# **Valorization of Agro-Industrial Waste into Bioactive Compounds: Techno-Economic Considerations**



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## **1 Current Context in Both Agricultural Waste (ACW) and Agro-Industrial Waste (AIW)**

As definition, agricultural waste (ACW) comes from the agricultural phase of the cultivation of certain species, while agro-industrial waste (AIW) results from the industrial processing of biomass (Portugal-Pereira et al. [2015](#page-16-0)). This is the base to quantify and identify the ways to face the problem. In the European Union, taking into account both ACW and AIW, around 89 million tonnes of biomass (from the agricultural production, postharvest, and processing stages) are wasted annually (Stenmarck et al. [2016\)](#page-16-1), and this value is expected to increase by 40% in 2020. However, this chapter is mainly focused in postharvest and processing stages, excluding the end of the food supply chain (retail and final consumption), which relates to retailers and consumers behavior.

If we analyzed just the AIW, this causes a serious disposal problem. For example, the juice industries produced a huge amount of waste as peels, the coffee industry produced coffee pulp as a waste, and cereal industries produced husks (Sadh et al. [2018\)](#page-16-2). All over the world approximately 147.2 million metric tonnes of fiber sources are found, whereas 709.2 and 673.3 million metric tonnes of wheat straw residues and rice straws were estimated, respectively, in the 1990s (Belewu and Babalola [2009\)](#page-14-0).

Specifically related to fruit processing industry, the proportion of AIW is significant, for example, depending on the location and method of harvest, the AIW is 30–50% for mango, 20% for banana, 40–50% for pomegranate, and 30–50% for citrus (Laufenberg et al. [2003](#page-15-0); Parfitt et al. [2010\)](#page-16-3). These percentages are clear and represent a relative number of wastes. However, if we think in terms of the scale of

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companies, the approaches could be different. For example, in micro and smallscale companies, processing waste is considered to be of negligible value compared to the processed material. On the contrary, for big companies the problem of waste is a priority, because they are paying to dispose their vegetable and food wastes in landfills. For example, in the case of an specific AIW (fruit processing wastes) in Europe, the disposal of 1 tonne of solid waste or  $1 \text{ m}^3$  of effluent costs \$28–60 dollars which includes a landfill tax of \$10 (Gendebien et al. [2001](#page-15-1)). On the other hand, in developing countries such as India, the average transportation cost was found to be \$11–15 dollars per tonne per trip (FICCI [2010\)](#page-14-1) which may indicate \$300 million dollars for total landfilling cost. If we add the environmental impact and the concept of corporate social responsibility, it is necessary to take into account that landfilling is also associated with risks of greenhouse gas emissions (Roggeveen [2010\)](#page-16-4). For example, global food processing waste-related greenhouse gas emission was found to be the third highest contributor after total emissions for China and the USA.

On the other hand, the United Nations Food and Agriculture Organization estimates that about 815 million people of the 7.3 billion people in the world were suffering from chronic undernourishment in 2016 (FAO [2017](#page-14-2)). This is the reason why the AIW and ACW must be used in the most efficient way and be valorized through its healthy and functional potential. Regarding that, in developing countries the majority of the fruit and vegetable processing information was found to be fragmented and insufficient, focusing on the execution of projects about biogas or compost production to obtain biofertilizer, which unfortunately does not take into account the complete potential of AIW. On the contrary, in developed countries, the fruit and vegetable processing waste was found to be fifth highest contributor (8% of total food waste) to overall food waste (Fava et al. [2015\)](#page-14-3), allowing carried out studies focused on AIW recovery (Pfaltzgraff et al. [2013\)](#page-16-5).

Finally, a key factor to recognize the opportunities of AIW and its valorization or added value is to identify the main sources or industries of each country or region. In the case of Chile, for example, AIW are generated in companies that produce fruit pulps, avocado oil, ready-to-eat salads, ready-to-eat meals, canned fruit, canned vegetables, and fruit juice, among others. Regarding this AIW, it is important to know which types of bioactive compounds are able to be extracted from them and how much is their value. This is also a key factor to take into account when a company must decide to invest in a new process or a new product. Table [1](#page-2-0) shows some bioactive compounds found in vegetable sources from AIW.

