The incubator does not provide start-ups with start-up capital.

EastLabs was founded in January 2012. The project is financed by Viktor Pinchuk, and receives 15% of each start-up authorized capital. The incubator offers a training program, three jobs for each start-up and investment in the amount of 20 thousand US dollars for development of the business.

The first incubator of ideas from the USA in our country, Founder Institute, with headquarters located in the Silicon Valley offers the curriculum, which actually prepares start-ups for incubators of later stages, such as EastLabs or Happy Farm. Founder Institute acquires 3.5% of the start-up shares at a market price. The first investment in the company ranges from $ 50 000.

Faster Capital from the UAE offers start-ups funding in exchange for a share in the project. As the incubator, Faster Capital provides assistance in assessing ideas, preparing feasibility study, market analysis, product development, sales and marketing as well as financial services until a start-up reaches the break-even point [13].

In 2016 the first Ukrainian Business InCUBubator for immature entrepreneurs initiated by Pryvatbank started its work. For months, the incubator collected more than 880 applications from participants who aim to start their own business or to expand the existing one. The projects were submitted by representatives of all oblasts (Figure 1) [14].
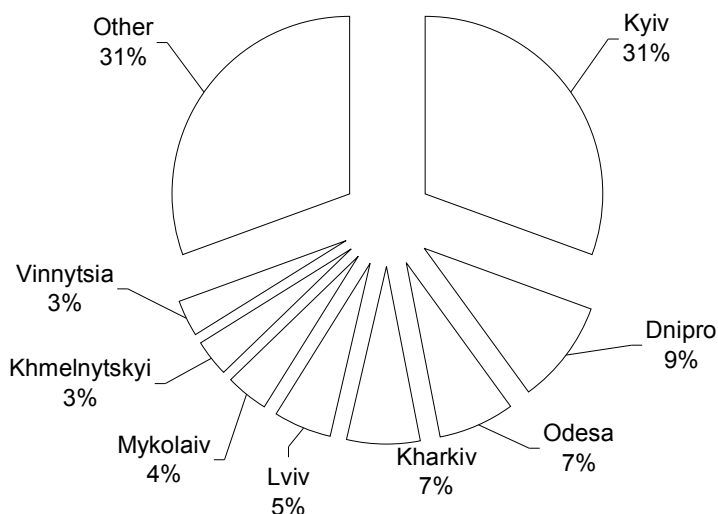

Figure 1. Number of projects registered with the Business Incubator by regions

According to Figure 1 the greatest number of start-up projects was submitted by Kyiv, Dnipro, Odesa and Kharkiv regions. The sectors, where entrepreneurs are to start their projects, are presented in Fig. 2.

Entrepreneurs associate most prospects for business with service sector. 17% of entrepreneurs would like to start their business in this sector. The second place is taken by trade prospects. 13% of applicants want to develop their business in this sector. Production, IT development and catering are third on the list of the most promising areas for Ukrainian small businesses [14].

The business incubator under consideration has generated a lot of interest from aspiring entrepreneurs. When choosing the finalists, the incubator management will consider possibilities of creating new jobs and implementing the project within six months.

Twenty finalists will have an opportunity to learn business and sales within a special Prometheus Program as well as to get support of experts and business coaches in organizing and planning their business, sales, accounting and legal issues.
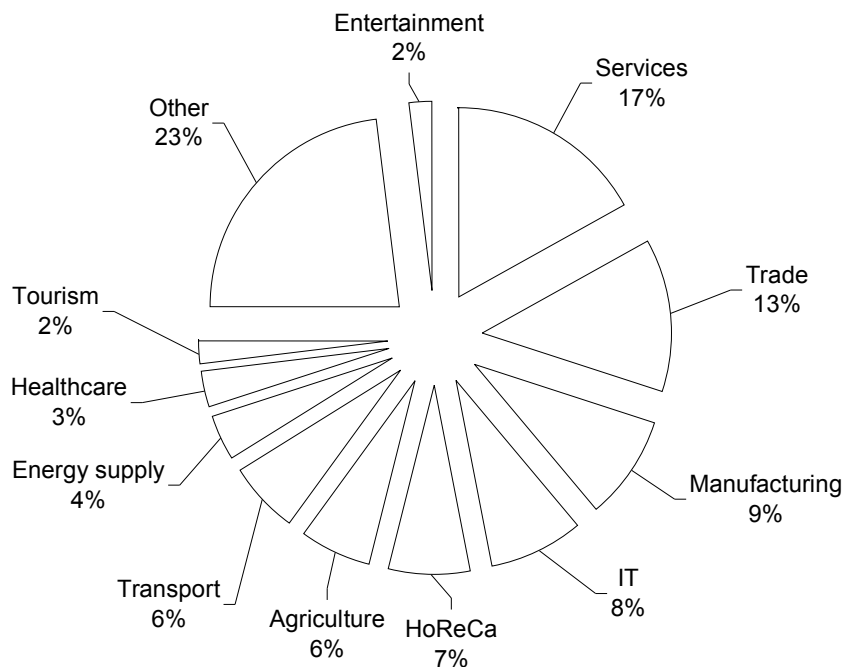
Figure 2. Sectors for project implementation registered with the Business Incubator (%)

Successful participants of the business incubator will receive financial and organizational support from the PrivatBank.

