

RYE AND OAT CRISPBREAD IMPROVEMENT WITH BIOLOGICALLY ACTIVE SUBSTANCES FROM PLANT BY-PRODUCTS

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Abstract

Vegetable processing in food industry results in significant number of by-products – peel, mark, bark, seeds still rich in bioactive compounds. The objective of this study was to investigate the stability of total phenolic content (TPC) and antioxidant activity after high temperature short time (HTST) extrusion cooking of a rye and oat- based matrix with addition of apple, carrot and pumpkin by-product flour (BPF) in various amounts (5%, 10%, 15% and 20%). Extrusion was performed with co-rotating twin-screw extruder (compression ratio 8:1) at Ltd MILZU. The main drive of extruder was provided with a 7.5 HP motor (400 V, 3 HP, 50 cycles). Temperatures for extrusion zones were 125 °C /135 °C /145 °C. TPC was determined using the Folin Ciocalteu method. Antioxidant activity was evaluated by free radical 2, 2-diphenyl-1-picrylhydrazyl (DPPH) antioxidant scavenging activity. TPC in cereal-based crispbread was 62.03 ± 0.15 mg GAE g⁻¹ DW before extrusion and 37.73 ± 1.96 mg GAE g⁻¹ DW after extrusion. Addition 20% of apple BPF increased TPC in crispbread to 193.92 ± 1.37 , carrot BPF 171.36 ± 6.97 and pumpkin BPF to 195.09 ± 4.68 mg GAE g⁻¹ DW after extrusion. Antioxidant activity of control (20% oats, 80% rye flour blends) sample was 0.516 ± 0.192 mg TE g⁻¹ DW but in samples with addition of 20% by-products, it was significantly higher reaching 0.926 ± 0.05 TE g⁻¹ DW in samples with pumpkin by-products after extrusion.

Key words: antioxidants, by-products, crispbread, extrusion, total phenolic content.

Introduction

Roughly one third of the food produced in the world for human consumption gets lost or is wasted. It constitutes approximately 1.3 billion tonnes per year. Around 100 million tonnes of food are wasted annually in the EU (Vaqué, 2015). If nothing is done, food waste could rise to over 120 million tonnes by 2020 (Turon *et al.*, 2018). Global quantitative food losses and waste per year are roughly 30% for cereals; 40 – 50% for root crops, fruits and vegetables (Vaqué, 2015). The amount of food lost or wasted every year is equivalent to more than half of the world's annual cereals crop (2.3 billion tonnes in 2009/2010).

The vegetable and fruit processing industry produces such by-products as peel, mark, bark, seeds that can be used in the manufacture of other foods. They contain a lot of biologically valuable compounds, such as fibre, micro and macronutrients,

organic acids. Food processing waste has the potential to be converted into useful products and utilized as supplements for the functional ingredient for consumers as a source of functional compounds.

Oats and rye are traditionally crops grown under Latvian conditions, which are valuable raw materials to produce many products, including crispbreads too.

The apple (*Malus domestica*) pomace is used as a substrate in several microbial processes for the production of organic acids, enzymes, and pigments (Figuerola & Mar, 2005). Apple polyphenols are frequently cited as important contributors in different models of human chronic diseases (Elleuch *et al.*, 2011). Apple pomace imparts nutritional benefits in the form of soluble dietary fibres, which are recognized for blood cholesterol-lowering functions (Paraman *et al.*, 2015). The antioxidant activity of apples is rooted in their ability to donate phenolic hydrogens

Table 1

Estimates of food waste in EU *(Stenmark *et al.*, 2016)

Sector	Food waste (million tonnes) with 95% CI**	Food waste kg per Person with 95% CI**
Primary production	9.1 ± 1.5	18 ± 3
Processing	16.9 ± 12.7	33 ± 2
Wholesale and retail	4.6 ± 1.2	9 ± 2
Food service, catering	10.5 ± 1.5	21 ± 3
Households	46.5 ± 4.4	92 ± 9
Total food waste	87.6 ± 13.7	173 ± 27

*EU-28 2012 from this quantitative study. Includes food and inedible ingredients.

**Confidence interval.

to lipid radicals, therefore generally considered to be more potent than as a chain-breaking antioxidant for inhibiting lipid peroxidation in food products thus prolonging their shelf life (Jiang *et al.*, 2001).

