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C O N T E N T

ACTIVITY WATER AND ANTIOXIDATIVE PROPERTIES OF WILD ONION FROM BOSNIA AND HERZEGOVINA

PRELIMINARY COMMUNICATION

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ABSTRACT
Wild onion is a vegetable plant recognizable as food and folk medicine. Its greater application in the food and pharmaceutical industry has found in last decades. In food industry wild onion is mainly used as a spice, while in the pharmaceutical industry it is a common ingredient in dietary supplements. Processing of a fresh wild onion is constantly increasing.
Active ingredients of wild onion are: raw vegetable fibers especially cellulose, allium compounds, chlorophyll, flavonoid, quercetin.
Wild onion is used in a fresh and processed condition. In most cases it is processed by drying at 40-50 °C for 5 to 10 hours, but also the active ingredients are extracted with various technological processes. Water content in the final product ranges from 6 - 10% and water activity from 0,17 to 0,21. Total phenolic content was expressed as mg of gallic acid in 100 g of raw material and it was estimated as an average value 561,013. The antioxidant capacity was expressed as EC50 value that represents amount of sample required for the reduction of 50% DPPH free radicals and it was estimated as an average value 6,032.
The content of the water was determined by drying. The water activity and color intensity were estimated by using instrumental methods. Antioxidant capacity was estimated by using of DPPH method and phenolic content by application of Folin-Ciocalteu calorimetry. Processing of fresh wild onion in the standardized dried semi-products may be significant due to the conservation of biological properties, and possibility of applications in the food and pharmaceutical industries.
Abbreviations: DPPH-2,2-diphenyl-1-picrylhydrazyl; EC50, concentration of antioxidant needed to reduce the original amount of radical by 50%.
Keywords: wild onion, active ingredients, food and pharmaceutical industry

1. INTRODUCTION

Wild onion eng. Ramsons, lat. *Allium ursinum* (ramsons, wild garlic, bear garlic) is a plant that belongs to the family *Liliaceae*. Wild onion is a widespread plant species in mixed beech and beech - fir forests of Bosnia and Herzegovina. It is a plant that grows 20 - 40 cm, and deeply in the soil it has a vertical and a thin bulb white or yellowish in color. The stem is erect, to some extent angular, no leaves on it and develops the sorts of cabbage family white star-shaped flowers. As for the smell and taste of wild onion, it can be determined by the strong smell of the garlic, and sometime it could be used to preserve the forest against negative impacts. Its taste is very similar to garlic, but it is stronger and more biting. Flowering time of plants is May and June. The most common parts of the plant are harvested, particularly its leaves and bulb (bulbus Allii ursini) that can be conserved [5,7].

Wild onion and other its edible parts are among plants, that are used for multiple purposes. They are a rich source of several phytonutrients, and recognized to have significant and wide biological activities. These biological activities are related to the thiosulfinates, volatile sulfur compounds which are responsible for the pungency of these vegetables.

Thiosulfinates are the best studied compounds arising from *Allium* species. Their finding was first reported by Wertheim (1844) and later by Semmler (1892) who identified the correct disulfide structure as the main component of distilled oil of garlic and onion[8,13].

The last decade has seen an enormous trend towards plant extracts such as essential oils, volatiles, and other molecules released by the secondary metabolism of plants. However, investigation on the biological activities of *Allium* compounds, as well as other phyto-compounds, and their mechanisms of action is still a major challenge for biochemistry, microbiology and food industries[5].

One of methods for determination of antioksidative properties of extracts is method of neutralization DPPH radicals. The principle of this method is that anti oksidans react with free DPPH radical (violet colored solution) and tranfrom it ito non – colored solution of DPPH-H (2,2-diphenyl-1-picrylhydrazyl). The level of nono-coloring indicates antioxidative potential of extract. Anti oxidans react with free radical and thus the reaction of chain oxidation has been broken donating hydrogen from group of polyphenols. In this way the final product has been obtained as very stabile and the reaction of lipide oxidation is stopped [15].

In 2000., gruop of authors, Aguirrezábal *et al*., compared the antioxidant effect of garlic with a mixture of nitrate, nitrite and ascorbic acid in dry sausage. They have found that garlic was as effective as the mixture of additives in inhibiting lipid oxidation. The antioxidant protection of diallyl sulfide (DAS), diallyl disulfide (DADS), S-ethyl cysteine (SEC), N–acetyl cysteine (NAC) in ground beef against lipid oxidation was studied by Yin and Cheng (2003). These authors found that the exogenous addition of these garlic-derived organosulfur compounds significantly delayed both oxymyoglobin and lipid oxidations[1,14].

As above mentioned and compared to garlic families, the wild onion is a plant which consists of a multitude of valuable biologically active substances[9,10].

The main chemical constituents contained in the wild onion are:

- alicilin, which has a strong antibiotic activity,
- essential oils with alisulfids, similar to garlic,
- biological catalysts,
- polysaccharides up to 15% (of the fruit sugar),
- water, as the main constituent, of 85-92%,
- potassium, about 270-310 mg/100 g,
- vitamin A (retinol), about 4000 mg/100 g,
- fatty acids, to a lesser extent,
- the essential amino acids, of which the most important is threonine, lysine, isoleucine,
- beta – carotene.

2. MATERIAL AND METHODS

In order to have good experimental data, which could be comparable to other reference materials, edible parts of wild onion, e.g. the dried leaves of wild onion were used in this paper. Materials for physical – chemical analyses for experimental work were taken from Eko Herb d.o.o. from Srebrenik.

The water content in the wild onion sample was determined by drying to constant weight at temperature of 150 °C, according to the methods determined by ISO 287: 2009.

Water activity in the sample of wild onions was measured using an Aqualab model CX-2, which works on chilled-mirror principle.

The most important criterion for evaluating the success of food dehydration process typically takes openness of the structure and the ability of rehydration[6]. Total phenols were determined by Folin-Ciocalteu colorimetry[2,3]. Antioxidant capacity was determined by DPPH method[4,11], using methanol as extract.

3. RESULTS

In the following table, the results of the water content and its' activity have been presented.

Table 1. Results of analyses of activity water, water content and index of rehydration of dry ramsons

No. of location from which samples were taken	aw	% water	Index rehydration
1	0,207	8,52	5,76
2	0,176	7,72	5,85
3	0,193	9,10	6,26

The water content in the wild onion, after constant drying on 105 °C, was different, and it varied from 7,72% to 9,10%. Sample no. 3. had the highest water content.
The lowest value of water activity was determined in the sample no. 2, of 0,176.
Based on obtained values for the water activity of all three samples of the wild-dried onions, calculated as a mean value, and the following values were obtained: an average value of water activity was 0.192. The index of rehydration was the for the sample no. 1., 5,76, but the highest for the sample no. 3, 6,26.

Table 2. The content of phenol components in the samples wild onion (mg gallic acid)

Number of locations from which are samples of wild onion taken	An average concentration of GAE per sample, mg of GAE per liter of extract	mg of GAE/100 g raw material
1 A	285,80	571,12
2 A	276,58	552,89
3 A	281,20	563,33

From the obtained values of total phenols for all three samples of dried wild onions, calculated the mean and expressed as milligrams of gallic acid per 100 grams of raw material and is 562,44. As it was shown in the table, no.2., the highest value of the phenol content in the samples of raw material was in the sample no. 1., 571,12, but the lowest in the sample no. 2. 552,89.
Compared to the results of extract, values of phenol content are lower and, and the highest value was for the sample no.2. 276,58, and highest for the sample no. 1. , 285,80.
The following diagram presents the results of the antioxidant capacity with concentration of extract of wild onion.

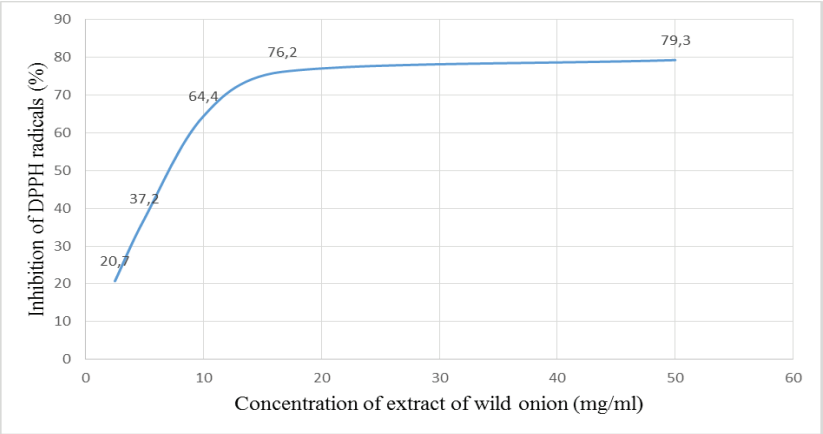

Diagram 1. Inhibition of DPPH radicals of extracts obtained from ramsons

The percentage of inhibition and EC_{50} are often used to express the quantification of antioxidative properties. As it has been presented on the diagram no. 1., the highest value of extract was for 50 mg 79,3%, while with concentration of 40 mg, inhibition value of activity of radicals was not too much lower, 76,2%. The value of the capacity of the antioxidant is expressed by the EC_{50} value which represents the volume of sample required for 50% reduction of DPPH free radicals.

a. Possible products of wild onions

Based on physical properties and the content of the some very important ingredients, there are several products which are made of wild onion, either as clean products or in combination with other raw materials and components.

The most common products on the basis of wild onions are based on the leaves of wild onions. Also, some are based on the bulbs of these medicinal plants, which are presented in the following table.

Table 3. Clean products and products with additives

Wild onions products	Products with accessories
Wild onions salads	Encapsulated ramsons
Pesto	Spreads
Pickled onion seeds	Soups
Tea	Stews
Herbal drops	Spirits
Noodles	Snacks
Spices	Crackers
	Pasta
	Butter

In table no. 3. Products as clean and with additions are given, and as it has been seen, the different products can be prepared based on ramsons, as fresh or dried.

4. CONCLUSION

As it is possible to make some conclusions, and based on the experimental work, and data available for wild onion, the following can be concluded:

- Wild garlic is good base for development different product which can be used either as food product or pharmaceutical product;
- As results of determination of ant oxidative capacity, it is possible to used wild garlic as a medicinal plant, which is rich in biologically

active ingredients and during drying process a certain amount is lost, but, of course, not to a significant extent;
- Extract of wild garlic has shown significant anti oxidative capacity compared to total phenol content, 285,80 mg GAE/g of extract;
- Based on the above mentioned data, that high value of anti oxidative capacity of extract of wild gralic in direct connection of high content of phenol compunds,
- Taking into account the data presented in whis work and clean products of wild garlic and products with additives, there is a great possibility of development of different products based on wild garlic originating from Bosnia and Hercegovina, particularly products derived from dried wild garlic.