The functions of incubators are constantly extended and modified; however, there are the major ones, which should be given as follows:

1. Business expertise for start-ups. Generally, in 90% of cases these services are provided to aspiring entrepreneurs to protect them against errors, which occur due to lack of confidence. It is therefore advisable that training and retraining of staff should be applied.
2. Financing customers. The more sources of funding are available, the better and more thorough consulting services are. Incubator experts' recommendations assist in obtaining loans or financing at early stages of company development.
3. Promoting economic development by increasing employment of population, business growth and formation of the infrastructure enterprises network. This explains the interest of regional administrations in development of incubators.

Business incubators take an important place in the innovation infrastructure. They are a tool of economic, social, structural and innovation policies.

The main advantage of business incubator for aspiring entrepreneurs, who experience financial difficulties, is that incubators provide them with protection and assistance on concessional terms, at below-market prices.

The important advantages of business incubator are a creative atmosphere, the image of a serious company, a list of required services, flexibility of management in the incubator.

To facilitate the development of business incubators in Ukraine, the Ukrainian Association of Business Incubators and Innovation Centres was created. It contributes to implementation of national, regional, local and international programs aimed at development of entrepreneurship by establishing and supporting business incubators, technology parks, business support centres and other innovative structures as well as persons engaged in provision of services in the field of entrepreneurship [10].

Promoting entrepreneurship within ukrainian agri-food sector can be a strategy towards country economic development.

In Ukraine the prospects of agri-food business incubators are determined by the following factors:

− Increasing demand of business structures for new training technologies, consulting and information support;
− Increasing demand of potential investors that not only should firms prove their steady material and financial position but also show an ability to dispose of investments provided to them;
− Credit policy of banks forbidding companies to take up loans to purchase fixed assets, especially buildings, office and other equipment which results in an increase of their costs and reduction of current assets;
− Pre-final stage of market formation which increases competition and makes business spend more time on sales of goods (services), diverting their attention from issues of functional management and strategic marketing;
− Time needed for start-ups to develop and adapt to the market under terms of the current fiscal policy.

As far as world experience of business incubators use is concerned, within the 1990-ies of the XX century approximately 80% of new jobs were created by small business in Europe and the United States owing to activities of business incubators. The need for business incubation is also stipulated by the socio-economic nature of small business: 14-30% of newly established small enterprises only survive during the first three years of work, while in a business incubator this number increases significantly and accounts for 85-86%. In order to encourage entrepreneurship, it is significant that business incubators ensure the provision of services at prices below the market level.

First business incubators appeared in the 1950-ies of the XX century in the United Kingdom [8]. However, the number of business incubators is the highest in the United States. As international experience shows, the most successful are the American, European and Asian models of business incubators. All the three models of business incubators are different. Most importantly, we should remember that incubator is a premise for implementation and generation of ideas of scientists, post-graduate students, University professors, engineers and innovators. Innovative "thoughts" and "ideas" are produced in symbiosis, which enables science to realize them within the industry in a short time and with immediate outcomes.

The American model is primary. The first modern business incubator, the Batavia Industrial Centre, was established in the USA in 1959 with the aim of increasing employment. One of the most successful business incubators in the United States includes [6]: business incubator to support FFVC high-tech companies in North Carolina, Affinity Lab in Washington to provide assistance to aspiring entrepreneurs, Alpha Lab in Pennsylvania to implement software and Internet projects.

In addition, the American model is characterized by a successful scheme of turning office centres of incubated enterprises into technology parks, in some cases – with the prospect of turning them into technology towns.

What is the difference between the American model of business incubators creation and the European one? The European model mostly aims to organize large corporations. A lot of time is spent on research and development, thus showing that even a small company could make a breakthrough and surpass large enterprises, despite their large scale and great amount of funds allocated for research and development.

Thus, the Swedish experience demonstrates that business incubator is an effective tool for development of business environment of industrial enterprises, premise for generation and implementation of innovative ideas on the basis of large companies [15].

Another feature of the Finnish and Swedish models of business incubation is government encouragement of commercialization of innovative scientific research of University and research laboratory scholars with reservation of their intellectual property rights.

By their internal content European incubators are more specialized, they do not scatter forces and follow a high-tech direction in their work, support the unemployed. The American style is more "aggressive", egocentric and focused on direct promotion of the company.

In Italy business incubators serve as job centres, environment for innovation and support for small business, sources of innovative technological developments and centres for surplus labour force engagement for large corporations. It is also worth noting that in Italy small innovative enterprises "grown" in business incubators provide activities of large industrial corporations in terms of innovation [3].

The largest Italian business incubator is BIC Lazio, whose major directions are as follows: development of the Liguria region, support for start-ups and extension of business projects, project management, and support for technology transfer and entrepreneurship with assistance of scientists from the University of Genoa [16].

The characteristic features of the German model of creation and functioning of business incubators is, firstly, a high quality of training entrepreneurs (only 5% of enterprises "grown" in business incubators go bankrupt); secondly, reorientation of business incubators from innovations to support for small and medium-sized businesses. The second feature is related to the fact that in Germany business incubators are primarily considered as a tool for fostering regional social and economic development.

The first German business incubator was created in 1983 on the basis of the Technical University in Berlin.

