CONTENT

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Transitioning to Zero Waste in Agro-Food Sector – Novel Solutions for By-Product Valorisation

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Abstract

Food industry is prompted to make a production eco-friendly and sustainable. Among other issues, by-products generated during processing received a great attention due to large quantities and valuable chemical composition – high contents of fiber, protein, and/or bioactive compounds. They are no longer considered as a waste, but as a valuable resource for food, feed and energy production. This article presents results gained through different projects conducted by the authors where solutions for the use of food industry by-products in food have been found. Brewer's spent grain, apple pomace, sugar beet pulp, oil press cakes, cocoa shell, citrus peel and even tobacco industry waste contain compounds that can be isolated and used in the form of extracts in food and other industries, but different ways of use of by-products "as such" are also shown on the examples of snacks, biscuits and chocolate, where not only problem of by-product disposal was resolved, but the nutritional values of these products were increased. Although projects were conducted locally, the results and findings can be applied worldwide in order to resolve food industry by-product issues.

Keywords: *Brewer's spent grain, apple pomace, sugar beet pulp, oil press cakes, cocoa shell, citrus peel, tobacco waste, extraction, snack, confectionary*

1. Introduction

Food industry is a large burden to the environment. It was estimated that app. 100 million tons of waste in food chain had been produced in EU-28 annually. In developed countries, 42% of waste is produced at the consumer level (in households), 39% in food production, 14% in food service and 5% in retail [1]. Food waste produces app. 3.3 billion tons of CO_2 annually, and food waste management requires significant resources, such as water, energy, labor, soil and money [2]. On the other hand, reduction of waste and by-product generation in food chain by ¼ globally could provide enough food to feed app. 870 million people, or 12% of current population [3]. These numbers indicate necessity for prompt reaction and major modifications and adjustments of food processing.

The framework was established in 2015, when United Nations published Sustainable Development Goals [4], which were adopted in national strategies worldwide. These goals need to be achieved by 2030. Therefore, any research directed towards lower use of toxic chemicals, efficient energy use, rational waste management and industry by-products is heartily welcomed on an international level. Both science and industry have been encouraged to seek solutions to utilize food industry by-products in such manner where firstly they would be used as food, followed by utilization in feed and finally in energy production.

As in other countries, waste disposal in Croatia represents an important national issue [5], so for the last couple of years researches focused on solving that particular issue are welcomed, especially those tackling the problem of different industrial waste.

Another important aspect is a high interest towards possible use and application of different by-products, especially from the food industry. These by-products often contain large quantities of bioactive components, vitamins, minerals, etc. and could be a highly valuable raw material for the food processing [6]. Producing food/products with added value in terms of health preservation and protection, improved consumers' diets and promotion of good health and nutrition is prioritized by the European food and drink manufacturers association.

Consequently, by-product utilization has become one of the fastest growing area of research because it represents a cheap and nutritiously highly valuable raw material, and by using it in subsequent industrial processes more efficient waste management is achieved, fully in line with the UN's Sustainable Development Goals. Also, economic efficiency of a particular production process is increased, because along with the reduction of waste, added value is achieved.

As a result, the price of thus produced food should decline, and better usage of resources could benefit targeting zero hunger in the World.

Additionally, the industrial innovation and responsible production are important drivers of today's research focused on the area of sustainable development. The emphasis has been also put on the potential of a number of new, innovative techniques, so called green extraction techniques and their possibility for application on various industrial by-products. Advantages of these techniques compared to conventional extraction include shorter processing time, without or with minimal organic solvent utilization, under significantly lower temperatures, which consequently improves the quality of the final product, higher energy efficiency, higher yield of extracted components and environment preservation.

Following this strategy, our research group decided to take part in seeking solutions to "return" by-products into food, at least partially, and by employing the "think globally – act locally" approach. By now, three major and several minor research projects of our team have been targeting by-products from local food industry in Croatia, eg. brewery, sugar production, apple processing, edible oil (from different raw materials) and chocolate production with two major goals: reducing food waste at processing level and enrichment of food products with nutritionally valuable components.

