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Winery Production Residues as Feedstocks within the Biorefinery Concept

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Abstract

The concept of biorefinery was introduced as a response to the global energy crisis and climate change resulting from industrialization. Wineries produce large amounts of organic residues (grape pomace, skins, seeds, vinasse, wastewater), which are potential feedstocks for biorefineries for the sustainable production of biofuels and bio-based products (chemicals, materials, biopolymers, food, feed, pharmaceuticals, nutraceuticals), while reducing the environmental impact, which is the core of the circular bioeconomy.

Keywords: *winery production residues, biorefinery, bio-based products*

1. Introduction

The circular bioeconomy, or the sustainable production of renewable biological resources and the conversion of these resources and waste streams into value-added products (biofuels and energy; chemicals and materials; food and feed; and cosmetics and pharmaceuticals)-(Fig. 1.), is considered a key element for the successful functioning of the European Union economies in the future [1].

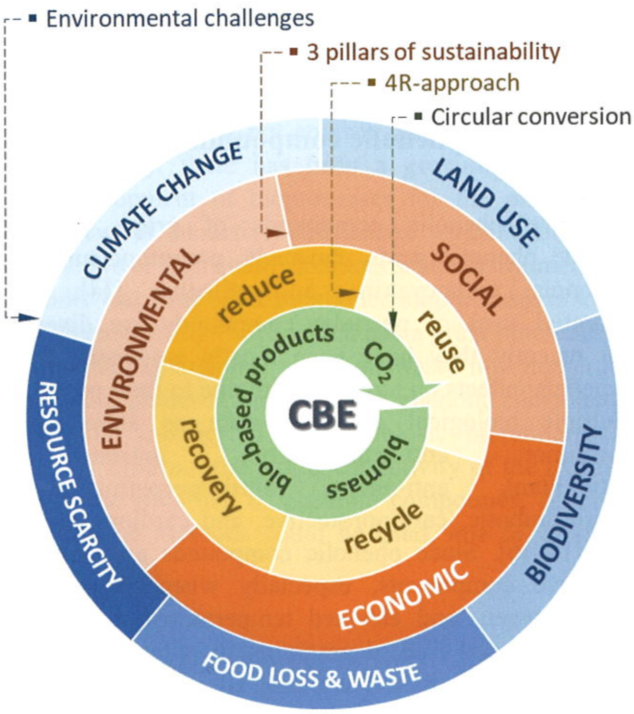

Fig. 1. Circular bioeconomy (CBE) as a solution for greatest environmental challenges (own illustration adapted from various sources: [2–4])

Indeed, current global challenges such as climate change, ecosystem degradation, and the increasing demand for food, feed, and energy require new methods of producing and disposing of production residues. In the transition from the current linear model of a bioeconomy based on an unsustainable "take-make-use-dispose" framework to a circular bioeconomy based on a 4Rs ("reduce-reuse-recycle-recover") framework, the development of biorefineries plays an important role. A biorefinery can be defined as an infrastructure facility that incorporates various conversion technologies (mechanical, thermochemical, chemical/biochemical, and biological) that produce a bio-based product from various biomasses such as lignocellulosic materials, algae, or food waste in a sustainable way, following ESG (economic, social and environmental) criteria. Particular emphasis is placed on cascading biomass use (Fig. 2.), i.e., using the same feedstock biomass to produce several different products within the same or different biorefineries to reduce waste production [2, 5, 6].

Wine industry is an important economic sector both in the world and in Croatia, in terms of wine production, but also in the development of wine tourism. Grapevine (*Vitis vinifera*) is one of the most cultivated crops in the world with an average annual grape production of 75 million tons in the last 10 years, while in Croatia it amounted to 148 thousand tons in the same period [7]. It is estimated that 70-80 % of grapes are processed into wine, leaving behind production residues of organic origin (grape pomace, wine lees), inorganic origin (diatomaceous earth, bentonite and perlite), wastewater and greenhouse gasses [8]. More broadly, wine industry production residues include grape shoots, leaves, and stalks as well as vinasse, a byproduct of the distillation of wine lees to produce ethanol [9]. In recent years,

