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Assessing of potential of Aronia Berries residue after juice extraction as a feedstock for platform molecules production

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The recovery of fruit industrial waste for the production of added value compounds is a topic of great importance for the application of circular economy principle. Pomace waste coming from Aronia melanocarpa industrial utilization is an interesting source of bioactive compounds such as dietary fibre, pectins, cell wall polysaccharides, vitamins, polyphenols, phospholipides. The extraction of bioactive substances has been carried out through an enzymatic approach followed by ultrafiltration technique. The obtained residues have been collected and characterized. The obtained data revealed the presence of free and complex sugars such as glucose, fructose, sorbitol, EHS and cellulose that could be considered starting feedstock for platform molecule production.

Key words: Aronia Melanocarpa, waste characterization, waste valorisation, carbohydrates conversion

INTRODUCTION

Industrial ecology concepts such as circular economy are considered leading principle for eco-innovation, aiming at "zero waste economy" in which waste are used as raw material for new products and applications. The large amount of waste produced by the food industry, have the potential to be reused into other production systems, trough e.g. biorefineries. Fruit pomace is a by-product of fruit industry that should be included in the circular economy concept. According to the literature, fruit pomace is a valuable source of nutritious components, such as proteins, fat as well as bioactive compounds such as dietary fibre, pectins, cell wall polysaccharides, vitamins, polyphenols, phospholipids [1]. In fact, during the manufacturing process of fruit juices, most of the above-mentioned components does not transfer to the juice and remains in pomace [2]. On the other hand, pomace may be a valuable source of interesting products such as simple and complex sugars, fats and organic acids that could be considered feedstock for platform molecules.

In the present work the case of Black chokeberry (Aronia Melanocarpa) has been studied. Usually, it is subjected to industrial processing for the production of juices or jams as it is a very rich source of substances exerting a beneficial impact on health, including mainly polyphenols (proanthocyanidins, anthocyanins, flavonoids, and phenolic acids). During the industrial process of extraction juice, a significant amount of pomace is produced (up to 16% of the mass of fruit being subject to processing) [3].

Herein we describe a process for the extraction of valuable compounds present in Aronia pomace and their potential conversion into added value compounds through thermo-chemical techniques.

EXPERIMENTAL

All chemical reagents were of analytical reagent grade and were used directly without further purification or treatment. Chokeberry (*Aronia Melanocarpa*) pomace was picked up at the juice producer Elkærholm (Egtved, Denmark).

Sugars were determined using a GS50 chromatography system (Dionex-Thermo Fisher Scientific, Sunnyvale, CA, USA) equipped with an AS50 autosampler, an ED50 pulsed amperometric detector using a gold electrode and a Carbopac PA10 analytical column (250 mm, 4 mm; Dionex).

Extraction of bioactive compounds: 60 g of chokeberry pomace were mixed with 3 L of acidified water (50 mM citric acid, pH 2.3) and homogenized with an ultra-turrax (30 min, 9600 rpm, ~323 K). The pectinase- based enzyme formulation Fruktozym® Flash-C (Erbslöeh Geissenheim AG, Germany) was added to the reaction mixture at a dosage of 2 mL kg^{-1}. The extraction continued for other 30 minutes at 323 K based on a previously optimized method. After this, the ultrafiltration process to collect the extract

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started using a tubular single-channel 25 kDa ceramic membrane (batch nr. 267449) from Atech Innovations Gmbh (Gladbeck, Germany). Two residues were collected at the end of the process (retentate and permeate).