In the following text, the major aims and results of (still ongoing) research that have been collected by now are reviewed.

2. Application of food industry by-products in development of functional and environmentally friendly extruded food products and additives

The project of the same name was funded by Croatian Science Foundation under the number HRZZ-IP-2013-11-1321. It lasted from 2014 to 2018 and it was focused on utilization of apple pomace, brewer's spent grain, sugar beet pulp and defatted oil press cakes (pumpkin, hazelnut, camelina, hemp) in production of modified flour, directly expanded products (flips) (Fig. 1) and cookies.

Corn grits were selected as the base material for the extrusion process, since this is commonly used raw material in snack production and corn flour has high glycemic index, making it less and less popular with consumers. Snacks and cookies were target products because they are widely consumed by all population groups, from children to elderly, and are energy dense, with low nutritive value. All by-products listed above are rich both in fiber and bioactive compounds and could reduce the caloric value of cookies and flips, while increasing fiber, vitamin and/or mineral contents. The review of composition and beneficial effects of some food industry by-products was given in detail by Jozinović et al. [7].

Fig. 1. Extruded corn snack without by-products, and with brewer's spent grain, sugar beet pulp and apple pomace

The first part of research included production of directly expanded snack (flips) in a laboratory single-screw extruder, enriched with apple pomace, brewer's spent grain and sugar beet pulp. Since all these by-products contain large quantities of water, they were dried in laboratory oven with forced air circulation at 60 °C and milled to pass through 2 mm sieve. Dried and milled by-products were added to corn grits in ratio of 5, 10 and 15% d.m. and moisture of mixes was set to 15%. Control sample was pure corn grits with 15% moisture. After equilibration, samples were extruded (at temperature profile: 135/170/170 °C, with 4:1 screw and 4 mm die) and dried at ambient conditions [8].

Although apple pomace changed the color of extrudates significantly compared to corn extrudate, it did not reduce expansion and increase hardness unlike other two by-products. Additionally, although hard, extrudates with sugar beet pulp were well expanded. The main fiber in brewer's spent grain, according to literature, is cellulose, and apple- and sugar beet pulp are significant sources of pectin. This led us to believe that pectin has an important role in expansion. Apple pectin has good gelling properties, unlike sugar beet pectin and this difference may have caused the difference in the hardness.

To explore this hypothesis, we prepared mixtures of corn grits with sugar beet pulp and brewer's spent grain with the addition 0.5 and 1% of commercial pectin and extruded them at the same conditions. The resulting extrudates were well expanded and had desirable hardness, with satisfactory results for sugar beet pulp at level of 0.5% pectin, whereas for brewer's spent grain 1% was needed [8]. This confirmed that pectin indeed has an important role in expansion. We assume this may be attributed to pectin ability to reduce fracture of cell walls by increasing their extensibility along with emulsifying and stabilizing effect on fats and proteins. The fact that sugar beet pulp pectin only contributed to expansion and not hardness may be attributed to the presence of large number of acetyl groups, its relatively small size and low average molecular weight, due to which it also has poor gelling properties.

The fiber analysis revealed significant increase of total fiber content in extrudates by addition of by-products, with the most pronounced effect of brewer's spent grain on insoluble and sugar beet pulp on soluble fiber. Snacks with 5% of by-products can have a health claim "source of fiber", while snacks with higher content of by-products can carry a claim "rich source of fiber". This is very important from the nutritional point of view and is significant improvement of otherwise nutritionally undesirable products [9].

Trained sensory panel evaluated samples with lower content (5%) of by-products only slightly lower than control sample, and, although samples with larger contents of by-products (10 and 15%) received statistically significantly lower grades, they were still in the acceptable range [8]. Here, we have to emphasize that snacks were not additionally aromatized nor salted, which would increase their palatability and overall sensory score.