The focus is clear; however, the way to achieve the aforementioned goals is not simple. Some modifications are needed to stabilize the AIW before to be processed. Some researchers are investigating both aerobic and anaerobic digestions as a tool to stabilize the AIW (Fernandez-Bayo et al. [2018\)](#page-14-4). On the other hand, if the goal is the functional compound from AIW, the stabilization must play the role of decreasing the biochemical reactions into the AIW and at the same time keep the benefits of the bioactive compounds. Some studies of AIW drying to recover bioactive compounds are focused in technologies as spray drying, freeze drying, and supercritical  $CO<sub>2</sub>$  drying (Santos-Rezende et al. [2018;](#page-16-6) Plazzotta et al. [2018](#page-16-7)). The cost of the abovementioned technologies is relatively high; however, conventional drying or

			Patent	
AIW	Products	Use/application	reference	Market price
Mango peels	Pectin, polyphenols	Gelling agent, stabilizing agent in fruit juices, preservatives	Taboada and Siacor (2013)	Commercial extract 25-30 (US\$/ $kg)^a$
Tomato processing by-products	Lycopene	Antioxidant, therapeutics	Lavecchia and Zuorro (2010)	Commercial extract 10% 55-60 (US\$/ $kg)^b$
Citrus peels	Dietary fiber, flavorant, oil	Nutritional supplement, food additive	Nafisi- Movaghar et al. (2013)	Commercial extract $20:1^{\circ}$ 60-70 (US\$/ $kg)$ <sup>b,d</sup>
Pomegranate husk	Site-specific inhibitors of histone methyltransferase	Lead compounds to develop anti-neoplastic and anti-HIV therapeutics	Kundu et al. (2011)	Commercial extract 20:1 <sup>c</sup> 55-70 (US\$/ $kg)$ <sup>b,d</sup>
Pomegranate peels	Polyphenols	Treatment of prostate cancer by increasing doubling time of a prostate-specific antigen	Liker (2014)	Commercial extract $20:1^{\circ}$ 55-70 (US\$/ $kg)$ <sub>b,d</sub>
Cranberry and pomegranate extract powders	Hydrolyzable tannins as antibacterial agents	POMcran capsules $(25 - 5000$ mg)	Mackler (2014)	Commercial extract $20:1^{\circ}$ 50-75 (US\$/ $kg)$ <sup>b,d</sup>
Grape seed extract	Polyphenols	Antiaging and cancer treatment	$\equiv$	$200 - 250$ (US\$/kg) <sup>e</sup>
Grape pomace extract	Polyphenols	Antiaging and cancer treatment	$\overline{\phantom{0}}$	180 (US\$/ $kg)^e$
Vegetable feedstock	Succinic acid	Food, agricultural, and pharmaceutical uses	$\equiv$	$1.7 - 3.7$ $(US\$/kg)^f$
Organic feedstock	Compost	Fertilizer	$\overline{\phantom{0}}$	25-33 (US\$/ $\text{yard}\text{)}^g$
Organic feedstock	Livestock feeding	Animal feeding	$\overline{\phantom{0}}$	$3.57 - 9.38$ (US\$/bushel) <sup>h</sup>

<span id="page-2-0"></span>**Table 1** Valorization of AIW and applications of its compounds

Source: Banerjee et al. ([2017\)](#page-13-0)