Chemical characterisation of the extraction residues: Upon the extraction protocol for bioactive molecules recovery, the resulting residues (retentate and permeate) were acidified using H_2SO_4 (4%) in order to stop the enzymatic activity. The acidified matrixes were kept under stirring at room temperature for 1 h. Then, 2 mL were filtered, diluted and analysed through IC-HPAD to determine free simple soluble sugars. [4]

The remaining part of the suspension was refluxed for 2 h. The obtained suspension was filtered by Whatman filter, and 2 mL of the filtered solution were diluted to a total volume of 200 mL with distilled water. The obtained solution was then analysed at IC-HPAD for sugar determination (hemicelluloses, starches and sugars released from pectins). [4]

Solid recovered from the filter were washed with distilled water and dried at 378 K for 24 h. Then, it was transferred into a glass tube and left in suspension with 5 mL of 80% H_2SO_4 at 277 K for 24 h. At the end, it was again refluxed for 2 h in an overall volume of 100 mL milli-Q water. The resulting suspension was cooled and filtered on a filtering crucible previously prepared and weighed. The filtered solution was diluted and analysed for sugar determination (cellulose). [4]

RESULTS AND DISCUSIONS

Aronia Melanocarpa is a very rich source of numerous substances [5]. Among that, the most important are the phenolic compounds (proanthocyanidins, anthocyanins, flavonoids, and phenolic acids), possessing antioxidative, anti-inflammatory, antiviral, anticancer, antiathero-sclerotic, hypotensive, antiplatelet, and antidiabetic properties.

The enzymatic degradation of plant cell-wall polysaccharides has been reported to facilitate the release of bioactive compounds into the extraction media [6] and to increase the filtration rate [7]. The enzyme products used for this purpose are typically pectinases, cellulases or proteases in single enzyme preparations or in blends.

In this work the isolation of bioactive compounds from plant waste has been carried out by using an enzymatic approach coupled to ultrafiltration: the extraction mixture obtained from enzymatic process (feed) was pumped to the membrane, the retentate was recirculated to the feed tank while the permeate (product) was collected separately. The ultrafiltration process was performed for 82 minutes, in which 677 g of permeate were collected. The permeate stream accounts for 22 % of the starting material and is rich in water-soluble small molecules. On the other hand, the retentate stream (88%) contains the particulate matter corresponding to the residual cell wall polysaccharide matrix.

The two streams obtained from such protocol, namely permeate and retentate, have been collected and characterized in order to check the presence of sugars, fat and lipids. The obtained results are summarized in Table 1.

Table 1. Chemical composition of the ultrafiltration streams

Constituents		Feed	Retentate	Permeate
Free Sugars (ppm)	Sorbitol	700	680	730
	Glucose	605	601	610
	Fructose	620	597	634
EHS (ppm)	Hemi-celluloses Starches Pectins	257	557	6
Cellulose (ppm)		85	293	6

The obtained data reveal the presence of free sugars, mainly sorbitol, glucose and fructose, that are equally distributed between the permeate and retentate and carbohydrates such as EHS (revealed by the presence of arabinose, galactose, glucose, xylose and mannose that are the main constituents of hemicelluloses, starch and pectin) and cellulose. Both the last two remain mainly in the retentate during the ultrafiltration process. The presence of such species increases the potential utilization of Aronia waste since they are all potential starting feedstock for added value products (Fig. 1).

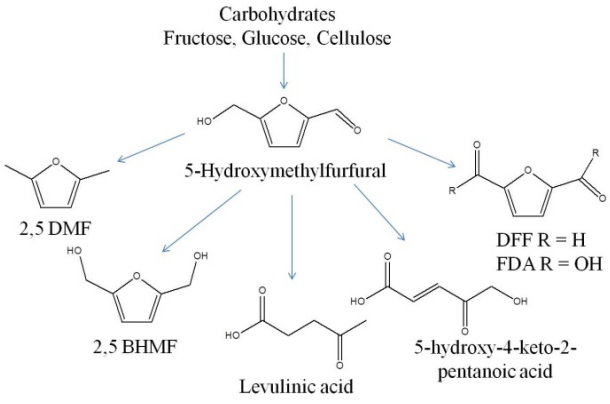

Fig. 1. Conversion of carbohydrates into added value products.