Unlike Asian business incubators, the American technology sector sells services: contact programming, business outsourcing and contact production. This is the model adhered to by India, China and other East Asian countries as well as Brazil and Mexico.

The main features of Chinese business incubators are as follows:
− their scale – business incubators are operators for a large number of businesses;
− extensive introduction of achievements of the American model of business incubation [15].

Venture companies are active participants of innovative activity. The activities of such enterprises are focused on research, innovation and financing of innovation projects, though, they carry high risks.

European venture capital is very different from the US by social and cultural characteristics: if the American mentality sees defeat as a challenge, which encourages you to move forward, the European businessman, who failed at least with one project, will be forever considered unprofessional. Accordingly, the development of innovative activity in Europe is different. Certainly, there is Cambridge University, which, like Stanford, gathered around dozens of high-tech companies, but this is due to the fact that it is a

relatively liberal Britain. The governments of France and Germany affect the economy and the market greatly, consequently, innovations in these countries are in the responsibilities of the state machinery, in other words, universities united in a single network, receive funds for innovative projects, acquiring similarity to American business incubators [6].

In the 1990-ies Internet incubators appeared. The number of business incubators is increasing due to active government support and high yield of incubators. Over the last ten years their number has grown from a few dozens up to 575, united within the National Business Incubation Association (NBIA). According to the NBIA, 87% of the enterprises, which have grown from business incubators, continue to work on the market. Without incubators, the share of operating companies can reduce to 50% [15].

The training and education programmes can enhance critical perceptions such as desirability, feasibility and conviction among farmers and inhabitants of cities to become entrepreneur in agri-food sector [17] .

Conclusions

The world and domestic experience of creation and activity of business incubators has shown that in the developed world they have become an indispensable characteristic of the market infrastructure, effective implementation of promising innovative business ideas and, consequently, a powerful engine of socio-economic development. Business incubators are an effective tool for creating small businesses and jobs, promoting cooperation of industrial enterprises and educational institutions. Moreover, business incubators encourage commercialization of new technologies and improve the image of the area of their functioning.

However, in Ukraine business incubation has not developed extensively and efficiently primarily due to ineffective government policies of encouraging business incubation development and scarcity of financial resources, lack of understanding of the role of business incubators as sources of business environment creation by many market actors.

One may have an impression that in Ukraine there is no real need for services of business incubators. In fact, technology parks, business incubators, innovation centres and similar organizations only deal with issues of infrastructure operation and "arrangement" of various benefits provision. Business incubators do not provide the service they are created for in the whole world, – assistance in creation and development of competitive companies, market leaders. The format of business incubators existence in Ukraine contradicts completely the successful world practice, where the focus is on provision of consulting, administrative and other management services for start-up company development.

For the process of business incubation to be successful, we suggest the following measures be taken:
− establishing a system of state policy to support organization and operation of business incubators;
− developing end-to-end projects for the network of business incubators in the regions of Ukraine;
− reducing the level of corruption;
− reforming the bureaucracy;
− joining organizational and economic effort for execution of complicated orders;
− stabilizing the political and economic environment as a core element of business development.

Business incubation creates a firm foundation for development of an integrated system of innovative entrepreneurship and allows building a model of the training process methodology of doing business successfully.

Everything is subjected to the principle of improvement, i.e., everything around us is constantly being improved and we hope that eventually our country's experience will be in demand, as sharing experience is an appropriate and productive way to improve potential.

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Towards Healthier Life: Changes in growing of health-friendly food crops and products in Lithuania before accession to EU and after

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Abstract

Introduction. The purpose of the article - based on analysis of statistical data to evaluate how the ratio of health friendly food crop changed before Lithuania entered EU in 2004 and after accession to the EU (2005–2017).

Materials and methods. The statistical data from Lithuanian National Statistical Office and Lithuanian Customs Office has been used. Data lines vary from 1995–2017, to 2004-2017. The content, comparative, statistical analysis, systematization, and scientific interpretation scientific methods have been employed.

Results and discussion. The analysis of statistical data shows the clear drift from traditional and healthier crops and products to ones that are easier to grow and are in demand in the World market. It was caused by the implementation of EU Common Agricultural Policy (CAP) financial mechanisms into Lithuanian agrarian policy. The direct payments for owning land, but not for growing particular crops, create a deficit in various types of food products, considered health inducing. Such a form of financial support of farmers made new EU Member States even more dependable on food import, than before accession into EU.

Because of the current form of agricultural support mechanism, it becomes a hard task to preserve traditional crop varieties in smaller new EU Member States, as it do not have a demand on a World market, so the growing of it seems unprofitable for the farmers at present moment. Unfortunately, if it will change in the future, the farmers will not have the capacity to renew the cultivation of these crops and it will be lost.

The EU CAP also serves as a mechanism for tackling unemployment in rural areas of EU Member States, promoting the agricultural business. Although, the current form of support mechanism, there a financial support is directly linked with the land farmer/ agricultural entity owns, creates a situation, there bigger and stronger farmers get more money, than the ones, that are weaker and own smaller land area. It increases the disparity between rich and poor and can lead to disappearance of smaller farmers.