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HISTORY OF TRAPPIST CHEESE

PROFESSIONAL PAPER

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Abstract
The original Trappist cheese, the product of the monastery of Marija Zvijezda in Banja Luka, has been produced for more than 130 years.
The specificity of this cheese is in its secret recipe which has been transferred orally from a monk to a monk. Another particularity of this cheese is that only monks who passed vows and are inside the order community can produce Trappist cheese.
As the production started in 1882, the cheese became a synonym for semi-hard cheeses in the area of South-Eastern Europe. After the Second World War, the monks produced it only for their own needs inside the monastery of Marija Zvijezda, and in this period there was neither opportunity nor interest by the legal representatives of that time to accurately describe its organoleptic characteristics and traits. Since the production of Trappist cheese has been revived in 2008, we can try to correct this injustice.
The characteristic of the Trappist cheese is the wheel weight 1,6-2,0 kg and it has a natural rind which is yellowish, thin and smooth. Its consistency is soft, elastic, mild and can be easily cut. The cut is smooth with or without very little holes, and the color is pale yellowish. Its aroma is clean, milk-specific, and it is moderately saline and easily soluble.
The fat content is about 32%, the water content is about 41% while the dry matter is 56%.
We can only wish that the Trappist monks continue the production of the Trappist cheese and that political circumstances will not influence it as it has been the case up to now.
Key words: Milk, Monastery of Marija Zvijezda, Trappist cheese

INTRODUCTION

This year the monastery of Marija Zvijezda will celebrate 132 years since the production of Trappist cheese began in Banja Luka. The cheese has been produced in all these years with more or less problems that followed the monks and their destiny in these areas. The production was interrupted only from 1996 to 2008 due to the sudden death of Father Mohor who knew the secret recipe and which he did not manage to transfer to his brothers.
The cheese production was revived again in 2008 when Father Tomislav went to France to the monastery of Mont-des-Cats and learned the technique of cheese making and brought back the recipe for cheese production.
After the Second World War, the property of the monastery was confiscated, monks had to leave and the name “Trappist” was taken away but not the secret of cheese making.
On the territory of the former Yugoslavia, each dairy owned by the state began the production of cheese called Trappist because this name was a synonym for quality and semi-hard cheese, but this production never had the approval of the monks. A particular problem then was the dairy of Banja Luka to which some cooperation was negotiated but which failed because the former government had its own experts who produced “better” and “original” cheese. Even now and as before, the Trappist monks have had problems in regards to the protection of their intellectual property, and many other producers have used this name illegally for some of their products. Today in the monastery we can also find notices to consumers where Trappist monks warned about the appearance of the original cheese and how it differs from forgeries.
Trappist cheese is standardized and we hope that Bosnia and Herzegovina will finally protect this product under the designation of origin and thus prevent

further illegal use of the Trappist name labelled on other semi-hard cheese.

The History of Trappist Order

Trappists belong to the monastic family that follows Christ by living according to the Rule of St. Benedict of Nurisa, the father of Western monasticism, the founder of the monastery Subiaco and Monte Cassino. The name "Trappists" was received by the reform movement that began in 17th century in French Cistercian monastery of Notre Dame de La Trappe in Normandy, under the guidance of Abbot Armand Jean le Bouthillier de Rance. This reform movement was inspired by the reform movement that began 500 years ago in the monastery of Cîteaux near Dijonin France. The aim of this movement was to influence changes in a loose lifestyle of the monks in many French monasteries. Therefore, the official name of Trappists is *Ordo Cisterciensis Strictioris Observantiae* (O.C.S.O.) which means the stricter observance of the Cistercian Order. Trappists are actually reformed Cistercians who have started their activities as an insignificant local reform movement, and today they serve in more than 100 monasteries in the world. It is less known that Trappists have a female branch which has 72 monasteries, mainly in Europe. The Trappists are a contemplative order in the Catholic Church that serves to God and to people in silence, prayer and physical work. Their motto is „Ora et labora"– pray and work. These silent monks and nuns devote their entire lives to God and their life path is governed by the cross (Ostojić, 1965).

The monastery of Marija Zvijezda is the only Trappist monastery which produces cheese on the right side of the Rhine River that is in the former countries of the communist bloc.

Often, the religious community of Trappist monastery is misplaced with Cistercist monks who were also engaged in different productions, including the production of different cheese types. Some documents mention that Trappist cheese was made in monasteries in Hungary, the Czech Republic, Slovakia, etc. (Sanders, 1954) which is not true because in these countries there were no Trappist monasteries.

The History of Trappist Cheese

The beginning of cheese production in Marija Zvijezda monastery is found in 1872, in a small dairy built by Father Franz and who called that cheese as a „Swiss". However, this cheese plant production did not last long due to animal diseases that caused the lack of milk.

The production of the original cheese began in 1882 when in the monastery in Banja Luka arrived Father Ignatius from the French monastery „Port-du-Salut". He trained his brother Luka in making cheese. At the beginning, the cheese was made only for the purposes of the monastery, and later it was made for markets in Austria and Hungary as well as for the whole Europe. It was very well known and it was awarded numerous prizes at fairs in Europe. At first, the monks processed the milk from their own farm and later they started to buy it from the local farmers.

There was an auxiliary dairy at Marija Zvijezda monastery, and the main dairy was established in Josipovac (today called Bosanski Aleksandrovac) where in 1887 a branch of Marija Zvijezda was opened.

However, the monks again encountered some problems, especially in the first year. First, because of the lack of expertise of cheese makers, they had initially problems with the quality of cheese. Therefore, in 1888 abbot Bonaventure the First sent brother Dositej to France to the local monasteries, especially in Port-du-Salut, to train in cheese making for one year. When he came back he taught his brothers about cheese production and they were obliged to keep the secret of production. The secret was transmitted orally from brothers to brothers or they would carry it with them into the grave. Kirin wrote about this: Even

though in the cheese making industry the Trappist cheese was dominantly present for the entire century, in our literature there are very little data about the technological process of making this cheese. Due to the secrecy of making cheese, there is no description of the original Trappist cheese from Banja Luka, so it can only be speculated.

This secrecy draws the following conclusion: "The quality of cheese and the art of its production are predicated largely on the method of its preparation. Specifically, a dozen specialists participated in the production of the cheese. Particular intervention was done by only one cheese maker. Each cheese maker knew his part of the job to perfection while the job of the others was a secret to him."

The success of the branch Josipovac prompted the Abbot Bonaventure to establish the second branch. The colonists were well developing economically in the colony Windthrst (today called Nova Topola).

The Trappists bought land from one colonist in 1893 and in that place they established the branch Marienburg – Marijin Dvor (Nova Topola). The cornerstone was set on March 18, 1893. In this branch, besides other buildings, a cheese making plant was opened. The local people brought milk and the monks processed it into cheese and butter.

Cheese production in both branches was developing successfully. Every day, 2.000-3.000 litters of milk were brought in. As the cheese plant was developing successfully, the purchase of milk rose up as much as 8.000 litters. The cheese production reached 100 – 120 tons per year. The excess of milk was pasteurized and transported to Banja Luka where it was offered for sale. The milk was much appreciated for its quality but also for the price. Specifically, it was cheaper than from other sellers.

The cheese was packed in packages of 4.8 kg and sent by post or railway to clients throughout the monarchy as well as beyond its borders. The Trappist monks were also the official suppliers for the royal palace in Belgrade.

H. Renner travel writer wrote: „Now the monastery.... deals with manufacture of the „Trappist cheese"which has a good reputation abroad as well. Since the monastery does not have enough cows, milk for the cheese making plant is taken from the close German settlements."

Up to now, there were no reliable data on the organoleptic properties of the original Trappist cheese, and its secrecy of production does not allow us to obtain an insight into the production technology. The assumptions by different authors were the same as today's Saint-Paulin cheese that is a successor of Port-du-Salut and Port-Salut (Kirin, 2003). Mainly, the research was done to study the chemical composition, the quality and organoleptic characteristics of semi-hard cheese, which were produced in the former communist dairies.

The cheese production was revived again in 2008 when Father Tomislav went to France to the monastery of Mont-des-Cats and learned the technique of cheese making and brought back the recipe for cheese production (Budimir, 2012).

MATERIAL AND METHODS

The research was done on the Agricultural Cooperative "Livač" which is located in Aleksandrovac in Laktaši municipality, Bosnia and Herzegovina. The cooperative is engaged in the production of raw milk. Since 2008, in a newly built space for cheese production, the Trappist cheese has been produced in collaboration with monk Tomislav Topić. The cooperative provides production material and auxiliary work force and the recipe is owned by the monastery of Marija Zvijezda. Currently, about 2,5 tons of Trappist cheese per month is produced. The cheese plant is

HACCP certified and has the ISO 2008:2009 certificate and is under the constant supervision of a veterinary inspection. Microbiological and chemical analysis (according to Gerber) of cheese was done at the Veterinary Institute of the Republic of Srpska „Dr. Vaso Butozan“ in Banja Luka.

Organoleptic Properties of Trappist Cheese

The Trappist cheese belongs to the group of semi-hard cheese types and is easily cut. It has somewhat stiffer consistency but is still soft enough; compared to the bad copies which are either too soft or too hard to cut. Unfortunately, because up to now it has not been possible to forbid the use of the name „Trappist“, on the market there are different cheese plants that make cheese types based on different recipes, and then they label it as „Trappist“.

The softness and ease of cutting comes from a special way of preparing and of course due to special conditions of its ripening. It is important to note that the original Trappist cheese ripens in special conditions, where it is handled with care and it is rotated and cleaned daily. The copies of Trappist cheese which can be found on the market are produced in a way that it is „dried“ for fifteen days and then it is delivered to the stores. The ripening time of the original Trappist cheese is between 75 and 90 days as a minimum and this allows it to have a special consistency and taste.

The cheese is produced exclusively in the form of a wheel, 19 cm in diameter and 7-9 cm size (Table 1).