Of particular interest is the presence of sorbitol that is one of the component of the *top added value*

chemicals from biomasses list: basing on data from the literature, among a series of fruits and berries, Aronia contains the highest concentration of sorbitol [8]. Sorbitol could be used as well (toothpaste, Confections and food, Ascorbic acid, Industrial surfactants, Pharmaceuticals) or as a platform chemical. The main uses are as source for ethylene glycol (EG), propylene glycol (PG), 1, 2-propanediol (1, 2-PDO), glycerol and lactic acid production [9]. Sorbitol is also suggested for the application of Aqueous Phase Reforming (APR) for the production of H_2 thus providing hydrogen needed in many other biorefining operations, such as hydrodeoxygenation [10]. Moreover sorbitol is a key intermediate in the production of liquid straight-chain alkanes such as n-hexane, n-pentane and their isomers which are also commonly known as gasoline alkanes [11] (Fig. 2).

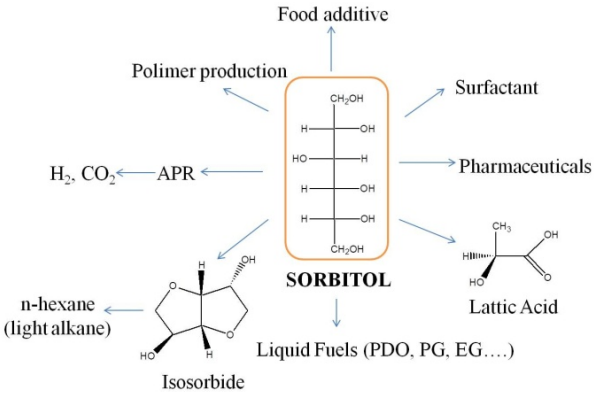

Fig. 2. Potential use of sorbitol.

CONCLUSION

Aronia Melanocarpa pomace coming from the industrial juice production has been studied in order to check the presence of bioactive molecules and other compounds to be used as feedstock for valuable product. Upon extraction of bioactive compounds by utrafiltration, the presence of interesting amount of sugars has been detected namely glucose, fructose, sorbitol, EHS and Cellulose. Potential pathway for the valorization of such compounds have been elucidated.

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REFERENCES

1. S. E. Kulling, H. M. Rawel, *Planta Med,* **74**, 1625 (2008)
2. M. S.K. Kołodziejczyk, J. Milala, *Industrial Crops and Products* **51**, 77 (2013)
3. B. Baranowski, A. Salamon, D. Michalowska, *Agris*, **16,** 100 (2009)
4. L. di Bitonto, G. Antonopoulou, C. Braguglia, C. Campanale, A. Gallipoli, G. Lyberatos, I. Ntaikou, C. Pastore, *Bioresource Technology* **266**, 297 (2018)
5. S. Borowska, M. M. Brz´oska, Comprehensive Review sin Food Science and Food Safety, 15, 982 (2016)
6. O. Gligor, A. Mocan, C. Moldovan, M. Locatelli, G. Crisan, I. C. F. R. Ferreira, *Trends in Food Science & Technology* **88**, 302-315 (2019)
7. S. Alvarez, R. Alvarez, F. A. Riera, J. Coca, *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **138**, 377-382 (1998)
8. H.J. Hofsommer, S.Koswig *Zum Nachweis von Aronia in schwarzer Johannisbeere. Flüssiges Obst* **72**, 289 (2005)
9. Y. Zan, G. Miao, H.Wang, L. Kong, Y. Ding, Y. Sun, *Journal of Energy Chemistry* **38**, 15, (2019)
10. J. So, Y. Chung, D. S. Sholl, C. Sievers, Molecular Catalysis, **475**, 110423 (2019)
11. A. Romero, A. Nieto-Márquez, N. Essayem, E. Alonso, C. Pinel *Microporous and Mesoporous Materials*, **286**, 25 (2019)