Conclusions. EU CAP fully achieves it' primary goal – to provide EU Member States citizens with safe and affordable food, but it does not fully fulfill (at least in new Member States) the secondary task – to stimulate the consumption of health inducing diet in EU.

Introduction

Thus, the EU food policy takes care of consumer protection and states that it is important not only to seek safe food consumption, but also to promote healthy food consumption. As EU is trying to be self-sufficient in food production, EU food policy (EU, 2007) and EU Common Agricultural Policy (CAP) become interconnected and partly follow the same goals, one of them – enhancing wellness of EU Member States citizens through providing access to cheap, safe and healthy food.

Moreover, in the context of the new EU financial period, it is particularly relevant to review the EU's common policies and to evaluate programs funded from the general EU budget. As for the EU CAP is allocated up to 38% from the general budget of the EU [1], plus some programs are also partly supported by the Member States themselves, so it is important both on a state and EU level to determine, how effectively the objectives of CAP are being implemented.

Taking into account the above mentioned topicality, the aim of this research paper is formulated as follows: based on analysis of statistical data to evaluate how the ratio of health friendly food crop changed before Lithuania entered EU (till 2004) and after accession to the EU (2005 – 2017). I order to achieve the aim of an article, three health-friendly crops and food products (fruits and vegetables, beef, fish) have been selected, what are commonly referred in a scientific publication, aimed at revealing food influence and its effects on health. There are also three crop cultures and products identified as unfavorable or less favorable to health, it is – pork, wheat, and sugar.

Article consists of three parts. The first part introduces the essence of the EU Common Agricultural Policy and a mechanism of financial support to EU farmers. Second part presents products, that. According scientific literature and EU Food Policy are considered health inducing and, in contrary, suggested to be avoided in order to keep healthy diet. The main results are presented in the third part of an article, there the analysis of a changing crop cultures and animal food products changes in Lithuania after the accession of EU is presented. All the findings and suggestions of an article are presented in the conclusions.

Materials and methods

With the regard to implement the aim of a article, we employed the content, comparative, statistical analysis, systematization, and scientific interpretation scientific methods. Systematization method helped us to prepare a theoretical background for our research. The content analysis initially dealt with 'the objective, systematic and quantitative description of the manifest content of communication' (Berelson, 1952) but, nowadays this concept has been expanded and also accommodates interpretations of latent content. We employed it during the official EU documents and scientific papers, aimed at revealing the EU Policy mismatches, analysis. Comparative analysis is a main tool for the researches in social sciences (Mahoney, Rueschmeyer, 2003) and can hardly be avoided in seeking the explanations of complex, dynamic, interconnected processes that not always can be described in simple causal-effect relations. This method was used combined with statistical data analysis in seeking to detect the trends of ongoing processes in Lithuanian agricultural sector and its causes. The logic of selecting products for the research is presented in the previous part of the article. The data lines vary because of availability of reliable data is different in different data bases of Lithuanian National Statistical Office and Lithuanian Customs Office. Scientific interpretation allowed us to look deeper into the causes and preconditions of current developments in Lithuanian agricultural sector, as well as to draw the overall conclusions.

Results and discussion

Essence of CAP

European integration, that started in 1951 by creating European steel and coal community, which was based on supranational authorities on independent states resources laid a foundation not only to peace in Europe (the main goal of European integration, which was obviously achieved, as Europe now faces more than 70 years of continuous peace – longest peaceful period in its his history), but also to one of the highest living standards in the world. This was achieved by combining a supranational authority's ability to coordinate and manage the interests of all involved parties on a strategic level with local governments' incentives and knowledge of local traditions, mentality and specifics of challenges faced by each citizen. European Coal and Steel Community evolved into European Economic Community in 1957, which main goal was expanded, compared to ECSC goal and included also the continuing growth of wellness of its respected member states citizens by creating common market, ensuring free flow of goods, services, capital and labor within its borders, fighting social exclusion, ensuring technology and innovations based economy growth and etc. One of a first challenges EEC faced – repeating food shortages in post war Europe [2]. Common challenges created prerequisites for applying a supranational authority's coordination into practice. Such a decision was implemented because of the following reasons: if EEC members would start solving such an important issue independently it would inevitably lead to protectionism, what would contradict not only to free market goal, but also to prerequisite of peace – a free access to all resources in all EU member states. Taking into account those possible negative effects and the importance of challenge – EEC food security, the first truly supranational authority in the World was created and implemented.

The Common Agricultural Policy, introduced in 1962, was aimed at providing Europeans with sufficient amount of food by supporting farm modernization and encouraging rural citizens of European Economic Community to stay in their villages and be engaged in agricultural activities instead of going into overcrowded cities and raise unemployment there. Even though taking into effect in 1966 as a compromise after one of the first major disagreements in EEC history (Empty Chair Crisis) it allocated 78% of the whole EEC budget [3]. Such a generous financial support mechanism for agricultural products producers (farmers) is based on an assumption, that food is a commodity, which does not fall under the typical economical rules. It is assumed, that lowering prices on food products would only barely increase its consumption, but a food shortage would boom the prices. So, to get bigger profits farmers may not produce so much food and get the same or even bigger amounts of money by creating food shortages and leaving a threat of malnutrition to poorer citizens of EEC, as even the small changes in food supply, could have substantial influence on prices. The solution was to financially support farmers in order to originate EEC with food production capabilities if for some reasons world market would become inaccessible. The chosen mechanism was very simple: the more you produce – more money you get. Such a financial support scheme created a food surplus already in 1970s. After main goal – providing EEC members with cheap and abundant food was accomplished, CAP was modified in order to guarantee employment in rural areas provide and to provide safe and nutritious food. Safe and nutritious food is one of the preconditions to the wellness of EU member states citizens, which is one of the main objectives of the whole EU [4]. It can be noticed, that achieving these two goals simultaneously created new challenges. With the aim to guarantee employment in rural areas, direct payment system to