The estimated market price is considering a format up to 25 kg

a https://[www.newdirectionsaromatics.com/products/fruit-extracts/mango-powder-fruit-extract.](http://www.newdirectionsaromatics.com/products/fruit-extracts/mango-powder-fruit-extract.html) [html](http://www.newdirectionsaromatics.com/products/fruit-extracts/mango-powder-fruit-extract.html)

b Summer, China

c 20:1, It has been used 1 kg of vegetable source to obtain 50 g of powder extract

d RuiHerb, China

e http:/[/www.polyphenolics.com/consumer/grape-seed-extract](http://www.polyphenolics.com/consumer/grape-seed-extract)/

f Shenyang East Chemical Science-Tech Co., Ltd.; Dalian Sinobio Chemistry Co., Ltd.; Guangzhou ZIO Chemical Co., Ltd

g https:/[/www.improvenet.com/r/costs-and-prices/composting](http://www.improvenet.com/r/costs-and-prices/composting)

https:/[/www.feednavigator.com/Article/2018/03/29/Feed-prices-forecast-to-rise](http://www.feednavigator.com/Article/2018/03/29/Feed-prices-forecast-to-rise)

drying using equipment like roller drum driers could be a most cost-efficient alternative to stabilize AIW in order to obtain its bioactive compounds as a potential added value.

#### **2 Valorization Approaches of AIW**

Valorization of AIW is currently focused on composting, livestock feeding, and other products with low-added value, as shown in Table [1](#page-2-0). There are many ways to decrease the amount of waste generated in this industry, some of them are reuse and recycle. However, in general both of them are options to valorize the residues into the same companies. Regarding that, this section is aimed to remark cases where the valorization is going forward, taking advantage from scientific studies to create new products with added value from AIW.

Some of the alternatives to valorize the AIW are the reuse and recycle. Reuse indicates the use of waste materials for other purposes without or with minor modification of their properties (Manzocco et al. [2016\)](#page-15-6). Direct reuse of AIW for soil amendment has been investigated by Clemente et al. [\(2015](#page-14-5)). However, it is difficult to put into practice due to the high biological instability of waste (Ajila et al. [2012\)](#page-13-1). On the other hand, recycle is a strategy based on the recovery of waste materials after a major modification of their characteristics (Williams and Anderson [2006\)](#page-17-1), which offers more possibilities than its reuse. Recycle strategies can be divided into strategies in which the whole waste mass is recycled and strategies in which specific compounds are extracted. Hence, the valorization on this chapter will be focused on the recycle strategies to extract specific bioactive compounds from AIW.

#### *2.1 Valorization from the Process*

The AIW contribution related with fruit and vegetable processing is more than 0.5 billion tonnes worldwide (Banerjee et al. [2017](#page-13-0)). The potential of those AIW in terms of bioactive compounds, antioxidant activity, and some other micronutrients makes this feedstock an important source of detailed studies. Some examples are the study of resveratrol from grape seeds and peels from wine industry (Fernández-Mar et al. [2012](#page-14-6)) and the valorization of pomace fractions from tomato paste to extract lycopene (Allison and Simmons [2017\)](#page-13-2).

In the case of lycopene extraction, there are many factors to be considered: drying method of the pomace, tomato varieties, and the characteristics of the cultivars, among others. In Table [2,](#page-4-0) the influence of different extraction methods in maximum lycopene recovery is presented.

Despite the abovementioned and the technologies used at laboratory level, the commercial technology to produce lycopene extract is solvent extraction using a mixture of ethanol and water. The commercial price of lycopene is 80–90 US\$/kg,

		Maximum lycopene yield (mg/g dry
Raw material	Extraction method	basis)
Raw tomato skins. separated	Acetone: hexane Soxhlet	770.8
Raw tomato skins. separated	Supercritical CO <sub>2</sub> , 27.58 MPa, 80 °C	644.1
Tomato pomace	Chloroform Soxhlet	820
Tomato pomace	Supercritical CO <sub>2</sub> , 40 MPa, $90^{\circ}$ C	459
Tomato pomace	Supercritical CO <sub>2</sub> , 46.0 MPa, 80 °C	314
Tomato pomace	THF, methanol	734
Tomato pomace	Chloroform	24.5
Tomato pomace	Supercritical CO <sub>2</sub> , 34.5 MPa, 86 °C	14.86
Tomato pomace	Hexane, acetone, ethanol, RT	19.8

<span id="page-4-0"></span>Table 2 Extraction methods in lycopene recovery from pomace<sup>a</sup>

a Extracted from Allison and Simmons ([2017\)](#page-13-2)

the commercial format is a red microencapsulated powder with 10% of lycopene, and the final powder is oil soluble.<sup>[1](#page-4-1)</sup>

The case of grape pomace valorization has been very important in the recent years because of the growing of wine industry. Since grape pomace can be regarded as an excellent and affordable source of polyphenolic compounds, some researchers have been studying technologies and strategies to extract the antioxidants from that source (Tournour et al. [2015](#page-17-2)). Figure [1](#page-5-0) shows the antioxidant activity (ORAC value) extracted from grape pomace from different cultivars of grapes in Portugal.