The second part of the project was focused on press cakes from oil production, specifically hazelnut, camelina, pumpkin and hemp. Considering that in the region around Osijek (Croatia) there are many small oil producers that produce cold pressed oils from afore mentioned raw materials, firstly, we conducted cold pressing of selected oils in a laboratory scale. Since significant amount of oil remained in the press cakes after the cold pressing and this would cause problems with sliding of material inside the extruder, press cakes were additionally defatted using supercritical fluid extraction (more about this process in the chapter below). Defatted oil press cakes were added to corn grits in 3, 6, and 9% (much less than afore mention by-products due to the negative impact on aroma in higher amounts). Pectin was added (1%) and expanded snacks were prepared. The effect on properties of extruded snacks was similar to above, with high sensorial acceptability [10].

Additional research involved exploring the potential of supercritical CO_2 extrusion in a single screw extruder (supercritical extrusion is normally conducted in twin-screw extruders). All defatted press cakes were added in the same manner as previously described, only without pectin. The hypothesis was that CO_2 would enable expansion at the exit of the extruder, however, this did not happen. Extrudates were not expanded at all, but pores were more evenly distributed and finer than in classically produced pellets. This led us to try secondary expansion of pellets and excellent results were achieved by microwave process [10]. The benefit of supercritical extrusion in production of secondary expanded products is that no puffing agents are needed, unlike with traditional process.

The third part of research was the production of modified flour and cookies enriched with extruded flour. For this part of the research, we focused on apple pomace and brewer's spent grain, based on the fact that apple is normally used in bakery and confectionary products and consumers are well adjusted to its taste, and brewer's spent grain is a source of ß-glucan, which has a positive effect on cholesterol level and postprandial glucose in blood according to EFSA health claims [11,12].

Firstly, corn grits were extruded with the addition of by-products in levels 15, 30 and 45%. Extrudates were milled and used in cookie production as a substitute for 5, 10 and 15% of wheat flour. The physico-chemical analyses revealed that such produced modified flour may be used in the production of cookies enriched with fiber up to 15% level, where all samples may carry a health claim "source of fiber", and some even a claim "rich source of fiber", without significant alterations in physical and sensory characteristics of cookies [13].

Encouraged by excellent results in this project, we decided to further explore potential of food industry by-products for extraction of bioactive components.

3. Application of innovative techniques of the extraction of bioactive components from by-products of plant origin

The project of the same name was funded by Croatian Science Foundation under the number HRZZ- 2017-05-UIP-9909. It started in 2018 and will last until 2023 and is focused on production of the extracts rich in bioactive components from selected by-products using different innovative green extraction techniques. Their application increases the extraction yield, higher content of bioactive components in the extracts, higher quality of the extract, and resource savings in time, solvents, etc. [14]. Each of the above mentioned extraction techniques has its advantages, so it is necessary to examine the process parameters of each extraction procedure and to compare them with conventional extraction methods to obtain a true insight about the impact of a particular method on the content of the bioactive components in obtained extracts.

Cocoa shell, tobacco industry waste and citrus peel are only some of the potentially valuable by-products that can be successfully used in the production of extracts rich in bioactive components and are therefore selected as raw materials in the project.

3.1. Focus on cocoa shell

During the processing of cocoa beans (*Theobroma cacao* L.), the cocoa shells, comprising at least 10% weight of cocoa fruit, is discarded. The cocoa shell is mainly used in animal feed preparation, fertilizers or as a fuel. So far, the cocoa shell has been the main source of dietary fiber [15], but new studies have also shown the content of some other valuable bioactive components such as phenolic compounds (Fig. 2). Phenolic components of this potential raw material have an antioxidant effect and protect cells from oxidative stress. Cocoa shell is also a potential source of proteins [16], theobromine, theophylline, caffeine [15] and water-soluble pectins [17]. Theobromine is a potential diuretic, stimulates kidney circulation and alleviates elimination of harmful substances in the urinary system [18]. Caffeine, theobromine and theophylline have a similar effect on the body such as stimulation of the nervous system, stimulation of the heart and bone muscles and muscle relaxation, but with different intensity. During the fermentation of cocoa beans, these compounds migrate into the cocoa shell, making it inadequate for use in animal feed. The relatively low fat content and low concentration of soluble sugars are an advantage of this potential raw material and make it a useful ingredient for functional energy-reduced foods [18]. This matrix is still insufficiently explored especially in Republic of Croatia and therefore in this project special attention will be given to research on this by-product.