Table 1. Organoleptic properties of Trappist cheese

Group	External appearance	Texture	Cutting	Smell and taste
semi-hard	wheel d=19 cm height= 7-9 cm weight 1,6-1,8 kg smooth rind, dry yellowish, thin	soft, elastic, mild easily cut plastic	smooth without or with very little holes pale yellow colour	clean milk–specific scent taste sweet, moderately saline easily soluble

The characteristic of the Trappist cheese is the wheel weight 1,6-2,0 kg and it has natural rind which is yellowish, thin and smooth. Its consistency is soft, elastic, mild and can be easily cut. The cut is smooth with or without very little holes, and the colour is pale yellowish. Its aroma is clean, milk-specific, and it is moderately saline and easily soluble.

According to Gerber, the fat content is about 32%, the water content is about 41% while the dry matter is 56% (Table 2).

Table 2. Chemical composition of Trappist cheese (according to Gerber)

Water	Dry matter	Milk fat	Milk fat according to Gerber	NaCL %
41,26	56,01	53,56	33	2

Some authors mention that the Trappist cheese is produced in the form of a block (Kirin, 2002) which is not true. All types of cheese which are made by Trappist monks are done in the form of a wheel. The authors note that this is cheese with rind which is usually protected by coating or as cheese without rind if it ripens and is shipped as a cheese packaged in foil or vacuum packed plastic bag, thereby

reducing the manufacturing abatement (Dorušić et al., 1976, Kirin, 2002). This was typical of forgeries, or for semi-hard cheeses that were made in dairies of former system, or of those that today illegally use this name. The Trappist cheese has a natural rind, and a special coating is used which is acceptable in terms of hygiene and health and which gives a yellowish colour of rind.

In the earlier papers, the authors state that the cheese has small holes once it is cut. The scent and taste of the cheese are described almost as in the original Saint-Paulina, as well as in the illustrated versions (Miletić, 1969, Sabadoš and Rajšić, 1980, Sabadoš, 1981). The original Trappist cheese once it is cut it does not have holes because of the production technology and the quality of milk which is used for its production.

Technological Process of Trappist Cheese

For obvious reasons, it is difficult to describe the technological process of Trappist cheese production. It is of utmost importance the quality of raw materials out of which the cheese is produced, meaning the hygienic and microbiological safety of milk. Furthermore, the production conditions must be of a high standard. Upon receipt of milk, a low pasteurization is done after which milk is cooled and cultures and rennet are added. Unfortunately for all, and fortunately for the cheese, the secret of the quantity and order of culture is known only to monks but not to all of them. Lay people do not know the quantities and types of cultures so they cannot describe this process. The written recipe is only in the Port-du-Salut monastery in France and is available only to the chosen monks.

After adding cultures the cheese is left resting to create a cheese curd after which the cutting starts. The cheese is moved to the cheese making table and it undergoes pre-pressing to separate whey. Often, semi-hard cheese types undergo the rinse of curd with water which is not the case with the Trappist cheese. After pre-pressing, the cheese is cut into an appropriate form; it is placed into a cheese mould and goes under pressing again. The cheese is pressed under certain pressure and after some time it is rotated and goes back under the pressure.

After completion of this process, the cheese is left to rest for some time and afterwards goes into brine which consists of water and salt concentration.

Once this phase is finished, the cheese is left on a shelf to drip and afterwards it is put into a pre-chamber. The first phase of cheese ripening has been done in this pre-chamber under adequate moisture and temperature conditions. After 40 to 50 days, the cheese is moved into another chamber with altered ripening conditions: lower temperature and slightly higher humidity. The ripening process ends with the optimal 75 to 90 days.

During the ripening process, the cheese is covered by coating and it is rotated and cleaned in the chambers daily. The cheese is cleaned and coated regularly, as well as the wooden holders and shelves on which the cheese ripens. Hygiene has a great influence on the ripening and the quality of Trappist cheese.

Instead of a Conclusion

Considering everything mentioned above, it remains to hope that the community of the monks of Marija Zvijezda monastery will continue to produce their cheese and that finally in Bosnia and Herzegovina the conditions will be set to protect the originality of the product according to the European standards.

This is also very important for other indigenous types of cheese that are made in Bosnia and Herzegovina because they represent a significant potential for the development of tourist and gastronomic offer. The protection of cheese will enable the milk production to increase and a greater value will be achieved. In addition to this, it will lead to hiring additional

population, either through a direct or indirect arrangement in agricultural production, tourism and other related industries.

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COMPARISON OF FIRST-ORDER AND NTH-ORDER KINETICS OF CO-COMPOSTING POULTRY MANURE WITH WHEAT STRAW

ORIGINAL SCIENTIFIC PAPER

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ABSTRACT
The objective of the study was to compare the kinetic models of first-order and nth-order for composting process of poultry manure and wheat straw. Composting process was carried out in two specially designed reactors with volume of 32 L under controlled laboratory conditions over 13 days. Experimental data was fitted with a first-order kinetic model and with an nth-order kinetic model. Both kinetic models were based on degradation of volatile solids content and four correction factors (temperature, moisture content, oxygen concentration, free air space). Comparisons of experimental and simulation results in general showed very good agreement during the whole duration of the process. For first–order kinetic model, the values of corrected reaction rate constants k were 0,0509 day^{-1} and 0,1037 day^{-1}, while the values of uncorrected reaction rate constants k' were 0,0498 day^{-1} and 0,1026 day^{-1}. For nth-order kinetic model, the values of corrected reaction rate constants k were 6,330e-10$\%^{-2.89}$ day^{-1} and 6,205e-08$\%^{-3.08}$ day^{-1}, while the values of uncorrected reaction rate constants k' were 6,023e-10$\%^{-2.89}$ day^{-1} and 1,817e-08$\%^{-3.08}$ day^{1}. The estimates of corrected reaction rate constants were generally higher than the estimates of uncorrected reaction rate constants. In some cases, the values of corrected reaction rate constant were much higher than the values of corrected reaction rate constant. The values of normalized root mean square error *NRSME* obtained in this study, ranged from 1,15% to 1,49% for first-order kinetic model, and 0,26% to 0,27% for nth-order kinetic model. The results showed that nth-order kinetic model is better than first-order kinetic model for describing of degradation of volatile solids in the composting process of the mixture of poultry manure and wheat straw.
Keywords: kinetics, composting, poultry manure, wheat straw, correction factors

INTRODUCTION

Composting is an effective way to recycle organic waste and to provide natural soil conditioning. During the first phase of the process contents of organic carbon are mineralized and easily metabolized by microorganisms, generating CO_2, NH_3, H_2O, organic acids, and heat.

The kinetic model can be used as a tool for studying the composting process on an industrial scale for optimization. The degradation rate of waste can be predicted using kinetic models of the process indicators (temperature, volatile solid content, moisture content, oxygen concentration, etc.). It is determined by using the reliable data obtained by experimental studies under controlled conditions. A review of the literature showed that the first-order equation is the most common form of description of the composting process[1]. Many researchers found that the volatile solid degradation follows first-order kinetics in the composting of different wastes.[1-7] The main advantage of the first-order kinetic model is the failure in the prediction of substrate degradation over the whole period of composting process.

The main objective of this study is to compare the kinetic models of first-order and nth-order for composting process of poultry manure and wheat straw, on the basis of the values of: uncorrected and corrected reaction rate constant, maximum and minimum differences between experimental and model results, normalized root mean square error, and time profiles of consumed volatile solid contents.

MATERIALS AND METHODS

Kinetic model

The composting reaction rate is described by the VS (volatile solids) degradation rate through the first-order kinetic model:

$$VSconsumed = [BVS_0] \cdot \left(1 - e^{-k' \cdot t}\right) \qquad (1)$$

where *VS* is the amount of VS consumed at time *t* (%), BVS_0 is the initial content of biodegradable volatile solids (%), *k′* is the uncorrected first-order reaction rate constant (day^{-1}).

k′ is defined as the product of *k* (corrected first-order reaction rate constant) multiplied by given environmental correction factors[2]:

$$k' = k \cdot F(T) \cdot F(MC) \cdot F(O_2) \cdot F(FAS) \qquad (2)$$

where *F(T)*, *F(MC)*, $F(O_2)$ and *F(FAS)* are corrections factors for temperature, moisture content, oxygen concentration and free air space, respectively.

The equation (3) is obtained from combination of equations (1) and (2):

$$VSconsumed = [BVS_0] \cdot \left(1 - e^{-k \cdot F(T) F(MC) F(O_2) F(FAS) t}\right) \qquad (3)$$

For describing the effect of temperature on reaction rate, the following equation was used[8]:

$$F(T) = \frac{(T - 71.6) \cdot (T - 5)^2}{(58.6 - 5) \cdot [(58.6 - 5) \cdot (T - 58.6) - (58.6 - 71.6)(58.6 + 5 - 2 \cdot T)]} \qquad (4)$$

Dependence of the reaction rate on oxygen concentration is given by the equation[1]:

$$F(O_2) = \frac{[O_2]}{F_{O_2}(20.95\%) \cdot (0.83 + [O_2])} \qquad (5)$$

where O_2 is the oxygen concentration (%).

Modeling the effect of moisture content on the reaction rate was carried out using the correction factor developed by Haug[2]:

$$F(MC) = \frac{1}{e^{(-17.684 \cdot (1 - [DM])) + 7.0622)} + 1} \qquad (6)$$

where is *DM* is the fractional dry matter of the composting material (-).

As a correction factor for free air space (FAS), the equation by Haug[2] was used:

$$F(FAS) = \frac{1}{e^{(-23.675\,FAS + 3.4945)} + 1} \qquad (7)$$

The free air space was calculated using the following equations[2]:

$$FAS = 1 - \frac{\delta_m \cdot DM}{G_s \cdot \delta_w} - \frac{\delta_m \cdot (1 - DM)}{\delta_w} \qquad (8)$$

$$G_s = \frac{1}{(V_s / G_s) + ((1 - V_s) / G_f)} \qquad (9)$$

$$\delta_m = \frac{C}{DM} \qquad (10)$$

where δ_m and δ_w are the densities of composting material and water (kg m^{-3}); G_s, G_v and G_f are the specific gravities of solids, volatile fraction of the solids (= 1) and fixed fraction of the solids (= 2.5); V_s is the volatile fraction of the solids (-); *C* is the bulk weight coefficient for the substrate (0.25).