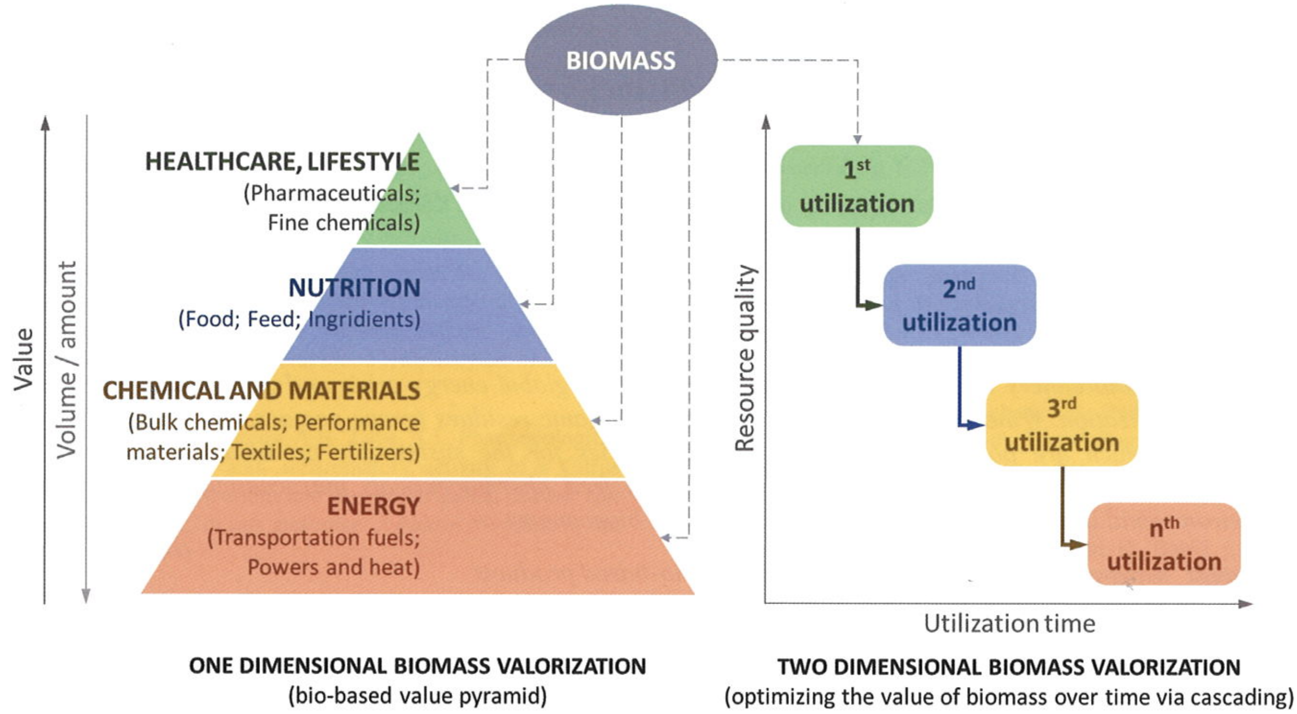

Fig. 2. Biomass valorization by circular bioeconomy (own illustration adapted from source [3])

grape pomace has been of particular interest because it is a raw material with low market value and a readily available natural source of polysaccharides, proteins, vitamins, minerals, fatty acids, fiber, oils, and biologically active compounds, including phenolic compounds [10]. Nevertheless, grape pomace is usually disposed of in landfills and vineyards or burned without a waste management strategy, which can cause numerous negative environmental impacts (hindered germination of plants in the soil, development of unpleasant odors, etc.) and economic losses.

This article presents some of the possibilities for the utilization of wine production residues within the concept of biorefinery.

2. Grape pomace

Grape pomace is the production residue of a winery, consisting mainly of skins, pulp and seeds, and may sometimes include stems. During wine production, 20 - 30 % of the mass of processed grapes remains as grape pomace [5]. The proportion of each component, as well as the chemical composition of the grape pomace, depends on the grape variety, geographical origin, agrotechnical growing conditions, and winemaking process. According to the literature, the proportion of grape seeds varies in the range of 15 - 52 $\%_{db}$ and the proportion of skin about 65 $\%_{db}$ of grape pomace [11]. According to the chemical composition, grape pomace is a lignocellulosic material containing 9.2 - 14.5 % cellulose, 4.0 - 10.3% hemi-cellulose and 11.6 - 42.2 % lignin. In addition, grape pomace contains 42.6 - 74.5% fiber, 7.0 - 23.5 % protein, 2.7 - 49.1 % sugar, and 4.8 - 6.7 % total phenols [12, 13]. Despite its rich chemical composition and multiple possibilities of its use (production of enzymes, biofuels, biopolymers, etc.), grape pomace is most often brought into context with phenolic compounds that can be used in various foods, cosmetics, and pharmaceutical products.