farmers (farming entities) was implemented. It focuses not on the production of agricultural products, but on a land owned (or leased) by the farmer and appears as payments per hectares of crop land or numbers of livestock. Direct payment system consists of two parts. One part, of direct payments is being paid regardless crop type and do not vary – a fixed amount of money per hectare. It can be presumed, what his part is being oriented at keeping EU citizens, engaged in agriculture at their farms, paying them and supporting rural employment in such a way. Plus, a constant and guaranteed payment provides farmers with predictable and stable cash flows, as farming is a risky business because of dependency on weather conditions. Second part is being paid according the crop variety, which has been planted. There is a room for maneuver for EU Member States governments to facilitate the cultivation of crops, what it considers to be more valuable to its citizens' health, o should be saved from disappearance [5]. But the tendencies observed show quite a different situation.

The selected type of support mechanism created prerequisites for EU inability to produce enough various food products to its citizens in nearest future. Farmers started to grow not the most beneficial crops to human health or to produce the most nutrient and healthy food products for inner EU market, but started growing crops, that require the least efforts to produce and can be easily sold in worldwide markets. The growing demand for biofuels encouraged some Lithuanian farmers to switch to rape growing thus reducing food crop area. CAP not only changed the traditional agricultural product portfolio of some EU member states, but even created a risk of disappearance of some traditional crops from the map.

It can't be said, what the governments of an EU Member States (especially newly accepted members) do not notice such a shift from more healthy crops to more desirable in international markets. It may seem, what biggest farmers or agricultural entities are solving one of the biggest problems of Central and Eastern Europe's countries – chronical budget deficit (in past 10 years Latvia, Poland, Hungary, Romania had budget deficit all 10 consequently years, Lithuania – 8 and etc. [6]. Growing crops, that are marketable worldwide creates foreign currency and cash flow incomes to the country, helps to fill in the budget. But it comes at the expense of changing portfolio structure of crops cultivated, what, indirectly influences the eating habits of EU member states citizens. Here we observe the dichotomy in objectives raised by CAP, and objectives achieved under its support mechanisms. In order to analyze, how CAP financial support mechanisms helped to achieve one of the main CAP and health promotion [7] objectives – to increase production and consumption of more healthy food - we made an analysis of statistical data in one of EU new comer Lithuania.

European health inducing policy

One of the main aims of EU is the wellness of citizens of all Member States. It consists not only of economic prosperity, which is unimaginable without healthy population, able of working creating and collaborating, but also of healthy aging and enjoying the life at any age. A lot of diseases and factors, causing disability, partial disability or constraints, interfering the satisfaction with the life lived relate to diet. It is the reasons, thy European Commission driven by the goal of enhancing the wellness of citizens of its Member States allocated 80 billion EUR of its budget to Horizon 2020 programs, one of them is promoting the "research on healthy foods and diets focuses on the nutritional needs and the impact of food on physiological functions and physical and mental performance. The activities aim at studying the links between diet, ageing, chronic disease and disorders and dietary patterns

and aim to identify dietary solutions and innovations leading to improvements in health and well-being" [8]. Such a focus on healthy food in EU clearly shows the actuality of the researches, aimed on revealing, how the EU promotes the healthy diet of its citizens. To contribute to this aim, we selected the following products presented in the article below and observed, how the EU CAP as one of the instruments to achieve main EU goals contributes to inducing healthy diet.

Products considered as having potential negative health effect

Malik et al. [9] research shows correlation between consuming animal fat (especially pork), added sugars and refined grains with increased endocrinal illnesses and obesity. Obesity leads to cardiovascular diseases, diabetes [10], more complicated pregnancy [11], lowers functional capacity of persons [12]. Wheat is considered less health-friendly, because it is usually consumed highly processed in final food products, what leads to high levels of gluten in it. Koning [13] emphasizes the toxicity of wheat gluten. Aronsson et al. [14] states, that gluten rich products, especially manufactured from highly processed wheat has long lasting negative effects on humans' health and twice fold increase the chances of celiac disease to children. Consuming gluten rich products lead to increased risk of allergic diseases [15]. It is advisable to substitute processed wheat products in order to lower the allergy [16], intestinal cancer [17], autism [18] [19] prevalence in society.

Pork fat is considered unhealthy and consumption of products, containing pork fat is not recommended both by European Food Safety Authority and World Health Organization [20]. Consumption of pork creates negative cardiovascular effects: coronary heart disease, stroke and hypertension. Also processed pork has adversely effect on oncological diseases - consumption of it can lead to colorectal cancer [21], although it is worth mentioning, what the clear mechanism how processed pork meat induces colorectal cancer is still unknown [22]. Higher levels of cholesterol in blood, which is closely linked with the consumption on triglycerides and fatty acids found in pork meat may lower the quality of life even for persons, who still did not develop such an adverse effect like cancer or coronary disease [23]. Such people show signs of earlier fatigue, are less productive.