Fig. 2. Bioactive components in cocoa shell and their potential health effects

3.2. Focus on tobacco industry waste

During tobacco production in the industry, large quantities of waste (leaves, parts of leaves) that cannot be recycled are produced. This waste is hazardous and represents a significant environmental problem [19]. Tobacco leaves (*Nicotiana tabacum*) contain pyridine alkaloids, primarily liquid nicotine [20]. Nicotine has a wide range of applications, including pharmaceutical, chemical, industries, as well as in the tobacco industry as the primary additive in cigarette manufacturing. It has antimicrobial and insecticidal activity, which is why it is used as a natural insecticide [21]. By reducing the nicotine level in the polluted solid to the level below the legal threshold using different extraction techniques, it would be possible to change the classification of waste from “hazardous” to “special” waste, which could then be simply removed as urban waste or further used as a starting material for extraction of bioactive components [19]. In addition, tobacco leaves contain carbohydrates, proteins, high concentrations of organic acids, glucosides, phenolic compounds, flavonoids, solanesol, and since waste is actually a parts of leaf of different granulation, all of the components are also found in the tobacco waste (Fig. 3) [21].

is rutin. Its potentially positive effect is manifested in reducing capillary, swelling and bruising and because of that it is used to treat venous insufficiency and to improve microvascular blood flow so tobacco waste can be an efficiently source for rutin extraction for the pharmaceutical industry [32]. This matrix is still insufficiently explored especially in the Republic of Croatia and therefore special attention to research on tobacco waste is given in the project.

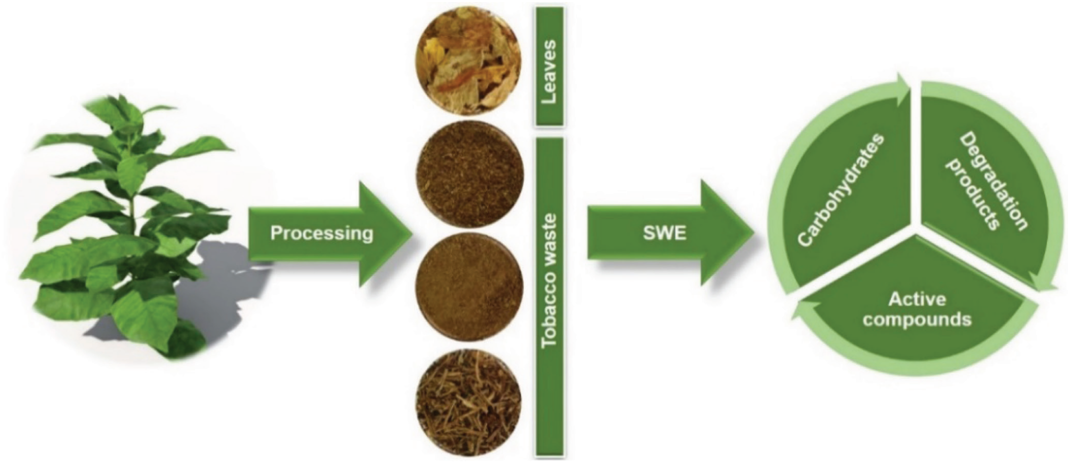

Fig. 3. Tobaco waste extraction (one example using SWE)

In tobacco, a high amount of solanesol is found. It is the terpene alcohol, consisting of nine isoprene units that play an important role in plant interactions with their environment, and it is a key intermediary for the pharmaceutical synthesis of supplements and ubiquitous drugs [22]. It has antioxidant, antibacterial, anti-inflammatory and anti-septic activity [23]. It is industrially important because it represents the starting material for coenzyme Q10 and vitamin K analogues [24]. Since coenzyme Q10 is present on the market in the form of dietary supplements to relieve pain caused by migraines [25], has protective role in Parkinson disease and other neurodegenerative diseases, a positive effect on regulation of blood pressure and glycemia in type 2 diabetic patients [26], solanesol demand is on the rise.