3. Bioactive phenolic compounds of grape pomace

Bioactive phenolic compounds of grape pomace include phenolic acids, flavanols, proanthocyanidins, flavonols, anthocyanins, and stilbenes [14]. The potential uses of phenolic compounds are diverse, but recently they have been mostly associated with beneficial effects on human health due to their potential multiple biological activities such as antiallergic, antitumor, anti-inflammatory, antimicrobial, antioxidant, anti-aging, antihyperpigmentation, antithrombotic, cardioprotective, and cardioprotective etc. [14–16]. Since phenolic compounds are unstable bioactive components, especially when exposed to light, oxygen, and elevated temperatures, they need to be protected from degradation in order to be used for further purposes. Therefore, all processes for the preparation of extracts rich in phenolic compounds from natural raw materials, including grape pomace (storage, sample preparation, extraction, stabilization of extracts), must be carried out under controlled and specified optimal conditions. Extraction is the first step in the isolation of phenolic compounds from raw materials and it depends on numerous process conditions (time, solvent concentration, temperature, etc.) that must be optimized to obtain maximum yields of biologically active phenolic compounds. Due to the structural diversity of phenolic compounds, there is no standardized method for their isolation [17], and application of eco-friendly methods are preferred. The most commonly used method for the preparation of grape pomace extracts is the conventional solid-liquid extraction along with the application of an appropriate solvent (ethanol, methanol, acetone, their mixture with water, etc.) which extracts the targeted easily soluble polyphenols. Recently, alternative solvent extraction methods have been developed, such as ultrasound assisted extraction, microwave assisted extraction, application of pulsed electric fields and pulsed ohmic heating, application of high voltage electrical discharge (cold plasma), pressurized liquid extraction and supercritical fluid extraction which have certain advantages such as better extraction yield, higher extraction rate, economic and energy efficiency, and lower negative environmental impact [17, 18].

During winemaking, only 30 % of phenolic compounds are extracted into the wine, while 70 % of bioactive phenolic compounds remain in the grape pomace. However, a significant proportion (98 %) of the phenolic compounds in grape pomace are incorporated or trapped in a complex lignin structure, making them difficult to extract using conventional extraction methods [19]. The extraction of trapped polyphenolic compounds requires additional processes of degradation, most common being acid hydrolysis or application of commercial enzymes, which increases the costs of production and/or is not environmentally friendly [20, 21]. Recently, there has been a growing interest in the development of bioprocesses for the production/extraction of bioactive substances which enable the production of high quality extracts in an environmentally friendly way. One of the mentioned bioprocesses is solid-state fermentation (SSF) which has a great potential for converting agricultural and food waste into numerous high-value products, including polyphenolic compounds, under the concept of lignocellulosic biorefinery. In order to maintain the biological activity of the extracts due to the presence of phenolic compounds, different stabilization methods could be used, one of which is encapsulation.

3.1. Solid-state fermentation

SSF is a process in which microorganisms grow on a moist, solid material under controlled conditions, without the presence of free water or with a minimal amount of free water [22]. Grape pomace is a suitable substrate for the cultivation of various microorganisms (yeasts, bacetria and fungi) under SSF conditions because it contains the nutrients necessary for their growth [23]. The filamentous fungi are the most commonly used microorganisam in SSF process especially those from fungal kingdom sub-division Basidiomycota and Ascomycota [24]. During growth on the substrate, microorganisms synthesize a number of enzymes (pectinase, cellulase, tanase, β-glucosidase, xylanase, etc.) [21, 25] that can degrade polymer structures and release phenolic compounds from the complex lignocellulose structure making them more readily available for extraction [20]. The efficiency of the SSF process is influenced by a number of factors such as type of bioreactor, substrate (chemical composition, moisture content, water activity, particle size, layer height), inoculum (concentration, culture age, morphology), carbon and nitrogen source, micro- and macro-elements, addition of inducers of synthesis of certain enzymes, mixing, temperature, pH and oxygen concentration. SSF can be implemented in different types of bioreactors (tray, packed beds, rotating disc or drums, fluidized bed, air-lift, immersion, etc.) [26, 27]. Tray bioreactors are a traditional type of bioreactor most commonly used in laboratory scale for enzyme production [28], for lignin degradation [28, 29], for the application of biologically treated material in the process of biogas production [30], and they are also used in commercial processes in various industries (production of fermented foods such as tempeh, or production of enzymes) [25, 26, 31]. The reason for this is simple design and operation, and easier scale-up compared to other bioreactors.