Malik and Hu [24] showed clear dependency between sugar consumption and increased risk of obesity, type 2 diabetes and cardiovascular diseases. Kearns et al. [25] also focus their research to coronary diseases and sugar intake, showing, that such a dependency has been observed for almost 50 years. American Heart Association [26] stresses sugar containing diet influence on children cardiovascular disease risk. Lowette et al. [27] showed, that a diet with high content of sugar may lead to adverse effects in human's cognitive function, impaired learning and memory. Similar results have been published by Hsu et al. [28].

Products recommended for a health inducing diet

The consumption of beef is preferential compared to pork and recommended in order to maintain healthy diet [29] [30]. The main focus on promoting beef meat lies not in its containment of high quality protein, iron, zinc, vitamin D, B3, B12, selenium and long-chain omega-3 fatty acids what have positive potential impact on human health, but also in its capability to substitute pork, considered not favorable in terms of healthy diet, in almost all traditional European dishes containing red meat. Also beef meat is considered much healthier than pork [31] as it is important dietary source of CLA, especially cis-9, trans-11 isomer, identified as an important health promoter factor including antitumor and ant

carcinogenic activities [32], beef also contains specific trans-fatty acids, that have potential protective properties against the development of coronary heart diseases [33].

Lampe [34] argues, that fruits and vegetables are the consistent parts of diet, which should be consumed most. The phenolics, found in fruits and berries show a wide range of antioxidant activities [35] and are thought to exert protective effects against major diseases such as cancer and cardiovascular diseases. Other researches [36] praise anthocyanins, found in berries and fruits, and its positive health effects. There are abundant of scientific literature [37], [38], [39] on positive effects of vitamins and minerals found in fruits and berries. Rodriguez-Casado [40] show fruits antimicrobial features.

Lithuanian Ministry of Health [41] strongly recommends increasing fish and fish products proportion in Lithuanians diet. Krumhout & de Goede [42] researching ω-3 fatty acids, found in fish concluded that there is strong evidence for a protective effect of ω-3 FA on fatal CHD and for some markers of atherosclerosis and thrombosis. Ω-3 fatty acids also reduced markers of ventricular fibrillation. Mozaffarian & Wu [43] research also confirms positive cardiovascular effects of diary consumption of fish fatty acids. Imhoff-Kunsch et al. [44] research showed what consumption of n-3 Long-chain Polyunsaturated Fatty Acid reduced risk of preterm delivery by 26%. Raji et al. [45] study showed positive effect of fish consumption to age-related brain gray matter loss. Butler et al. [46] research shows a positive link between fish consumption and neuropsychological performance. Gil & Gil [47] found, that fish consumption is associated with lower markers of inflammatory processes.

Changes in growing of health-friendly food crops and products in Lithuania between 1995 and 2017

Pork. Production of pork meat, that traditionally was on an equal terms (or was produced a bit less compared to beef in Lithuania) in production in Lithuania has increased significantly in the first years after Lithuanian entrance to EU. The increase is about 20 percent. The following growth was limited be swine fever, that occurred in 2009 and once again in 2016. After this event, following EU regulation, as a preventive countermeasure to avoid future outbreaks of this disease the liquidation of all pigs grown in small and medium farms was implemented. These actions eliminated a competition that was starting to occur in Lithuanian pork production sector, reserving this market only to bigger producers and other EU member states farmers. The growth in pork meat production correlates with the decrease in beef production, which was traditional in Lithuanian cuisine, has long-lasting traditions and is not, only a good substitution to pork in almost all meals, but is also considered much healthy than pork.

Beef. The production of beef meat has dropped by 22 percent on average if comparing periods from 1995 to 2004 and from 2005 and 2017. The biggest drop in agricultural production of beef was in the first years Lithuania entered EU, from 2005 to 2013. In this financial perspective the production of beef in Lithuania decreased by 30 percent. During the financial perspective, which begun in 2014 (should last until 2020) the production of beef stabilized at around 73 percent of pre entrance to EU level.

Production of fresh pork meat in Lithuania

Year	Quantity, thousands of tons	Year	Quantity, thousands of tons
1995	115,5	2004	136,3
1996	109,9	2005	148,4
1997	107,7	2006	151,3
1998	116,6	2007	141,2
1999	112,7	2008	104,8
2000	102,8	2009	84,4
2001	88	2010	103,9
2002	116,3	2011	108,9
2003	125,5	2012	111,8
		2013	122,9
		2014	118,9
		2015	121
		2016	105,8
		2017	100,3

Production of fresh beef meat in Lithuania

Year	Quantity, thousands of tons	Year	Quantity, thousands of tons
1995	146,2	2004	97,6
1996	139,1	2005	110,1
1997	150	2006	93,4
1998	141,1	2007	112,4
1999	127,5	2008	90,6
2000	125,9	2009	88
2001	79,9	2010	89,6
2002	74,8	2011	86,4
2003	86,3	2012	84,8
		2013	77,1
		2014	82,8
		2015	93,1
		2016	88,9
		2017	85,3