The following equation was proposed as the nth-order kinetic model:

$$-\frac{dVS}{dt} = k' \cdot VS^n \qquad (11)$$

Combining the equation (11) with the equation (2) the following equation was obtained:

$$VS = \left(\frac{-\frac{dVS}{dt}}{k \cdot F(T) \cdot F(MC) \cdot F(O_2) \cdot F(FAS)} \right)^{\left(\frac{1}{n}\right)} \qquad (12)$$

Normalized root mean square error *NRSME* (%) was calculated using the equation[9]:

$$NRSME = \frac{RMSE}{[BVS_0]} \cdot 100 \qquad (13)$$

where *RSME* is the root mean square error (-), $[BVS_0]$ is the initial biodegradable volatile solids content (-).
The *VS* (volatile solids) content data was used to calculate the profiles of *VS* consumption against time for each reactor, using the following equation[2]:

$$VSconsumed = \frac{[VS_i]-[VS_t]}{(100-[VS_t])\cdot[VS_i]}\cdot 10^4 \quad (14)$$

where *VS consumed* is the *VS* consumed in the process time *t* (%), $[VS_i]$ is the initial concentration of *VS* (%), $[VS_t]$ is the concentration of *VS* at process time *t* (%).

Applied numerical method and software
Using the nonlinear regression method with the Levenberg-Marquardt algorithm[10], the kinetic parameters were estimated from the experimental data obtained from the process in reactors.
For determining the values of reaction rate constants and for prediction of volatile solid contents, the numerical software package Polymath[11] was used.

Experimental materials
Poultry manure and wheat straw (Table 1), mixed in two different ratios (Ratio 1 - 73.5% PM+26.5% WS; Ratio 2 - 78.0% OM+22.0 WS), were used as the experimental material (Table 2). The straw was cut into 2.5 cm long pieces. Poultry and straw were mixed manually for 30 min, in order to achieve better homogenization of material.

Table 1. Characteristics of poultry manure and wheat straw before mixing (three measurements, mean ± standard deviation)

Composting Material	Moisture (% w.b.)	Volatile solids (% d.b.)	Ph	Electrical conductivity (dS m^{-1})
Manure	65,31±1,97	71,37±1,35	8,27±0,09	3,94±0,05
Straw	10,42±0,83	87,38±1,78	7,87±0,03	1,94±0,04

w.b. – wet basis; d.b. – dry basis

Table 2. Characteristics of poultry manure and wheat straw after mixing (three measurements, mean ± standard deviation)

Reactor	Moisture (% w.b.)	Volatile solids (% d.b.)	pH	Electrical conductivity (dS m^{-1})
1	59,22±1,67	77,66±2,25	7,95±0,08	2,84±0,20
2	67,17±0,64	73,75±0,20	8,17±0,08	3,55±0,13

w.b. – wet basis; d.b. – dry basis

Experimental reactors
Two specially designed reactors with volume of 32 L (0,48 height x 0,30 internal diameter m), made of high density polyethylene, were used for the experiment.
The reactors were insulated with a layer of polyurethane foam (1 cm of thickness).

Measurements and analysis
The air compressor was used for constant aeration (0,6 L min^{-1} kg^{-1} OM). The measurement of airflow was carried out using airflow meters (Valved Acrylic Flowmeter, Cole-Parmer, USA). In the reactors, the temperature was measured in

the intervals of 15 min through thermocouples type T (Digi-Sense, Cole-Parmer, USA), placed in the middle of the substrate. Thermocouples were connected through the acquisition module on a laptop. The oxygen in the exit gas mixture was measured by an Orsat O_2 analyzer (W. Feddeler, Germany) in each reactor. Moisture content and volatile solids were determined according to APHA[12]. The composting material was mixed several times per day. After mixing, the samples were taken every day at the same time, from different places in the reactor (top, middle, and bottom). Each analysis was done in triplicate with calculation of the mean value. The experiments were performed in duplicate.

Statistical analysis

Statistical analysis (ANOVA analysis, and the least significant difference for mean at 95%) was performed with a statistical package STATGRAPHICS[13], on data obtained in the composting mixture at the different composting times.

RESULTS AND DISCUSSION

The time changes of volatile solid content, temperature, oxygen concentration and moisture content in both reactors are shown in Figure 1. These data were used for parameter estimation and for prediction of volatile solid contents. There were statistically significant differences ($P<0,05$): in volatile solid content for the first ten days, in temperature from the first to thirteenth day, in oxygen concentration for the first ten days, in moisture content for the whole period of the process.

The values of corrected reaction rate constant k and uncorrected reaction rate constant k' correspond to literature values of other researchers.[1,9,14,15] On the other hand, the values of normalized root mean square error *NRSME* in this are less than the values in the above mentioned studies. This finding confirms the fact that laboratory composting is generally faster than full-scale composting. Superior performance in laboratory systems was attributed to a better management of the environmental process conditions, which was around 50% more efficient than in full-scale systems[16].

In both models, the values of corrected reaction rate constant k are greater than the values of uncorrected reaction rate constant k' (Tables 3 and 4). These differences are caused by the differences between operational and environmental conditions of optimum conditions, the greater differences between them means the greater differences between k and k'. Also, the values of normalized root mean square error *NRSME* for the first-order kinetic model both for the corrected reaction rate constant k and for the uncorrected reaction rate constant k' are greater than the same values for the nth-order kinetic model.

Comparisons of the experimental and simulation results in general showed very good agreement during the whole duration of the process (Figure 2).

The kinetic model with nth-order showed better prediction performance than the first-order kinetic model.

The maximum and the mean differences between the experimental values and the model for the first-order kinetic model were 4,65% and 0,36% for the first reactor and 4,94% and 0,36% for the second reactor.

The maximum and the mean differences between the experimental values and the model for the nth-order kinetic model were 1,23% and 0,03% for the first reactor and 1,34% and 0,01% for the second reactor.

Some discrepancies were noticed immediately after the thermophilic phase and during the cooling phase which are related to the degradation of hardly biodegradable compounds. A possible solution to this problem may be in performing more experiments and more

sampling, both with different and under the same experimental conditions in reactors (reproducibility of experiments).

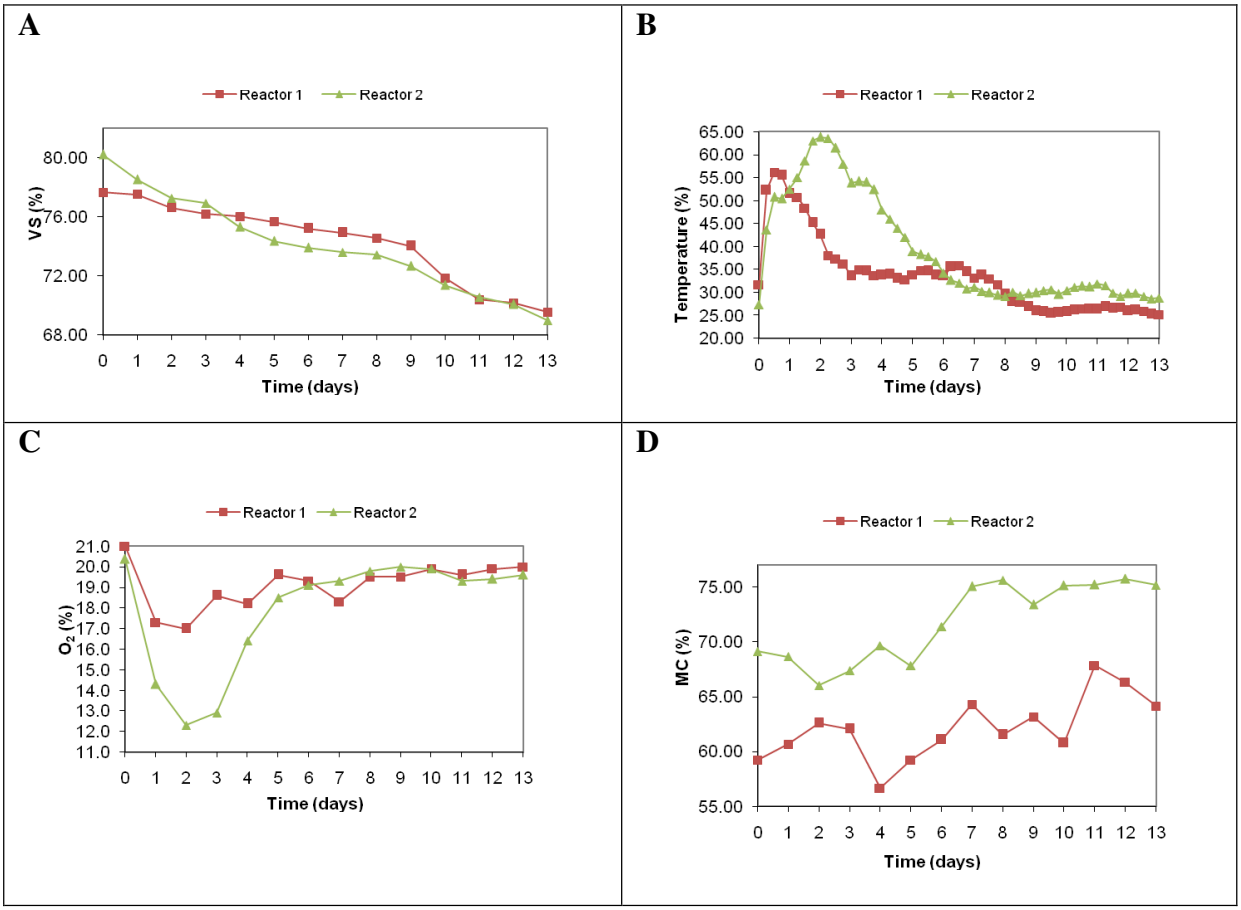

Figure 1. Changes of process parameters during the process: a) volatile solid content, b) temperature, c) oxygen concentration, d) moisture content.