Clorogenic acid is used as an additive in beverages, food, cosmetics as well as in medical substances. In addition, it has antibacterial and antiviral properties and is a natural antioxidant and anticancer agent [27]. Caffeic acid is one of the natural phenolic compounds widespread in plant materials, and recently, pharmacological studies have shown that caffeic acid has antioxidative [28], anti-apoptotic [29], antidepressive [30] and anti-cancer effect [31]. Tobacco industry waste is a potential raw material for producing of caffeic acid. One of the most important flavonoids found in tobacco

3.3. Focus on citrus peels

One of the main by-products of citrus peel is essential oil. In our project, essential oils are produced by different extraction techniques from selected types of different citrus peels (special Croatian varieties) which have not yet been explored. Along with aroma compounds, citrus peel is also rich in phenolic components, such as phenolic acids and flavonoids. The most common flavonoids present in the citrus peel are hesperidin, naringin, narirutin and neohesperidin [33]. Hesperidin is found in citrus, as well as in peel in high concentrations, especially in sweet orange and lemon [34] and possesses different properties, such as positive effects on vascular or cardiovascular system [35], protective effect in case of exposure to radiation [36], anti-inflammatory [37], anticancer [38], antimicrobial [39], antioxidant [40] and a negative impact on fertility [41]. Hesperidin can be used as a dietary supplement primarily in combination with other components such as vitamin C. Also naringin, a flavonoid found in higher concentrations in the citrus peel is determined [33]. Naringin has a number of positive effects on human health and life, such as antioxidative [42], anti-inflammatory [43], anticancer [44], gastroprotective function [45], positive effect on cardiovascular disorder [46], diabetes complications, bone diseases [47] and allergy [48].

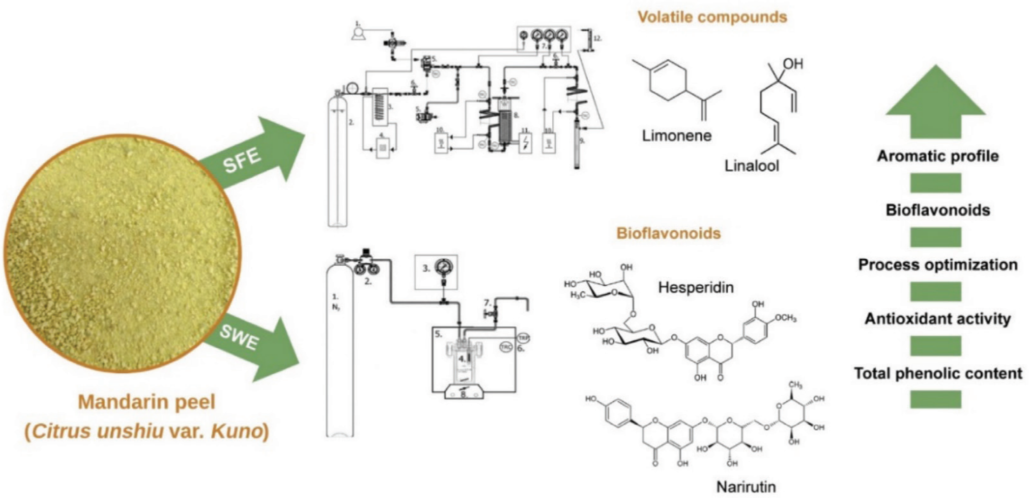

Fig. 4. Mandarin peel extraction (one example using SWE and SFE)

The innovative green extraction techniques in this project are applied in the isolation of different bioactive components from selected by-products with finding the potential applications in other industries. One example is given in the Fig. 4 for the extraction of bioactive compounds from mandarin peel variety Kuno using two different extraction techniques: SFE for the isolation of nonpolar volatile compounds and SWE for the extraction of polar bioflavonoids.