3.2. Encapsulation

Encapsulation is the process where the active matter or their mixture is coated with a polymer that protects it from negative external influences (physical, chemical, and biological degradation). Coatings may vary in their origin and properties, but preference is given to those that are generally recognized as safe (GRAS). The choice of coatings depends on the encapsulation method used and the encapsulation objective, e.g., masking of undesirable odors, maintenance of storage stability, targeted delivery, and controlled release of the active ingredient during digestion [32]. Polysaccharides (cellulose and its derivatives; plant exudates such as gums, starches, and starch derivatives; seaweed extracts such as alginates), proteins of plant or animal origin, and lipids are most commonly used for encapsulation of biologically active extracts. Of particular interest is the use of coatings isolated from natural sources, including food industry residues, such as soy and whey protein isolates, Arabica gum, gelatin, and starch, which is important for developing sustainable encapsulation processes.

Various encapsulation techniques are known, such as spray drying, freeze drying, extrusion, ionic gelation, emulsification, molecular inclusion, and coacervation [33]. The most commonly used encapsulation techniques are spray drying with maltodextrin as coating and ionic gelation with sodium alginate and calcium chloride.

4. Bioproducts based on winery residues

Products that can be made from grape pomace or individual parts of it (seeds, skin, stems) can be divided into primary and secondary products. Primary products include e.g. grape pomace extract rich in phenolic compounds, pellets, grape seed oil and enzymes. Secondary products can be produced by using primary products or by processing and converting primary products under the biorefinery concept (bioethanol, biogas, electricity and heat, bio-based materials) (Fig. 3.). Grape pomace extracts rich in phenolic compounds can be further used for a wide range of functional products such as food (e.g. functional cookies), pharmaceutical products (dietary supplements) or cosmetic products (creams), positively affecting the stability, organoleptic and technological properties of the functional product [15, 34]. Functional products are becoming increasingly important due to the increased awareness of the importance of consuming functional products to prevent modern disorders and diseases (diabetes, cancer, cardiovascular and neurodegenerative diseases). Functional products are products that naturally contain or are enriched with biologically active ingredients. Biologically active substances from natural sources are preferred over synthetic compounds, which can often be carcinogenic [8].

Grape seed oil is the best known commercial product from the production residues of the winery, which can be obtained by pressing or extraction. Being rich in antioxidants (vitamin E) and unsaturated fatty acids, it is very stable and is used in cooking and as a base oil in cosmetics, food and pharmaceutical products [10].

Grape pomace can be used in various feed formulations, but due to its high content of insoluble lignin and indigestible polysaccharides (cellulose, hemicellulose, pectin), this requires pretreatment by biological, chemical, or physical methods, or a combination thereof [11]. Even when grape pomace is used as a biofertilizer, pretreatment (e.g. composting) is required to obtain the appropriate properties (high content of nitrogen, potassium, and phosphorus, organic matter for soil nutrition without negative environmental impact).

In addition, it can serve as a substrate for the production of enzymes (cellulase, pectinase, xylanase,