Table 3. Estimated values of k, k' and NRSME for first-order kinetic model

Reactor	k (day^{-1})	k' (day^{-1})	*NRSME* for k (%)	*NRSME* for k'(%)
1	0,0509	0,0498	1,49	1,51
2	0,1037	0,1026	1,15	1,10
Mean± standard deviation	0,0773±0,037	0,0762±0,037	1,32±0,24	1,31±0,29

Table 4. Estimated values of k, k' and NRSME for nth-order kinetic model

Reactor	k (%$^{1-n}$ day^{-1})	k' (%$^{1-n}$ day^{-1})	*NRSME* for k (%)	*NRSME* for k'(%)	Reaction order
1	6,330e-10	6,023e-10	0,44	0,27	3,89
2	6,205e-08	1,817e-08	0,34	0,26	4,08
Mean± standard deviation	3,13e-8±4,3e-08	9,39e-9±1,2e-08	0,39±0,07	0,265±0,007	3,98±0,09

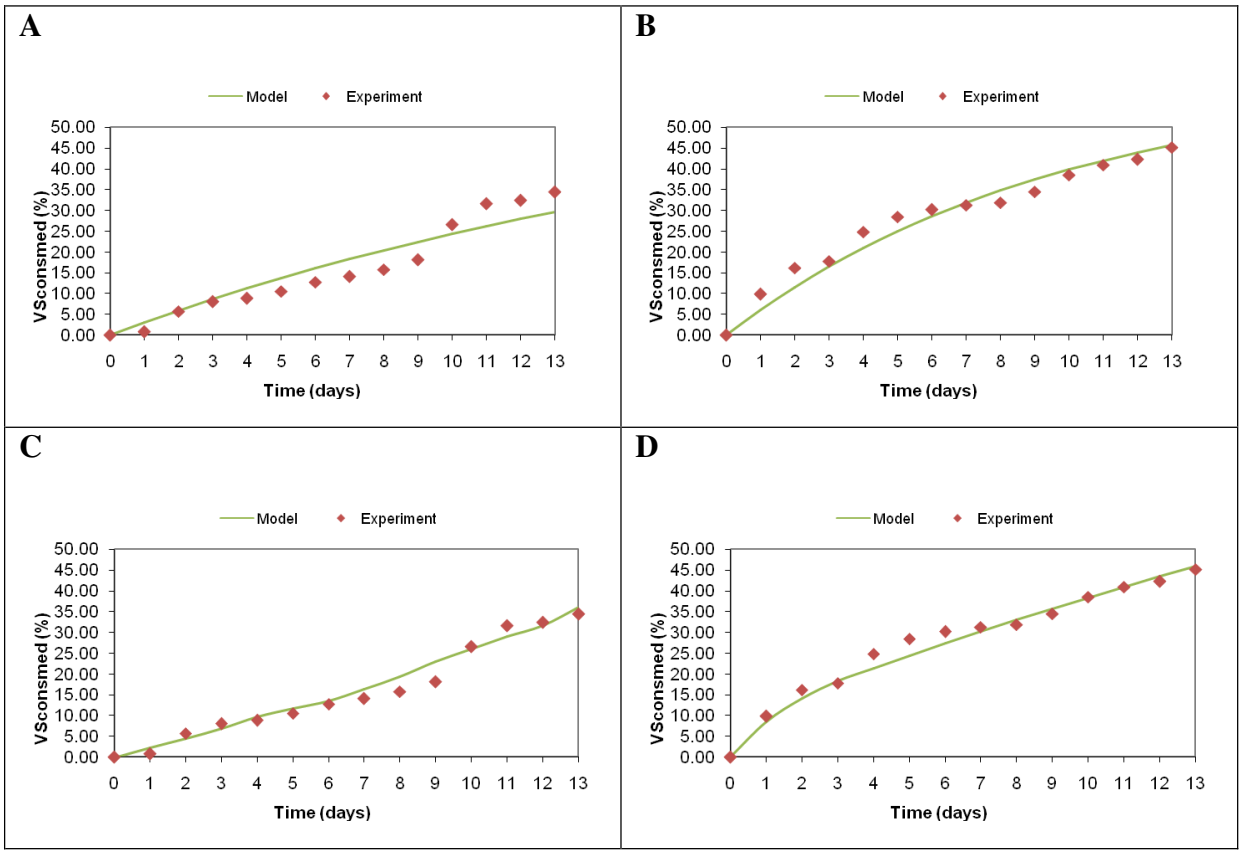

Figure 2. Comparison of experimental and simulation results: a) reactor 1, first-order model, b) reactor 2, first-order model, c) reactor 1, nth-order model, d) reactor 2, nth-order model.

CONCLUSIONS

1. For first-order, the values of corrected reaction constant k were 0,0509 day^{-1} and 0,1037 day^{-1}, and the values of uncorrected reaction constant k' were 0,0498 day^{-1} and 0,1026 day^{-1}.
2. For nth-order, the values of corrected reaction constant k were 6,330e-10%$^{-2,89}$ day^{-1} and 6,205e-08%$^{-3,08}$ day^{-1}, and the values of uncorrected reaction constant k' were 6,023e-10%$^{-2,89}$ day^{-1} and 1,817e-08%$^{-3,08}$ day^{-1}. The values of reaction orders are 3,89 and 4,08.
3. Comparisons of the experimental and simulation results in general showed very good agreement during the whole duration of the process.
5. According to the results (maximum and minimum differences between experimental and model data; normalized root mean square error *NRSME*), the kinetic model with nth-order showed better prediction performance than the first-order kinetic model.
4. In both models, the values of corrected reaction rate constant k are greater than the values of uncorrected reaction rate constant k'. The values of normalized root mean square error *NRSME* for the first-order kinetic model both for the corrected reaction rate constant k and for uncorrected reaction rate constant k' are greater than the same values for the nth-order kinetic model.
5. Future research will be focused on the effects of correction factors on composting kinetics and optimization of the process.

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THE INFLUENCE OF ANTIOXIDANTS ON OXIDATIVE STABILITY OF SUNFLOWER AND OLIVE OIL

ORIGINAL SCIENTIFIC PAPER

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ABSTRACT
Oxidation of vegetable oils has been recognized as a major problem in edible oils; it causes a change in the chemical, sensory and nutritional properties. In this study the effect of addition of natural antioxidants (in concentration of 0,2%) on the oxidative stability of extra virgin olive oil, high-oleic sunflower oil and their mixtures (80:20, 50:50) were investigated. The two types of 100% natural rosemary extracts (OxyLess CS and StabilEnhance OSR) and green tea extract were used as natural antioxidants. Oxidative stability of vegetable oils, their mixture and oil with and without added antioxidants was investigated using the Schaal Oven test. The test results are shown in peroxide value over 4 days of the test. High-oleic sunflower oil has better stability to oxidation due to the high proportion of oleic acid. The research results show the higher antioxidant activity of a rosemary extract Oxy'Less CS in relation to StabilEnhance OSR and green tea extract. The addition of rosemary extract StabilEnhance OSR (0,2%) leads to a very little increase in the stability of oils and their mixtures in relation to the oil without added antioxidants. Application of used antioxidants increases the oxidative stability of the tested vegetable oils and their mixtures.
Keywords: Vegetable oils, Oxidative stability, Green tea extract, Rosemary extract.

INTRODUCTION

Vegetable oils are products that are subject to rapid undesirable changes (enzymatic and microbial processes and chemical reactions), resulting in deterioration of the oil. Oxidative deterioration of vegetable oils during storage implies a lot of undesirable reactions (polymerization, hydrolysis, isomerization, cyclization, etc.)[1]. Oil oxidation can appear faster or slower depending on the composition of vegetable oils, storage conditions and the presence of substances that speed up or slow down spoilage[2]. Composition of oleic, linoleic and linolenic acid in the oil affects oxidative stability[3,4]. Odor of oxidized oil is attributed to primary and secondary oxidation products[5,6]. The products of oxidation impair sensory properties of oils (an unpleasant odor and flavors)[7]. Hydroperoxide, which is the major oxidation product, decomposes to secondary products, such as esters, aldehydes, alcohols, ketones, lactones and hydrocarbons[8]. Additionally, certain oxidation products are potentially toxic at relatively low concentration[3]. Oil oxidation can be determined by oxygen depletion, peroxide value, volatile compounds, conjugated diene content and flavor scores[9,10]. Oxidation stability or sustainability of vegetable oils is a time during which oil can be saved from the oxidation process. Knowing the sustainability of oil is important in order to pre-determine the period during which oil can be preserved from more pronounced oxidation and for determination of the time limit of oil usage. Various researchers emphasize that the sustainability of vegetable oils depends on the type of oil, fatty acid composition and the amount of natural antioxidants in the oil. In practice, the most commonly applied methods for the determination of the oxidation stability are based on accelerated oxidation of oils, which are Schaal Oven test, AOM test and Rancimat test [11-15]. Extra virgin olive oil is produced by mechanical pressing fruity olives (*Olea europea* L.) in which the composition is dominated by oleic fatty acids, contains natural antioxidants such as tocopherols, carotenoids, sterols and

phenolic compounds. Boskou[16], and Ashton[17] reported that high oleic sunflower oil may decrease the risk of coronary heart disease by decreasing low density lipoprotein (LDL) cholesterol. Genetic modification of sunflower oil, to decrease linoleic acid and increase oleic acid, could increase the oxidative stability during storage and deep - fat frying, as well as improve health benefits. This oil has a high stability to oxidation and spoilage, wide application in extending the viability of finished products, as well as multiple usage of the oil during frying foods without major changes in its quality [1].

The aim of this study was to investigate the oxidative stability of extra virgin olive oil, sunflower oil with high oleic content, and their mixtures and the effect of the addition of natural antioxidants to change the oxidation stability.

MATERIALS AND METHODS

To test the oxidation stability of extra virgin olive oil, high oleic content sunflower oil and mixtures (80:20, 50:50) was used. Rosemary extract Oxy Less CS and StabilEnhance OSR, and green tea extract were supplied from Naturex (France). The initial testing of the chemical characteristics of the tested oils was carried out by standard methods.

Free fatty acids

Acidity of vegetable oils is a result of hydrolysis of triacylglycerol lipolytic enzyme activity, expressed as a percentage (%) of free fatty acids. Free fatty acids (FFA) in vegetable oils were determined by standard method ISO 660:1996, which is based on the principle of the titration with sodium hydroxide solution. The result is expressed as a percentage (%) of free fatty acids calculated as oleic acid.

Peroxide value

Peroxide value (PV) is an indicator of the degree oxidative deterioration of vegetable oils. Determination of peroxide is one of the most applied methods for the examination primary oxidation products of vegetable oils. Peroxide value of the oils was determined by the standard method ISO 3960:1998. The result is expressed as mmol O_2/kg oil.

Schaal Oven test

This is one of the oldest tests to determine the oxidation stability (sustainability) of vegetable oil. Tested samples of vegetable oils are heated in a thermostat at a temperature of 63 °C and are accompanied by an increase of PV or sensory changes resulting from oil oxidation spoilage. Changes are monitored at specified time intervals. The results of the oxidation stability of the tested vegetable oils, applying this test are shown as PV after a certain time of the implementation of the test (4 days). This test is suitable for comparison of different vegetable oils on the oxidative stability and sustainability. Results of Schaal Oven test give us the nearest data to estimate the actual sustainability of vegetable oils.