The carrot (*Daucus carota*) pomace is a by-product obtained during carrot juice processing and rich source of β -carotene and contains thiamine, riboflavin and minerals (Kaur, Kaur, & Ahluwalia, 2014). Carrot is a significant source of phytochemicals, including phenolic compounds and carotenoids (Arscott & Tanumihardjo, 2010).

Pumpkin (*Cucurbita pepo*) peel is rich in pectin and is an excellent source of β -carotene, which the body converts into the important antioxidant of vitamin A. Pumpkin contains biologically active components such as polysaccharides, proteins and peptides, phenolic compounds, terpenoids and sterols. Pumpkin seeds are rich in carotenoids, including lutein, carotene, and including β -carotene too. The seed oil is rich in unsaturated fatty acids, as linoleic, oleic, and saturated as palmitic, and stearic acids. The oil is also rich in vitamin E, including both γ -tocopherol and α -tocopherol (Mala, 2016). Pumpkin can also be processed into flour, which has a longer shelf-life.

One of the usages of the by-products might be their incorporation in the manufacture of extruded products. The production of foodstuffs by the extrusion method is a way to turn starchy products (grains, potatoes) into readily available and usable products such as breakfast cereals, pasta products, snack bars, chips.

The objective of this study was to investigate the stability of total phenolic content (TPC) and antioxidant activity after high temperature short time (HTST) extrusion cooking of a rye and oat- based matrix with addition of apple, carrot and pumpkin by-product flour (BPF) in various amounts (5%, 10%, 15% and 20%).

Materials and Methods

The study was realised at the scientific laboratories of the Faculty of Food Technology at Latvia University of Life Sciences and Technologies and in JSC MILZU.

For development of crispbread as raw materials 1880 type rye flour (JSC Dobeles dzirnavnieks), oat flour, apple pomace, seeds and peel, carrot pomace and peel and pumpkin peel and pomace were used.

By-products obtained from local juice producers were dried in a microwave – a vacuum dryer “MUSON-1” (Russia) according to the developed program. The necessary amount of microwave energy (magnetron minutes) was calculated according to the weight, moisture of by-products. Dried by-products were ground to a powder by the grinder FOSS KNIFITECTM 1095 (Germany) for 30 seconds each grind. After that they were sieved through 2 mm sieve. TPC content was determined in dried carrot, apple,

pumpkin by-product flour, in rye and oat flour for crispbread production.

Control samples were prepared from rye flour, oat flour (80: 20) and water 17%, based on the recipe of LTD Milzu. Experimental samples were prepared with addition of apple, carrot and pumpkin by-product flour (BPF) 5%, 10% and 15%, 20% to dry ingredients of cereal, a part of cereal flour was replaced.

Samples were prepared with a co-rotating twin-screw extruder (compression ratio 8:1) at LTD MILZU. The main drive of extruder was provided with a 7.5 HP motor (400 V, 3 HP, 50 cycles). Temperatures for extrusion zones according to developed technologies at LTD Milzu were 125 °C /135 °C /145 °C.

Coded samples are displayed in Table 2.

The moisture content of selected material was determined with Memmert equipment Modell-100-800 (Germany) according to standard LVS EN ISO712:2010 A.

The total phenolic content of the extruded product extracts was determined according to the Folin-Ciocalteu spectrophotometric method with modifications. Extraction was performed by the method described by Tomsone and Kruma (Tomsone & Kruma, 2017).

Antioxidant activity of the extruded product extracts was measured based on scavenging activity of the stable 2, 2-diphenyl-1-picrylhydrazyl (DPPH) radical. The radical scavenging activity was expressed as Trolox equivalent (TE) 100g⁻¹ DW of extruded material.

All analysis was performed in triplicate, and results are presented as a mean value \pm standard deviation (SD). Statistically significant differences between results were calculated at the level of confidence $\alpha=0.05$.

The one-way analysis of variance was analysed by Microsoft Excel 2010.

Results and Discussion

Antioxidants are of twofold interest as for food scientists and health professionals and there has been a convergence of interest among researchers in these fields as the role of antioxidants in the diet and their impact on human health has come under attention (Mala, Sathiya, & EKurian, 2016). Antioxidants defend against oxidative injury and are therefore believed to provide protection against various diseases – different types of cancer and coronary heart diseases (Uddin & Ahmad, 1995).

Among the most valuable bioactive compounds in vegetable by-products peel, bark, mark seeds and cereals are the phenolic antioxidants (Awika, 2003).