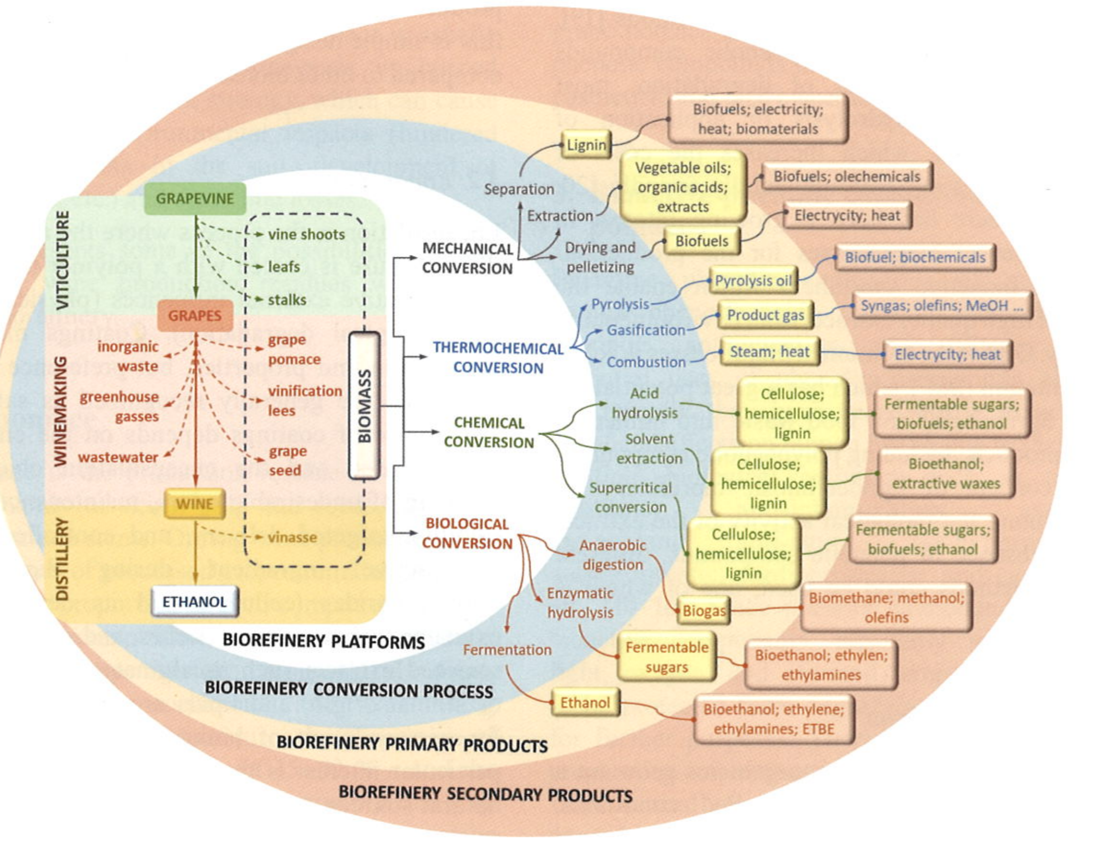

Fig. 3. Biorefinery concept applied od winery (own illustration adapted from various sources: [2, 5, 9, 35])

β-glucosidase, exo-polygalacturonase, laccase, lignin peroxidase, manganese peroxidase) from grape pomace in SSF process with various microorganisms or can be used as an inducer for enzyme synthesis in submerged fermentation [9, 21].

Due to its chemical composition and high energy value, grape pomace can be used for the production of biofuels (pellets, biochar, bioethanol, biogas) as an alternative to fossil fuels. Grape pomace pelletization, in which involves drying the pomace to a moisture content of less than 12 %, yields biofuel that can be used to generate heat and electricity in wineries or other facilities. Biochar from grape pomace is usually produced by thermochemical processes or pyrolysis. Hydrothermal carbonization can be used as an alternative to pyrolysis, especially for biomass with a higher moisture content. Apart from being a source of energy, it can be used to improve the chemical, biological, and physical properties of soil and to remove pollutants from wastewater [5, 36]. In the production of bioethanol from grape pomace, unlike sugar feedstocks, it is necessary to pretreat them with chemical, thermochemical, or biological processes to break down a complex lignocellulose structure into simple sugars, from which bioethanol is formed by fermentation. The production of biogas from pomace is possible through the process of anaerobic co-digestion with manure with prior degradation of lignin by some of the mentioned conversion processes [5]. Grape pomace can also be used as filler for the production of polymeric multicomponent composites [37].

Vinasse is potential feedstock for the production of tartaric acid, which is used as a preservative in the food industry, as well as lactic acid and xylitol [9]. Grape pomace and vinasse can be used as substrate for the production of protein-rich fungal biomass.

The *skin* of grapes can be used for the production of natural dyes which can be later used in textile industry [38].

Wastewater from wineries can be used as a substrate for the cellulose production as well as for single-cell proteins production that can serve as food or feed additives [9].