Statistical analysis

One-way analysis of variance (ANOVA) and multiple comparisons (Duncan's *post-hoc* test) were used to evaluate the significant difference of the data at $p < 0,05$. Data were expressed as average value of two repetitions.

RESULTS AND DISCUSSION

The obtained values of measured quality parameters (FFA, PV) indicate that the tested vegetable oils and their mixtures are good quality and they are in accordance with national regulations.

Test results for oxidative stability of extra virgin olive oil, high oleic sunflower oil, their mixtures in ratios of 80:20 and 50:50, and the impact of the addition of natural antioxidants are shown in Tables 1 - 4. The increase in peroxide value (PV) during 4 days with Schaal Oven test indicates oxidative deterioration of the oils. Greater stability to oxidative deterioration (lower PV) after four days of the test can be seen in high oleic sunflower oil compared to extra virgin olive oil and their mixtures (higher PV). Better resistance high oleic sunflower oil to oxidative deterioration is explained by the high proportion of monounsaturated oleic fatty acid (79%). Smith et al.[18] studied the oxidation and thermal stability of high oleic sunflower oil compared to sunflower oil (linoleic type), soybean oil, corn oil and peanut oil. They determined that high oleic sunflower oil (5,5% linoleic acid) has better oxidation and thermal stability of sunflower oil (71,6% linoleic acid). Addition of 20% and 50% high oleic sunflower oil in extra virgin olive oil result with a mixture of oil higher oxidation stability compared to pure olive oil. The results of testing oils and their mixtures with the addition of natural antioxidants (0,2%) indicate a positive effect on the oxidation stability of oils. Table 1 shows the oxidative stability of extra virgin olive oil with the addition of natural antioxidants. The addition of rosemary extract OxyLess CS leads to greater resistance according to oil deterioration. After four days of test, slightly lower PV was obtained in oils with antioxidants (green tea extract and rosemary extract StabilEnhance OSR) compared to oil without antioxidants. Green tea extract antioxidant has a better ability to protect against oxidation compared to StabilEnhance OSR.

Table 1. Oxidative stability of extra virgin olive oil determined by the Schaal Oven test during 4 days every 24 hours

Time (h)		**0**	**24**	**48**	**72**	**96**
Antioxidant	**Concentration (%)**	**PV (mmol O_2/kg)**				
Extra virgin olive oil	0	2,67^a	3,57^b	4,11^c	4,46^d	4,75^e
Oxy´Less CS	0,2	2,67^a	2,93^b	3,05^b	3,40^c	3,50^c
StabilEnhance OSR	0,2	2,67^a	3,54^b	3,68^b	3,89^c	4,21^d
Green tea extract	0,2	2,67^a	3,41^b	3,44^b	3,98^c	4,11^c

FFA – 0,11%
Data are expressed as mean value of replication (n=2)
The same letter in the same row indicates no significant differences (Duncan's test, $p < 0,05$)

Oxidative stability of high oleic sunflower oil with and without added antioxidants is shown in Table 2. The results indicate that the addition of rosemary extract OxyLess CS and green tea extract in this oil provide higher efficiency protection against oxidative deterioration (lower PV) compared to the addition of rosemary extract StabilEnhance OSR. The best protection of this oil gives OxyLess CS where obtained PV after four days of the test is lowest.

Table 2. Oxidative stability of high oleic sunflower oil determined by the Schaal Oven test during 4 days every 24 hours

Time (h)	**0**	**24**	**48**	**72**	**96**

Antioxidant	Concentration (%)	PV (mmol O_2/kg)				
High oleic sunflower oil	0	0,96^a	2,39^b	2,67^b	3,80^c	4,28^d
Oxy´Less CS	0,2	0,96^a	1,56^b	1,79^c	1,95^c	2,23^d
StabilEnhance OSR	0,2	0,96^a	2,28^b	2,41^b	3,42^c	4,05^d
Green tea Extract	0,2	0,96^a	1,57^b	1,71^b	2,03^c	2,42^d

FFA – 0,18%
Data are expressed as mean value of replication (n=2)
The same letter in the same row indicates no significant differences (Duncan's test, $p < 0,05$)

The addition of high oleic sunflower oil (20%) in extra virgin olive oil is the oil mixture (20:80) with greater stability to oxidative deterioration. This mixture of oils after four days of the test has a slightly lower PV 4,64 (mmol O_2/kg) compared to the extra virgin olive oil. Table 3 shows the effect of the addition of antioxidants on oxidative stability of mixture high oleic sunflower oil and extra virgin olive oil in the ratio of 20:80. The obtained values of PV, which represents the degree of oxidation of the oil during the four days of the test, showing that addition rosemary extract OxyLess CS to mixture of oils better protects the oil from oxidative deterioration resulting in better stability of the oil mixture compared to oil mixture with added extract of green tea. The addition of rosemary extract StabilEnhance OSR slightly enhances the oxidative stability of the oil mixture compared to the sample without added antioxidants.

Table 3. Oxidative stability of high oleic sunflower oil and extra virgin olive oil mixture (20:80) determined by the Schaal Oven test during 4 days every 24 hours

Time (h)		0	24	48	72	96
Antioxidant	**Concentration (%)**	**PV (mmol O_2/kg)**				
Oil mixture 20:80	0	2,45^a	3,11^b	3,63^c	4,49^d	4,64^d
Oxy´Less CS	0,2	2,45^a	2,82^b	3,03^c	3,14^c	3,21^c
StabilEnhance OSR	0,2	2,45^a	2,96^b	3,52^c	4,17^d	4,55^d
Green tea extract	0,2	2,45^a	2,96^b	3,43^c	3,61^c	3,95^d

FFA – 0,13%
Data are expressed as mean value of replication (n=2)
The same letter in the same row indicates no significant differences (Duncan's test, $p < 0,05$)

The addition of 50% high oleic sunflower oil in extra virgin olive oil results with a mixture with better stability. This mixture of oils (50:50) after 4 days of the test has a lower peroxide 4,51 (mmol O_2/kg) compared to mix ratio 20 : 80. Table 4 shows the results of oxidation stability mixture of oil with the added test antioxidants. Rosemary extract OxyLess CS have the best protect efficiency of oil mixture from oxidative deterioration followed by green tea extract and StabilEnhance OSR.

Table 4. Oxidative stability of high oleic sunflower oil and extra virgin olive oil mixture (50:50) determined by the Schaal Oven test during 4 days every 24 hours

Time (h)		**0**	**24**	**48**	**72**	**96**
Antioxidant	**Concentration (%)**	**PV (mmol O_2/kg)**				
Oil mixture 50:50	0	2,25^a	2,74^b	3,47^c	3,87^d	4,51^e
Oxy´Less CS	0,2	2,25^a	2,35^a	2,42^a	2,46^a	2,96^b
StabilEnhance OSR	0,2	2,25^a	2,67^b	3,22^c	3,44^c	4,42^d
Green tea extract	0,2	2,25^a	2,41^a	2,75^b	2,93^b	3,26^c

FFA – 0,15%
Data are expressed as mean value of replication (n=2)
The same letter in the same row indicates no significant differences (Duncan's test, $p < 0,05$)

CONCLUSIONS

Based on the results from the research of the oxidation stability of vegetable oils and their mixtures with and without the addition of natural antioxidants the following conclusions can be carried out:

High oleic sunflower oil shows greater stability and resistance to oxidative deterioration due to a larger share of oleic fatty acid. Addition of 20% and 50% high oleic sunflower oil in extra virgin olive oil results with a mixture of oil with higher oxidation stability compared to pure olive oil.

Application of the tested natural antioxidants (0,2%) increased oxidative stability of vegetable oils and their mixtures.

From the this study it can be concluded that the addition of rosemary extract OxyLess CS in 0,2% has the best protection efficiency for the tested oils and their mixtures compared to the green tea extract and StabilEnhance OSR.

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PROPERTIES OF CORN EXTRUDATES WITH ADDITION OF CHICKPEAFLOUR

ORIGINAL SCIENTIFIC PAPER

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ABSTRACT

Extrusion is a significant process in the food industry, where corn grits is often used as the main raw material to which various types of flours can be added to increase nutrition value and to improve physicochemical properties. Chickpea (*Cicer arietinum* L.) is one of the world's most important grain legumes because it is a valuable source of protein, minerals and vitamins, and plays a very important role in human diets in many areas of the world.

The aim of this study was to determine the effect of chickpea flour addition (5%, 10% and 15%) on properties of corn grits extrudates. Samples with 15% of moisture content were extruded in the laboratory single screw extruder at temperature profile 135/170/170 °C, using a screw with compression ratio 4:1 and die with 4 mm diameter. Obtained extrudates were air-dried, and physical and rheological properties were determined.

The obtained results showed that the addition of chickpea flour to corn grits resulted in increase of expansion ratio (ER) and fracturability, whereas bulk density (BD) and hardness of extrudates decreased. Addition of chickpea flour and extrusion process resulted in significant colour change, where the total colour change (ΔE) increased proportionaly to the chickpea level, with more pronounced change in extruded products. After extrusion process, peak, hot and cold viscosity decreased in all samples, and the extruded samples were less prone to retrogradation.

Keywords: extrusion, corn grits, chickpea flour

INTRODUCTION

Extrusion is a frequently used process in the food industry, it is considered as the HTST procedure („high temperature short time"), and is used for production of various types of products, including pasta, snacks, breakfast cereals, confectionery and other products, as well as for modification of starch and flour[1, 2]. The basic raw material for the production of a large number of these products consumed by vast population is corn grits. Targeting improvement of the nutritional value and physico-chemical properties, numerous studies with the subject of replacing corn grits with flours of other grains, pseudocereals, legumes and dried fruit and vegetables were conducted[3]. Chickpea (*Cicer arietinum* L.) is one of the world's most important plant species of the legume family, because it is a valuable source of protein, minerals and vitamins, and has a very important role in the human diet. More than 70% of world's production and consumption of chickpea is in India, but it is important in many other countries of Asia, Africa, Europe and America. The crude protein content of chickpea, which is in range 137-340 g/kg d.m., largely depends on a cultivation method. Chickpea contains 562-788 g/kg total carbohydrates, expressed on dry matter, of which the starch, total sugars and fibers are the major components[4]. Chickpea starch is slowly digestible, what in the human diet leads to a low glycemic index. Therefore, it may have an important role as a low-glycemic functional ingredient in a healthy diet[5]. In view of these positive properties, the aim of this study was to investigate the influence of chickpea flour addition on properties of corn grits extrudates.