Scientists Dar, Sharma and Kumar reported a significant decrease in total phenolic content during barley flour extrusion (Dar, Sharma, & Kumar, 2014)

Table 2

Composition of experimental samples

Sample	Composition
Control crispbread	Rye – 80%, oats – 20%
ABF5	95% – Control crispbread, 5% – ABF*
ABF10	90% – Control crispbread, 10% – ABF
ABF15	85% – Control crispbread, 15% – ABF
ABF20	80% – Control crispbread, 20% – ABF
CBF5	95% – Control crispbread, 5% – CBF**
CBF10	90% – Control crispbread, 10% – CBF
CBF15	85% – Control crispbread, 15% – CBF
CBF20	80% – Control crispbread, 20% – CBF
PBF5	95% – Control crispbread, 5% – PBF***
PBF10	90% – Control crispbread, 10% – PBF
PBF15	85% – Control crispbread, 15% – PBF
PBF20	80% – Control crispbread, 20% – PBF

*ABF – apple by-product flour.

**CBF – carrot by-product.

***PBF – pumpkin by-product.

while others show an increase or no change for both phenols and antioxidant activity. Some reports also indicate that extrusion may partly depolymerize some high molecular weight polyphenols like proanthocyanins into lower molecular weight forms (Awika, 2003). A study on dark buckwheat flour reported no changes in antioxidant activity after extrusion at 170 °C (Nayak *et al.*, 2011). Another study showed a significant reduction in antioxidant activity for 60 – 68% and for TPC 46 – 60% in extrusion of barley flour (Altan, McCarthy, & Maskan, 2008).

TPC content was determined in dried carrot, apple, pumpkin by-product flour, in rye and oat flour for crispbread production.

TPC in rye flour was 71.38 ± 11.01 , in oats 24.64 ± 1.68 , in by-product flour ranged from 132.44 ± 11.88 mg of GAEg⁻¹ DW in carrots, 160.23 ± 6.89 mg of GAEg⁻¹ DW in pumpkins, to 187.79 ± 12.63 mg of GAEg⁻¹ DW in apple by-product flour. Results about dried pumpkin TPC reported by Pricina and Karklina (2014) was 672.19 mg GAE 100 g⁻¹ (Pricina & Karklina, 2014). For carrots some authors show

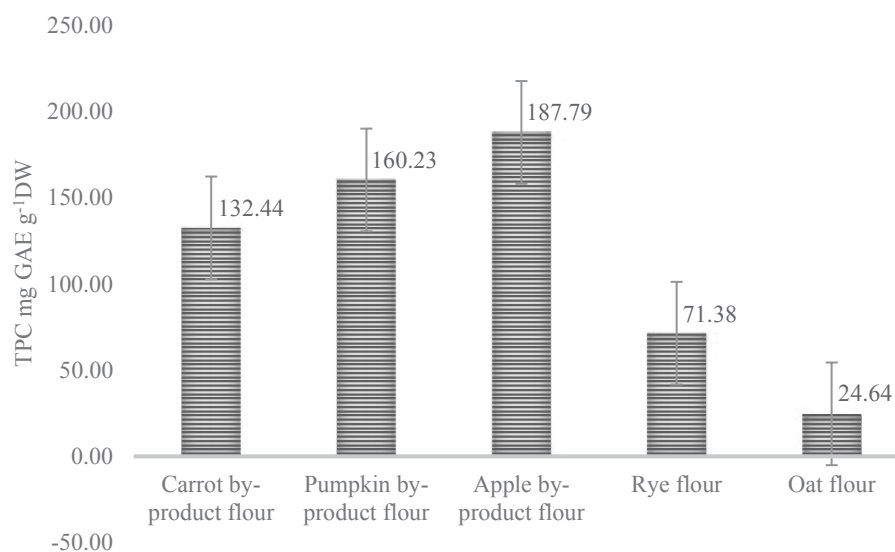


Figure 1. TPC content in rye flour, oat flour and by-product flour.