Another example of valorization is the case of producing succinic acid from natural resources (Dessie et al. [2018\)](#page-14-7), which use AIW to carry out a solid-state fermentation. The succinic acid produced represents an added value product, which could be used in food, agricultural, and pharmaceutical industries. Other studies focused on the AIW valorization to produce succinic acid, explore the characteristics of the biomass feedstock and evaluate if mixed food waste is especially appealing as it represents less resource competition than more homogenous food waste fractions (Rex et al. [2017](#page-16-9)).

The AIW could be also a by-product from the process. For instance, the defatted soybean meal from the soybean oil industry could be used to obtain isolated soy protein. The high amount of protein of defatted soybean meal is interesting for the current market taking into account the food trends to plant-based diet. The protein content of defatted soybean meal is 45.7% w/w. There are several types of products derived from isolated soybean protein: dairy-based products including infant formula, beverages including liquid soy milk and fruit drinks, soups and sauces, energy bars, meat analogs including vegetarian food products, breads and pastries, breakfast

<span id="page-4-1"></span><sup>&</sup>lt;sup>1</sup><http://es.hsfbiotech.com/micro-encapsulated-powders/lycopene/lycopene-10-cws.html>

<span id="page-5-0"></span>

**Fig. 1** Extraction of antioxidant activity from grape pomace from different grape cultivars: *TR* Tinta Roriz; *TF* Touriga Franca; *TNac* Touriga Nacional; *Mix* mix red grape pomace. Gray columns represent the ethanol/water extracts (80:20 v/v); and black columns represent the aqueous suspension (Tournour et al. [2015\)](#page-17-2). ORAC (oxygen radical absorbance capacity) represents the value of antioxidant activity

cereals and other nutritional food products, and protein drink for muscle building and weight-gaining purposes (Lai et al. [2017\)](#page-15-7). On the other hand, there is another type of applications of added value products from AIW. For instance, in the last few years, there is a growing interest to encompass from material as bioabsorbent (Sud et al. [2008\)](#page-17-3) to rhizobial inoculant production (Ben Rebah et al. [2007](#page-14-8)).

Also, there are some bioactive compounds that are demanded for the market, and they could be included in AIW, for example, pectin, dietary fiber, polyinsaturated lipids, essential oils, flavonoids, and peptides, among others (Banerjee et al. [2017\)](#page-13-0). Also structuring agents, mainly referring to colloidal polymers with interesting gelling or viscosant properties, can also be selectively extracted from AIW (McCann et al. [2011](#page-15-8)). Some recent studies relevant to bioactive extraction (e.g., carotenoids, essential oils, polyphenols, anthocyanins) from AIW using novel technologies include the use of ultrasounds, supercritical carbon dioxide, microwaves, and pulsed electric fields (Amiri-Rigi et al. [2016](#page-13-3); Jacotet-Navarro et al. [2015](#page-15-9); Rabelo et al. [2016;](#page-16-10) Zhou et al. [2015](#page-17-4)). For these reasons, extraction of specific compounds from AIW could be an affordable, sustainable, and profitable strategy for industries (Galanakis [2012;](#page-14-9) Laufenberg et al. [2003](#page-15-0)).