MATERIALS AND METHODS

Corn grits was kindly supplied by company "Žito" Ltd. Osijek, produced in 2012. Chickpea was purchased in a local supermarket (producer: DO-IT BV, Prins Hendrikweg 19, 3771 AK Barneveld, NL), and milled in a laboratory mill IKA MF10 with 2 mm sieve. Control sample of corn grits and mixtures of corn grits with chickpea flour (5%, 10% and 15% of chickpea) were prepared at 15% moisture content and stored in plastic bags in a refrigerator at 4 °C, in order to even distribution of moisture. Before the extrusion process the samples were removed from the refrigerator and allowed to equilibrate at room temperature. The samples were extruded in a laboratory single-screw extruder Brabender 19/20 DN (Brabender GmbH, Duisburg, Germany), at this regime:

- screw: 4:1;
- die: 4 mm;
- temperature profile: 135/135/170 °C.

The obtained extrudates were air-dried overnight and analysed.

Expansion ratio (ER) was determined according to Brnčić et al.[6], where *ER* is calculated according to the equation 1:

$$ER = \text{extrudate diameter (mm)/die diameter (mm)} \quad (1)$$

Bulk density (BD) was determined according to the method of Alvarez-Martinez et al.[7], and calculated according to the equation 2:

$$BD\ (g/cm^3) = 4m/\pi d^2 L \quad (2)$$

where m is mass (g) of a lengh L (cm) of extrudate with a diameter d (cm).

Hardness and *fracturability* of extrudates were determined by texture analyzer TA.XT2Plus (Stable Microsystem, United Kingdom) using the method „Measurement of the hardness and fracturability of pretzel sticks", according to Jozinović et al.[8].

For the measurement of colour and viscosity, extrudates were ground in the laboratory mill IKA MF10 using sieves with openings 2 mm.

Color was measured according to Jozinović et al.[9], using Chroma Meter CR-300, KonicaMinolta, Japan with granular materials attachment.

Pasting properties were measured by using Micro Visco-Amylo-Graph (Model 803202, Brabender Gmbh & Co KG, Duisburg, Germany), according to the method of Jozinović et al.[9]. The flour suspensions (10% d.m., 100 g total weight) were heated at 7,5 °C/min from 32 to 92 °C, held at 92 °C for 10 min, cooled at 7,5 °C/min to 50 °C, and held at 50 °C for 1 min.

All statistical analyses were carried out using software program STATISTICA 10.0 (StatSoft, Inc, USA). Experimental data were analyzed by analysis of variance (ANOVA) and Fisher's least significant difference (LSD) with significance defined at $P < 0,05$.

RESULTS AND DISCUSSION

Figure 1 shows the influence of extrusion process and chickpea flour addition on expansion ratio (ER) of corn extrudates. It is evident that the addition of chickpea leads to increase of ER, but it was lower when the proportion of chickpea in the mixture was higher. The increase in expansion of extrudates based on chickpea and rice flour with addition of Fenugreek (*Trigonella foenum – graecum*) is found in the study conducted by Shirani and Ganeshanaree[5]. They determined the largest expansion ratio at extrudates with a ratio of chickpea: rice 70:30. In accordance with the results of this research, the increase in the share of chickpea above 70% decreased the expansion ratio. The reason for this may be

a high proportion of protein and fiber in chickpea in relation to rice. The proteins act on the degree of expansion via its ability to influence distribution of water into the matrix and through its macromolecular structure and conformation, which affects the properties of elongation during the extrusion cooking[10]. Similar results were obtained by Martinez-Serena et al.[11], and Onwulata et al.[12], who investigated the effect of whey protein concentrate addition in the extrusion of corn starch and rice, and found reduction in expansion at higher protein concentrations. The reason for this may be a modification of the viscoelastic properties of the dough as a result of competition for the available water between protein and starch, which leads to slowing down of starch gelatinization, and consequently to a lower moisture content and expansion of the product.

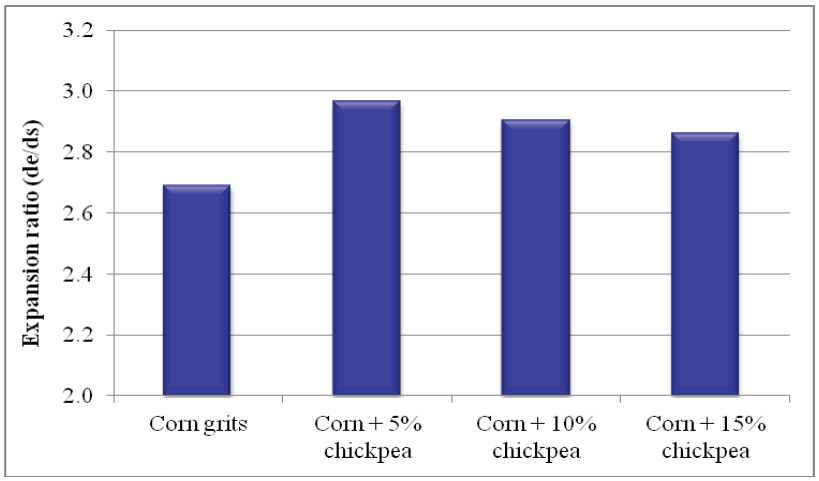

Figure 1. Effect of chickpea flour addition on expansion ratio (ER) of corn grits extrudates

Figure 2 represents how the extrusion process and chickpea flour addition affect the bulk density of the samples. It is apparent that the addition of chickpea decreased bulk density compared to control samples of extruded corn grits. In addition, it can be seen that bulk density of the extruded mixture of corn grits and chickpea slightly increased with the increase of proportion of chickpea flour in mixture. The results obtained by measuring of bulk density are in accordance with the results of measurements of expansion - extrudates with the lower expansion had the higher bulk density. These results are consistent with the results of other investigations.[12-14] Pastor-Cavada et al.[13] investigated the influence of wild legume additions on physical and nutritional properties of extruded products based on whole grain corn and brown rice. They concluded that addition of raw materials rich in fiber and protein in flour materials causes an increase of bulk density. The research conducted by Wang and Ryu[14] showed that the bulk density of extruded corn grits decreased with increasing content of corn fiber in mixture. *Texture properties* of extrudates were measured by texture analyzer TA.XT2Plus, whereby results for hardness and fracturability were obtained. From Figure 3 it can be seen that the hardness of extruded corn grits was higher than the hardness of a mixture of corn grits and chickpea, wherein the hardness increased with the increase of the share of chickpea. The texture of extrudates is the subject of numerous studies. Research by Petrova et al.[15] showed that the hardness of extruded lentil grits increases with increasing moisture content due to reduced

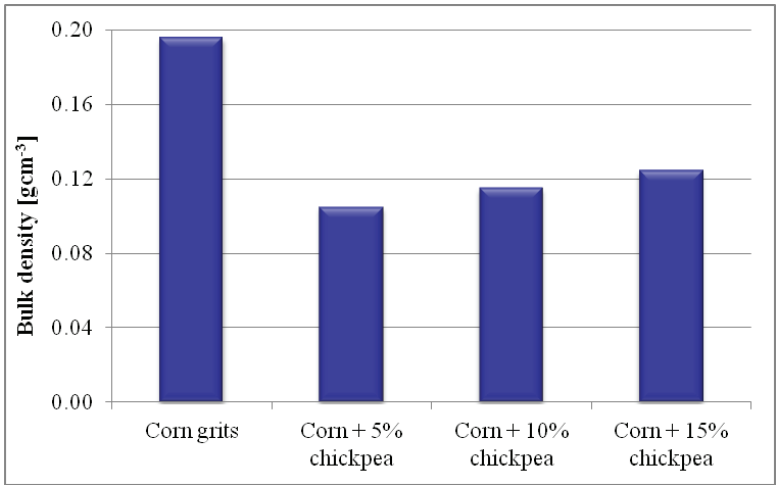

Figure 2. Effect of chickpea flour addition on bulk density (BD) of corn grits extrudates

elasticity of the dough, resulting in reduction of specific mechanical energy and reducing gelatinization and expansion, and increasing the bulk density and hardness of the extrudates. Li et al.[16] studied the textural changes in soybean and corn extrudates. They found that increasing the share of soybean in mixture and the increase of screw speed significantly decrease the hardness of extrudates, while the increase of moisture content increases it. This shows that increasing of soybean proportion in mixture requires a corresponding increase of moisture content to obtain desired hardness of final product. Reducing hardness of extruded snack products based on chickpea with decreasing moisture content was shown by the investigation conducted by Meng et al.[17]. In addition, Figure 3 shows that with addition of chickpea fracturability slightly increased, and it was slightly lower for mixtures with higher chickpea content.