Grain: Wheat and rye. The most drastic changes are being observed in grain growing in Lithuania. Historically rye was more prevalent in Lithuania, than wheat [48]. It has become a part of Lithuanian traditions, as traditional rye bread or rye vodka, as well, as other dishes ("kleckai" (kind of rye dough dumplings) and etc.) are included into the list of Lithuanian national heritage. Unfortunately, the trends in agricultural production in Lithuania put these products under risk of disappearance, as the growing of rye has decreased dramatically. The trend, of shifting from rye to wheat in Lithuania was observed even before entrance into EU (Table no. 3), but after accession then CAP came into effect, the substitution of rye with wheat in the portfolio of Lithuanian farmers became dangerous from the traditions saving side. Lithuania has already lost one of very important traditional crops – flax has disappeared from list of crops grown by Lithuanian farmers, although flax has been an important crop in Lithuania [49] for centuries.

Table 3

Harvest of wheat and rye in Lithuania in thousands of tons

Year	Wheat	Rye	Rye/wheat ratio	Year	Wheat	Rye	Rye/wheat ratio
1995	637,3	239,3	266,3%	2004	1430,2	140,6	1017,2%
1996	936,2	286,8	326,4%	2005	1379,4	108,3	1273,7%
1997	1127,4	348,2	323,8%	2006	809,8	90	899,8%
1998	1031	348,7	295,7%	2007	1390,7	165,2	841,8%
1999	870,9	260,9	333,8%	2008	1722,5	204,9	840,7%
2000	1237,6	311,4	397,4%	2009	2100,2	207,9	1010,2%
2001	1076,3	231,1	465,7%	2010	1710,4	87	1966,0%
2002	1217,6	170,2	715,4%	2011	1869,3	85	2199,2%
2003	1204,1	147,1	818,6%	2012	2998,9	156,6	1915,0%
				2013	2871,3	96,5	2975,4%
				2014	3230,6	85,3	3787,3%
				2015	4380,3	107,8	4063,4%
				2016	3844,5	77,5	4960,6%
				2017	3917,4	63,1	6208,2%

The shrinking part of rye in crop structure in Lithuania also has a negative health effect. Rye bread, compared to wheat bread, has some positive effects. One of them – lowers the level of cholesterol in blood [50]. The cholesterol is seen as one of the prerequisites for cardiovascular diseases, that are responsible for more than a half of deaths in Lithuania [51]. It is important to mention, that both rye and wheat contain gluten, but traditionally rye was used in Lithuania in a much less refined form and all the traditional Lithuanian dishes are being prepared from much less refined rye than nowadays consumed wheat.

Such a huge growth in wheat production, what has overcome the needs of Lithuania by 2,5 mln. tons has a quite simple explanation. Wheat is a commodity, traded in a world market, has a demand Worldwide as owing to globalization processes Western – style food is getting popular even in regions, previously dominated by Asian or African cuisine [52] [53]. Such a situation is quite comfortable for EU decision makers, as helps to maintain positive trade balance of EU (wheat is much easily traded abroad than rye), helps to keep

low levels of unemployment in rural areas of EU members (especially new ones) at low costs, do not require to relocate big manufacturing facilities from older EU members to new ones in order to tackle unemployment. The promotion of production of low value-added products (agricultural production) in new EU member states do not create a competition to older EU members in terms of economic competitiveness, makes them dependent on older EU members, somehow diminishing the influence of new EU members on decision making process in Brussels.

Fruits and berries. Trends in fruits and berries (because Lithuanian National Statistical Office provides data only on apple, pear, black, red, white currant, cherry, plum, strawberry and raspberry production in Lithuania, only data of these fruits and berries is taken into consideration. It should be mentioned, that reliable and accurate statistical data on fruits and berries production in Lithuania appeared only after accession to EU. Because of that reason, data from 2005 has been analyzed. As 2005 and 2006 show similar results, it can be presumed, that in previous years harvests appeared to be on a comparable levels) show the same negative trend. According Lithuanian National Center for Health Encouraging and Disease Prevention [54] fruits and berries are among products, whose consumption should be promoted on a country scale, as it has positive health benefits.

Table 4

Harvest of fruits and berries in Lithuania in thousands of tons

Year	Fruits and berries, thousands of tons
2005	224,4
2006	231,5
2007	100,7
2008	171,6
2009	133,5
2010	84,4
2011	116
2012	164,2
2013	143,7
2014	137,4
2015	168,3
2016	151,6
2017	162,9

Although statistical data shows a high decrease in Lithuanian production of traditional local fruits and berries (see Table No. 4). The production levels of these agricultural products after entrance to EU is only at the level of 2/3 of previous production and do not show the signs of recovery as a big part of apple orchard has been abandoned or destroyed in order to use the land for wheat and rape growing and it takes form 5 to 7 years, till newly planted orchards become productive, even if the initiatives in promoting local fruit production would occur. The results shown in a table are not so disappointing because of growing harvests of black currant, whose export is booming [55]. Such an artificially created deficit in fruit and berries production was covered by fruit import. Main Lithuanian fruits and berries import partners after accessing EU became Spain and Italy.