In the cascading approach (Fig. 4.), the product with the highest value is produced first, then the second-highest, and so on. In this context, the solid residue of grape pomace or seeds left after the extraction of phenolic compounds or oil production is still rich in nutrients such as proteins and fiber and can be further processed

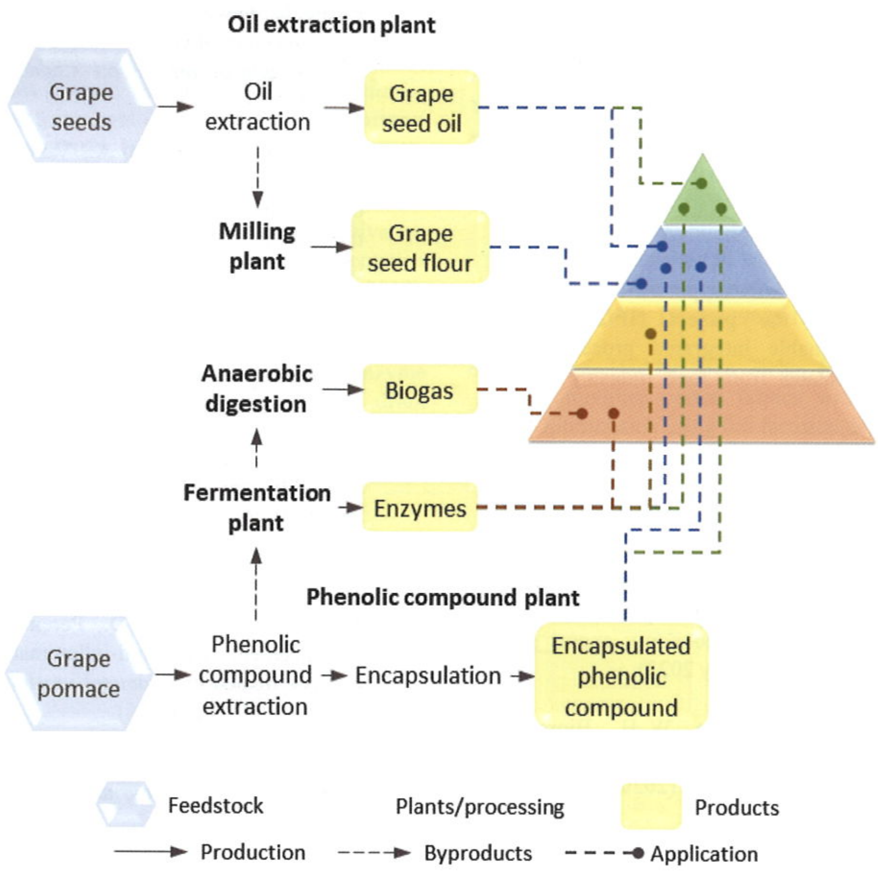

Fig. 4. Scheme of a cascading biorefinery proposal based on main winery residues

into flour, which can be used as an additive in bakery products or as a feed ingredient. In addition, this residue can be used for the production of pellets with a slightly lower heating power than the original grape pomace and for the production of biochar. In addition, the grape pomace remaining after SSF process can be used for bioethanol and biogas production.

5. Conclusion

The circular bioeconomy through the concept of biorefinery offers the possibility of efficient use of biomass, including organic residues from wineries, for the sustainable production of high value-added products. The advantages of the circular bioeconomy over the linear one are better resource and environmental efficiency, lower greenhouse gas emissions, reduced dependence on fossil resources, and valorization of waste biomass. This approach focuses on recycling, reusing, reducing, and recovering (4R-approach), and maintaining a sustainable production process to produce useful organic products. Since biorefinery requires capital investment to economically justify the conversion of industrial residual biomass into high value products, integrated technologies must be introduced to produce multiple products within a biorefinery concept (co-production of bioenergy such as bioethanol, biogas, electricity, heat, and bioproducts such as biochemicals, biomaterials, bioplastics, food, feed). The use of winery residues through cross-sector integration and cascade use of feedstocks has the potential for full valorization into high value products within the biorefinery concept.

Acknowledgments: This work was supported by the Croatian Science Foundation under the project (IP-2018-01-1227) "Development of a sustainable integrated process for the production of bioactive isolates from food industry residues" (POPI-WinCEco).

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