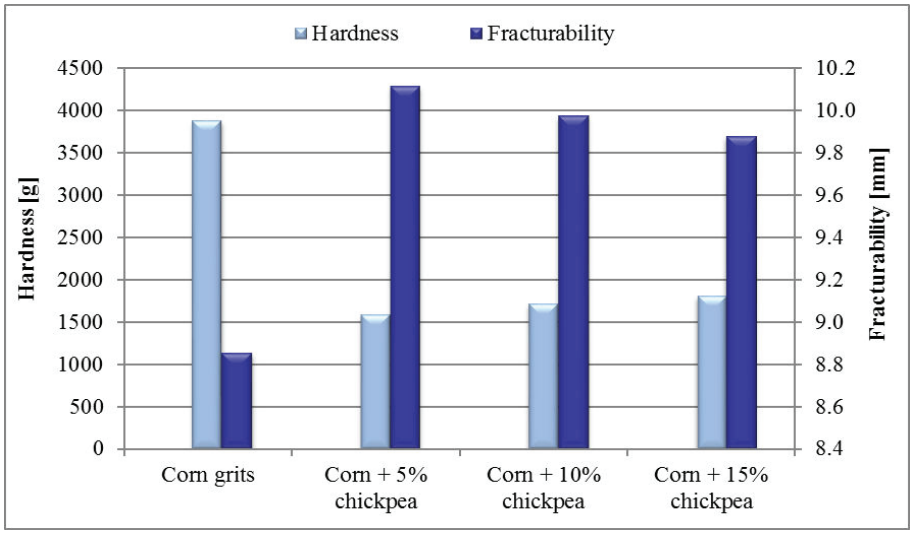

Figure 3. Effect of chickpea flour addition on texture properties of corn grits extrudates

Results of measuring the influence of extrusion process and chickpea flour addition in corn grits on color properties are presented in Table 1. Color is determined by chromameter in CIELab and LCh color spaces. Primarily, it can be seen the differences in color between the extruded and non-extruded samples. By observing the parameter *L**, which refers to the lightness, it can be seen that its values decreased, i.e. the samples were darkened. The values of parameter *C*,

which is used to describe the color saturation, decreased after performing extrusion, whereby the values were lower when the proportion of chickpea in the mixture was higher. Values of the parameter *a** were positive for all non-extruded samples and extruded mixtures, indicating that these samples were in domain of red. In the case of non-extruded samples, the maximum value had a mixture with 5% chickpea (0,69 ± 0,05), while the lowest had a mixture with 15% chickpea (0,21 ± 0,02). For extruded samples situation was reversed, i.e. the highest value was observed in a mixture with 15% chickpea (0,80 ± 0,06), and the lowest in mixture with 5% chickpea (0,27± 0,02). The only negative value was obtained for the extruded corn grits (2,19 ± 0,02), and this sample was in domain of green. All *b** values were positive, indicating that samples were in domain of yellow. Values were higher for non-extruded samples, but in the both cases decreased with increasing chickpea content. Values of the parameter *h°*, which show the hue, are in the range from 0° (red), through 90° (yellow), 180° (green), 270 ° (blue) back to 0°. For investigated samples *h°* values ranged from 92,70 ± 0,02 for extruded corn grits, to the minimum value of 88,84 ± 0,08 for extruded mixture of corn grits with 15% chickpea flour. So, the parameters a* and b* are confirmed, because obtained values for h° indicate that the color of samples was in domain of yellow and red, or in green domain in the case of extruded corn grits sample. The main reason of color change during the extrusion process is formation of Maillard products. The influence of extrusion parameters and application of different raw materials on the color of extruded products is subject of numerous studies[18-21]. Shirani and Ganesharanee[5] in their investigation showed that addition of chickpea flour during the extrusion process leads to darkening, which is in accordance with these results.

Table 1. Effect of extrusion process and chickpea flour addition in corn grits on color change

Sample	Non-extruded samples					
	L*	**a***	**b***	**C**	**h°**	**ΔE**
Corn grits	82,41 ± 0,04 [a]	0,36 ± 0,06 [b]	47,74 ± 0,06 [d]	47,74 ± 0,06 [d]	89,56 ± 0,07 [b]	
Corn + 5% chickpea	82,56 ± 0,03 [b]	0,69 ± 0,05 [c]	43,82 ± 0,08 [c]	43,82 ± 0,08 [c]	89,10 ± 0,06 [a]	3,93
Corn + 10% chickpea	82,59 ± 0,03 [b]	0,22 ± 0,02 [a]	43,34 ± 0,01 [b]	43,34 ± 0,02 [b]	89,70 ± 0,02 [c]	4,41
Corn + 15% chickpea	82,91 ± 0,02 [c]	0,21 ± 0,02 [a]	40,98 ± 0,10 [a]	40,98 ± 0,10 [a]	89,66 ± 0,08 [c]	6,78
Sample	**Extruded samples**					
	L*	**a***	**b***	**C**	**h°**	**ΔE**
Corn grits	81,82 ± 0,02 [d]	-2,19 ± 0,02 [a]	46,49 ± 0,02 [d]	46,54 ± 0,01 [d]	92,70 ± 0,02 [d]	2,91
Corn + 5% chickpea	77,89 ± 0,03 [c]	0,27 ± 0,02 [b]	40,61 ± 0,03 [c]	40,61 ± 0,03 [c]	89,53 ± 0,04 [b]	8,44
Corn + 10% chickpea	77,70 ± 0,02 [b]	0,33 ± 0,02 [c]	39,04 ± 0,02 [b]	39,05 ± 0,02 [b]	89,60 ± 0,03 [c]	9,89
Corn + 15% chickpea	76,42 ± 0,05 [a]	0,80 ± 0,06 [d]	38,88 ± 0,06 [a]	38,89 ± 0,05 [a]	88,84 ± 0,08 [a]	10,7

In Table 2 the effect of extrusion process and chickpea flour addition on viscosity of mixtures based on corn gritsis shown, which is determined by Brabender Micro Visco-Amylo-Graph. From the results it can be seen that the extrusion led to a significant decrease in peak viscosity (which indicates the maximum viscosity after gelatinization of starch) in all samples. Addition of chickpea caused a reduction of peak viscosity in extruded and non-extruded samples. After heating to 92 °C there was a decrease in viscosity for all samples. In non-extruded samples viscosity was higher for mixtures with chickpea flour and it increased proportionally to the increase of chickpea content, while in the case of extruded samples viscosity was lower in the mixtures with chickpea, wherein viscosity values of mixtures were higher again for samples with higher content of chickpea. After 5 minutes mixing at 92 °C, in the case of non-extruded samples, viscosity is increased again to the approximately initial values, while in extruded samples viscosity continues to decrease. The low values of *breakdown* (*breakdown = peak viscosity - viscosity at 92 °C / 5 min*) in non-extruded samples indicate a good stability during mixing at high temperatures. On the other hand, extruded samples showed less stability at high temperatures, which is particularly related to mixtures with higher content of chickpea. After cooling to the temperature of 50 °C there was a significant increase in viscosity for all samples as a result of starch retrogradation. The tendency of retrogradation can be read from the values of *setback* (*setback = viscosity at 50 °C - viscosity at 92 °C / 5 min*). Based on the obtained results it can be seen that non-extruded samples are significantly more prone to retrogradation compared to extruded samples. In case of non-extruded samples, retrogradation tendency increased with the increase of chickpea content, while in the case of extruded samples mixtures with chickpea showed significantly lower tendency to retrogradation compared to the control sample of corn grits. Effect of extrusion process on rheological properties of different types of flour is the subject of numerous studies. Nascimento et al.[22] in their research studied the influence of semi-defatted sesame oil cake on viscosity of corn expanded extrudates. Paste viscosity of raw corn grits showed high peak viscosity at 95 °C and high setback viscosity, while samples with sesame oil cake flour presented a bimodal shape viscosity at 95 °C with a mild drop during cooling step. Carvalho et al.[23] concluded that the viscosity of paste depends to a large extent on the degree of gelatinization of the starch granules and the rate of molecular breakdown. To the similar observations came Duarte et al.[24] in the research about addition of soybean hull in corn extrudates. They found that increasing the soybean hull content resulted in reductions in cold and peak viscosity values. A decrease in the peak viscosity values could be the indication of the effect of fibre during extrusion, which may have contributed to the increase in starch damage.

Table 2. Effect of extrusion process and chickpea flour addition in corn grits on rheological properties

	Corn grits	**Corn + 5% chickpea**	**Corn + 10% chickpea**	**Corn + 15% chickpea**
		Non-extruded samples		
Peak viscosity [BU]	736,0 ± 3,0 ^{c}	673,5 ± 3,5 ^{b}	645,0 ± 3,0 $^{a, b}$	609,0 ± 23,0 ^{a}

Viscosity at 92 °C [BU]	111,5 ± 2,5 [a]	112,0 ± 8,0 [a]	129,5 ± 16,5 [a]	147,5 ± 9,5 [a]
After mixing at 92 °C [BU]	736,5 ± 2,5 [c]	672,5 ± 1,5 [b]	643,5 ± 11,5 [b]	596,0 ± 19,0 [a]
Viscosity at 50 °C [BU]	1096,5 ± 2,5 [a]	1089,5 ± 14,5 [a]	1208,0 ± 1,0 [b]	1223,5 ± 48,5 [b]
After mixing at 50 °C [BU]	1098,5 ± 3,5 [a]	1131,0 ± 16,0 [a, b]	1169,5 ± 19,5 [b]	1138,0 ± 11,0 [a, b]
Breakdown [BU]	0,0 ± 0,0[a]	2,0 ± 0,0 [a]	4,0 ± 4,0 [a]	18,5 ± 0,5 [b]
Setback [BU]	356,5 ± 5,5 [a]	436,5 ± 13,5 [a, b]	550,0 ± 2,0 [b, c]	606,0 ± 68,0 [c]
Extruded samples				
Peak viscosity [BU]	148,5 ± 4,5 [b]	114,5 ± 9,5 [a]	140,0 ± 10,0 [a, b]	138,5 ± 3,5[a, b]
Viscosity at 92 °C [BU]	91,5 ± 3,5 [b]	0,0 ± 0,0 [a]	8,5 ± 8,5 [a]	14,5 ± 7,5 [a]
After mixing at 92 °C [BU]	67,0 ± 4,0 [b]	0,0 ± 0,0 [a]	0,0 ± 0,0 [a]	0,0 ± 0,0 [a]
Viscosity at 50 °C [BU]	191,5 ± 3,5 [b]	41,0 ± 11,0 [a]	65,0 ± 13,0 [a]	72,0 ± 7,0 [a]
After mixing at 50 °C [BU]	197,5 ± 4,5 [b]	50,0 ± 11,0 [a]	76,5 ± 10,5 [a]	80,0 ± 6,0 [a]
Breakdown [BU]	81,5 ± 0,5[a]	114,5 ± 9,5[b]	140,0 ± 10,0 [b]	138,5 ± 3,5 [b]
Setback [BU]	119,5 ± 0,5 [b]	37,5 ± 11,5 [a]	62,0 ± 13,0 [a]	69,0 ± 7,0 [a]

CONCLUSION

Investigation was conducted to determine the possibilities of application of chickpea flour in production of extruded products based on corn grits. Chickpea flour addition in corn grits resulted in the increase of expansion ratio (*ER*) and fracturability, but reduction of bulk density (*BD*) and hardness of extrudates. Furthermore, addition of chickpea flour and extrusion process resulted in significant colour change, where the total colour change (ΔE) increased proportionaly to chickpea level, with more pronounced change in extruded products. After extrusion process, peak, hot and cold viscosity decreased in all samples, and the extruded samples were less prone to retrogradation. Based on the foregoing it can be concluded that chickpea flour can successfully be added to the corn grits in order to produce final products of snack type, as well as modified flour, by extrusion process.

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