Table 5

Import of fruits and berries to Lithuania in millions of Euro

Year	Import of fruits and berries, mln. EUR	Year	Import of fruits and berries, mln. EUR
1999	61,6	2004	89,8
2000	63,4	2005	109,2
2001	63,2	2006	191,2
2002	65,4	2007	244,6
2003	75,2	2008	352,1
		2009	256,8
		2010	350,2
		2011	415,5
		2012	505,3
		2013	542,2
		2014	508,8
		2015	564,7
		2016	365,4
		2017	422,1

It corresponds to some alternative economic ideas [56] that newly accepted EU members become an open market for products from older member states.

Sugar beets. Even though sugar has been considered very harmful to humans health, and products, containing high to moderate amounts of sugar (sweets, chocolates, cakes, pies and etc.) are banned in Lithuanian schools and kindergarten, its production do not decrease after Lithuanian access to EU. Sugar beets production drop in 2008 was influenced by bankruptcy of one of the biggest Lithuanian sugar producers, which could not to withstand competition from other EU sugar producers, but not by common EU policy. Stable sugar beets production is maintained through quota system.

Fish. The results of fish catches are affected by quota system implemented in a whole EU and based on pre-Entrance levels of catches of each member state. It is not very thorough, as before entering the EU, some of newly accepted member states had an outdated fishing fleet, some disorder in an organization of fishing activities. Such a situation resulted in lower catches of fish in open seas for particular period. It was reflected in quotas that are lower than a potential of some new member states to enhance their fishing capabilities. Because of that, new member states are locked in lower fish catches having no legal rights to catch more fish and to deliver it to states consumers.

It is worth mentioning, what data on fish catches was provided by Eurostat and for the moment of preparation of an article an official data on Year 2017 was not available.

Summarizing the above mentioned, we can state, that the aim of supporting the healthier diet of an EU citizens is not fully achieved by current form of CAP, as it do not guarantee the basis for healthy diet – the production of health inducing agricultural products at least in new EU Member States. It shaped the portfolio of grown agricultural crops and in that way, what it even can raise an assumption, that Common EU agricultural policy serves

not as a trigger for more healthy, nutritious food production, which should contribute to a higher levels of EU member states citizens living quality, but as a tool to help to improve a EU foreign trade balance by growing easily sold in Worldwide markets low value added products in new EU Member States.

Table 6

Sugar beets production in Lithuania in thousands of tons

Year	Sugar beets production, thousands of tons	Year	Sugar beets production, thousands of tons
1995	692,4	2004	904,9
1996	795,5	2005	798,5
1997	1001,9	2006	717,1
1998	949,2	2007	799,9
1999	869,9	2008	339,1
2000	881,6	2009	682
2001	880,4	2010	706,7
2002	1052,4	2011	877,8
2003	977,4	2012	1003
		2013	967,1
		2014	1014,4
		2015	619,5
		2016	933,5
		2017	956,9

Table 7

Catches of fish in Lithuanian territory or by ships with Lithuanian flag in thousands of tons

Year	Catches, thousands of tons	Year	Catches, thousands of tons
2000	77.077	2004	160.222
2001	148.977	2005	138.166
2002	149.388	2006	153.113
2003	155.246	2007	149.733
		2008	157.104,9
		2009	150.094,6
		2010	138.244,7
		2011	137.085
		2012	70.195,04
		2013	74.802,81
		2014	148.842,76
		2015	72.432,13
		2016	105.738,74

Conclusions

CAP is an effective tool in providing citizens of EU Member States with safe and affordable food. It also acts as a social support mechanism, ensuring livability of rural areas by enhancing employment in farming industry through the financial support system. Although, it can be noticed, that CAP implementation mechanism does not pay too much attention to the crops and products grown by farmers' portfolio structure, and only focuses on effective use of land. Such an attitude leads to a situation, that farmers start to grow crops, not the most favorable for Member States citizens' health, but the most appreciated in the World market. This creates a big surplus of agricultural products of one or other variety (typically not the most health inducing) and creates a big deficit, or even threatens of disappearance of other varieties.

The big focus on agricultural sector, caused by the CAP financial mechanisms is also twofold. On the one hand, it helps to tackle unemployment in rural areas and to keep the living standards in rural areas comparable to at least the living standards of a middle class in urban areas, on the other hand, it locks the citizens of rural areas into low value-added industry, which is primarily dependent on EU financial mechanisms for survivability, so very sensitive to any changes in Brussels policy. Such a big and obvious risk may slow the investments into rural areas, as no one can guarantee, that EU attitude towards CAP and its financial mechanisms will not change and affect the return on investment.

It can be presumed, although it requires deeper researches to fully substantiate, that CAP acts as a tool to make newcomers of EU more compliant. It is hard to stand firm on contradictory position in EU negotiations, because employment, living standards and quality of life in rural areas in home countries of EU newcomers is dependent on current CAP financial mechanisms and even the small adjustment in policy may have significant consequences which countries cannot afford.

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The Editorial Board of scientific periodical
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Requirements to all texts:
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Size of the article – 10–15 pages in Microsoft Word 2003 and earlier versions with filename extension *.doc (!)
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Мова статей – англійська.

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В Ukrainian Food Journalвзято за основу загальноприйняте в світі спрощене оформлення списку літератури згідно стандарту Garvard. Всі елементи посилання розділяються **лише комами**.

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