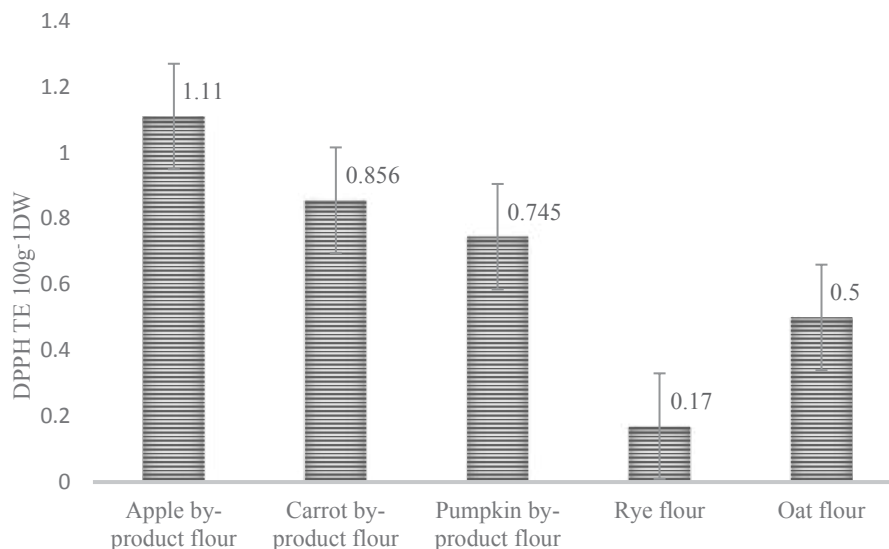


Figure 2. DPPH antioxidant activity in by-products, rye and oat flour.

results ranging from 331.00 to 366.00 mg GAE g⁻¹DW (Arscott & Tanumihardjo, 2010). The difference in results is probably due to the application of different drying methods (Henriques, Guiné, & Barroca, 2012) as phenolic compounds are heatlabile and can break at the exposure to high temperatures.

The polarity of plant radical scavenging components is important factor defining extracts antioxidant activity.

The antioxidant activity of dried by-products, using DPPH assay, was 0.86 ± 0.07 TE 100g⁻¹ DW in carrots, 0.75 ± 0.02 TE 100g⁻¹ in pumpkin and 1.11 ± 0.05 TE 100g⁻¹ DW DPPH antiradical activity in apple by-

product. The DPPH is a stable free radical commonly used to determine the radical scavenging activity or antioxidant properties. The highest antioxidant activity was determined in apple by-product flour as apple by-products contain seeds rich in antioxidants and fatty acids in comparison with peel and bark (Leyva-Corral *et al.*, 2016). Antioxidant activity is inhibited by many factors, mostly the composition of phenolic compounds in product, both phenolic compounds and carotenoids are strong in vitro antioxidants (Arscott & Tanumihardjo, 2010). The phytochemicals present in apples such as carotenoids, vitamins, flavonoids, quercetin, catechin, phloridzin and

Table 3

TPC and DPPH content in experimental samples for crispbread production

Samples	DPPH, TE 100 g ⁻¹ DW		TPC, mg GAE·100 g ⁻¹ DW	
	before extrusion	after extrusion	before extrusion	after extrusion
Control crispbread	0.24 ± 0.06	0.52 ± 0.09	62.03 ± 0.15	37.73 ± 1.96
ABF5	0.28 ± 0.01	0.44 ± 0.03	68.01 ± 0.07	78.57 ± 1.23
ABF10	0.32 ± 0.04	0.58 ± 0.06	74.00 ± 0.05	95.74 ± 1.89
ABF15	0.36 ± 0.03	0.78 ± 0.07	79.98 ± 0.03	156.98 ± 2.80
ABF20	0.41 ± 0.02	0.88 ± 0.06	85.96 ± 0.08	193.92 ± 1.37
CBF5	0.28 ± 0.09	0.54 ± 0.08	65.34 ± 0.11	122.08 ± 3.96
CBF10	0.29 ± 0.07	0.59 ± 0.06	68.64 ± 0.11	133.47 ± 4.73
CBF15	0.33 ± 0.04	0.83 ± 0.05	71.95 ± 0.09	160.70 ± 2.96
CBF20	0.36 ± 0.05	0.95 ± 0.01	75.25 ± 0.05	171.36 ± 6.97
PBF5	0.26 ± 0.07	0.78 ± 0.10	66.15 ± 0.11	177.73 ± 5.09
PBF10	0.29 ± 0.02	0.83 ± 0.04	70.27 ± 0.13	182.32 ± 6.01
PBF15	0.31 ± 0.05	0.88 ± 0.05	74.39 ± 0.09	188.28 ± 6.57
PBF20	0.34 ± 0.08	0.93 ± 0.05	78.51 ± 0.12	195.09 ± 4.68

Table 4

Pearson's coefficients between TPC and antioxidant activity before and after extrusion

Correlation between group	Samples with apple BPF	Samples with carrot BPF	Samples with pumpkin BPF
<i>TPCBE/TPCAE</i>	0.98	0.98	1.00
<i>TPCBE/DPPHBE</i>	1.00	1.00	1.00
<i>TPCAE/DPPHAE</i>	0.98	0.99	0.99
<i>DPPHBE/DPPHAE</i>	0.98	0.98	1.00

TPCBE – TPC before extrusion
TPCAE – TPC after extrusion
DPPHBE – DPPH before extrusion
DPPHAE – DPPH after extrusion.

chlorogenic acid act as strong antioxidants (Shanmugam *et al.*, 2017).