4. Cocoa shell as a raw material in food production

With good results of the previous projects and chocolate factory on hand, we tried to further valorise cocoa bean shell. Namely, the shell represents up to 20% of cocoa bean [49] and is discarded prior or after the roasting of cocoa beans. It has application in animal feed, for mulching in agriculture, biofuel production and as an adsorbent. Despite this, it still represents a major load for the environment due to limitations: low bulk density makes it very light and wind spreads it easily abroad; it contains methyxantines that are harmful for some animals and have to be extracted before inclusion into feed; polyphenols inhibit microflora and microbial biofuel production is limited [50]. Therefore, we tried to put it “back into food”. Firstly, we continued with extrusion experiment and added it to corn grits in the ratio of 5, 10 and 15% d.m. and expanded it directly as described above (Fig. 5). Obtained extrudates were darker and harder than control sample, but acceptable for consummation, with increased polyphenol content [51].

Fig. 5. Extruded corn snack with added cocoa shell.

Further investigation is oriented towards chocolate and chocolate-like products within an ongoing project “Application of cocoa husk in production of chocolate and chocolate-like products (UIP-2017-05-8709)” financed by Croatian Science Foundation. Current scientific researches in the chocolate technology largely deal with polyphenol content in the products [52], influence of growing conditions and origin of cocoa beans [53], cocoa bean processing [54] and chocolate processing [55] on polyphenol and/or aroma profile and increase of polyphenol content in chocolate by addition various additives of plant origin, rich in polyphenols [56].

Cocoa shell has also been in focus of scientific research as a source for extraction of polyphenols, theobromine, dietetic fibre, pectin; in preparation of milk beverages, enzymes, as an adsorbent in water purification and biogas production substrate. Furthermore, it was used to enrich cookies and bread, as well as in production of muffins enriched with cocoa husk fibre. Cocoa husk polyphenols were antioxidants in frying oil and cooked beef [10,15]. As far as members of this research group are aware, scientific researchers have not dealt with cocoa husk application in chocolate.

Cocoa husk is not used in current chocolate production processes above 3% since it influences aroma (high content of polyphenols), high fibre content makes it coarse and difficult to reduce particle size and if used in quantities exceeding 3%, it makes problems with viscosity.

Firstly, we tried to explore if HVED (High voltage electrical discharge) treatment would be a beneficial technique in decontamination and disintegration of the husk. We came to some interesting findings, from polyphenol content [49], where we determined that virtually all caffeic acid is extracted into water during HVED treatment, unlike (+)-catechin, (-)-epicatechin, (-)-epicatechin gallate, 10 – 90% of which was retained in the husk. Also, we determined reduction of the contents of acrylamide and HMF in cocoa husk to quantities below the limit of quantification, or even below the limit of detection [57] and explained HMF and acrylamide content reduction in the treated husk by different chemical mechanisms [58].

In parallel, we have produced dark and milk chocolates with cocoa husk (Fig. 6). The content of the husk was 5, 10 and 15% for dark and 2.5 and 5% for milk chocolates. These percentages were selected based on EU legislation for quality of chocolate, where we aimed to obey the legitimate cocoa butter and non-fat cocoa solids content. The addition of both treated and untreated cocoa shells resulted in softening and darkening of samples, which could have a positive effect for consumers. However, the particle size distribution and rheology were negatively affected, which could pose the problem in the industry [58].

Conclusions

From the results listed above, it is evident that food industry by-products have a great potential to be used as a raw material in food industry and as a source of bioactive components for pharmaceutical industry. The results of the presented project research will contribute to solving the problem of large quantities of organic waste, having both environmental and financial effects. Research on industrial scale is needed in order to adjust processes where necessary and to maximize usage of plant raw materials. Special emphasis in the projects is on the possible commercial valorization of the research results and on the technology transfer of those scientific results to the industrial level.

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Fig. 6. Laboratory production of chocolate – refining in a ball mill, tempering and moulded chocolate.

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