TPC and DPPH were determined for experimental samples with by-products before and after extrusion. Temperatures for extrusion zones according to developed technology at LTD Milzu were 125 °C /135 °C /145 °C, and water added to dry matter was 17%. Results are shown in Table 3.

TPC content was determined before extrusion to predict the changes of TPC activity. In oat rye (control) crispbread TPC decreased after extrusion. Phenolic compounds are heatlabile and can break at the exposure to high temperatures. Viscidi and others (2004) reported a significant loss of TPC during extrusion of oat cereals (Viscidi *et al.*, 2004). In the sample from rye and oats blends (80:20), – control crispbread TPC content after extrusion decreased and varied from 62.03 ± 0.15 before extrusion to 37.73 ± 1.96 mg GAE·100 g⁻¹ after extrusion. Scientists Biel and others have reported losses of up to approximately 60% of phenolic compounds in extruded oat samples, compared to its respective raw sample (Biel *et al.*, 2011). Extrusion increased TPC for all samples with added plant by-products (Table 3). In crispbreads with addition 5% of pumpkin by-product TPC increased from 66.15 ± 0.11 to 177.73 ± 5.09 mg GAE·100 g⁻¹, addition 5% of apple by-product to control sample increased TPC from 68.01 ± 0.07 to 78.57 ± 1.23 mg GAE·100 g⁻¹ after extrusion and addition 20% of ABF increased TPC from 85.96 ± 0.08 to 193.92 ± 1.37 mg GAE·100 g⁻¹. Addition of 20% of PBF increased TPC from 78.51 ± 0.12 mg GAE·100 g⁻¹ before extrusion to 195.09 ± 4.68 mg GAE·100 g⁻¹ after extrusion.

This increase of polyphenol contents after heating is because of the high antioxidant activity after high temperatures during HTST process. The formation of phenolic compounds might be because of the availability of precursors of phenolic molecules by non-enzymatic interconversion (Camire, 2011). Another explanation for the higher TPC after heating is an increased formation of anthocyanin of browning

compounds caused by the Maillard reaction at high temperatures (Basto *et al.*, 2016).

The polarity of plant radical scavenging components is important factor defining extracts antioxidant activity.

The reduction in total phenolic content may be attributed either to the decomposition of phenolic compounds due to the high extrusion temperature. Addition of apple, pumpkin and carrot by-products increased the antioxidant activity in all samples as carotenoids and phenolic compounds are the predominant phytochemicals in all varieties of vegetables and fruits (Konrade *et al.*, 2016).

For all crispbread samples correlation between groups of samples prior to extrusion and after extrusion was very strong 0.91<r<0.99, (p<0.05). To obtain higher TPC and DPPH, it is recommended to add 20% of by-products but further studies are necessary to understand how addition of by-products to cereal crispbreads change the texture, mouthfeel, colour and other physical and sensory features.

Conclusions

Addition of plant processing by-products increased TPC and the antioxidant activity in all samples of rye and oat-based crispbreads. Extrusion increased TPC content in samples with 20% ABF to 193.92 ± 1.37 mg GAE·100 g⁻¹ DW, with 20% CBF to 171.36 ± 6.97 mg GAE·100 g⁻¹ DW, 20% PBF to 195.09 ± 4.68 mg GAE·100 g⁻¹ DW. Comparing the control sample, the antioxidant activity increased after extrusion of rye and oat-based sample when carrot and pumpkin by products were added, except 5% apple BF decreased TPC to 0.44 ± 0.03 mg GAE·100 g⁻¹ DW probably of different chemical composition of ABF. The highest antioxidant activity was in samples with carrot by-products (0.95 ± 0.01 TE 100 g⁻¹DW), and pumpkin by products 0.93 ± 0.05 TE 100g⁻¹ DW 20% addition respectively. Therefore, apple, carrot and pumpkin by-product flour is a good source of natural bioactive compounds and could be used as functional

ingredients in production of crispbreads based on oat and rye flour.

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