On the other hand, before to extract bioactive compounds or structuring agents from AIW, the strategy to stabilize them is drying. Flours can be obtained from drying processes, and they can be used as an ingredient for the formulation of products rich in functional compounds such as polyphenols and fiber (Ferreira et al. [2015\)](#page-14-10). The main advantage of this recycle strategy is that valuable products such as adsorbents and functional flours are obtained from low-cost raw materials. However, the main issue is the high cost required for AIW drying, due to the high water content. As a consequence, the production of AIW flour is affordable only if high valueadded ingredients and products are developed (Ratti [2001](#page-16-11)). To have an estimation of the cost to dry AIW, Karam et al. [\(2016](#page-15-10)) have stablished the energy consumption of different drying technologies, for example, diseccant drying (6 KW/kg of AIW), freeze drying (15–20 KW/kg of AIW), and vaccum drying (5 KW/kg of AIW).

Another example of valorization is rice bran, which was previously being considered as an AIW, as the rice kernel (white rice) is an important product where the major income from rice comes from this part. Rice germ and bran are usually being considered as by-products, until researchers found that rice bran oil has good composition of monounsaturated and polyunsaturated fatty acids which turns to be health beneficial to humans (Kochhar and Gunstone [2002\)](#page-15-11). Rice bran, a part of the rice kernel that contains pericarp, aleurone, and subaleurone fractions, is a byproduct of rice milling. It is estimated that the world annual production of rice bran amounts to 76 million tonnes (Chiou et al. [2013\)](#page-14-11). Rice bran oil has been commercialized now in India, the USA, Thailand, and many more. The benefits of rice bran oil have been discussed by many researchers, which have been summarized by Friedman ([2013\)](#page-14-12): anti-allergic activities, anti-cholesterol activities, anti-diabetic activities, producing liquid-solid or semisolid form of product from rice bran oil (e.g., shortening or spreads), and regulation of the immune system. These benefits are related to rice bran composition in terms of bioactive compounds, which is summarized in Table [3](#page-6-0).

Bioactive compound or	Amount or activity of bioactive	
extract	compounds	<b>Benefit</b>
Phenolic acids	$2101 \mu g/g$	Antioxidant
$\alpha$ -Tocopherol (vitamin E)	$71 \text{ mg/g}$	Antioxidant
Rice bran extract	Inhibition of Vibrio cholerae, Vibrio vulnificus, Salmonella spp., Shigella spp., Escherichia coli, and Staphylococcus aureus	Antibiotic activity
Pigmented rice brand extract, cycloartenyl ferulate from rice bran oil-derived	Capture immunoglobulin E (IgE)	Antiallergic an anti-inflammatory activity
MG-3 arabinoxylan rice <b>bran</b>	Ameliorate hepatocellular carcinoma	Anticarcinogenic effect
Tocotrienol-rich fraction of rice bran	100 mg/day during 6 weeks	Anticholesterol effect
Stabilized rice bran	20 g daily during 12 weeks	Antidiabetic activity

<span id="page-6-0"></span>**Table 3** Bioactive compounds in rice bran

Source: Friedman [\(2013](#page-14-12))

### *2.2 Valorization from the Artisanal Fishery to Food Industry*

From a social point of view, fisheries and aquaculture industry provide employment to a major part of the population in several coastal provinces of many countries. This activity is physically demanding and in many cases is not well remunerated in developing countries. On the other hand, a big amount of waste is obtained from the cleaning process of fishery products, which could be used for other food applications. Hence, valorization of the underutilized and invasive species along with fishery by-products and wastes generated from these industries can enhance the industry's value chain, which can improve the profitability of the products. Also, valorization and production of various high-value pharmaceuticals/nutraceuticals (marine oils, omega-3 fatty acids, proteins, amino acids, enzymes, chitin, chitosan, and astaxanthin) from these resources can maximize the economic viability of the industry while addressing issues of waste management and environmental sustainability. Currently, polyunsaturated fatty acids mainly omega-3 fatty acids are obtained from marine fishes with high fat content. Specifically, fish oil derived from blue fish is rich of both eicosapentaenoic acid (EPA, C20:5n-3) and docosahexaenoic acid (DHA, C22:6n-3) (Ciriminna et al. [2017](#page-14-13)). High demand has motivated researchers to pursue new sources of these fatty acids, improve existing extraction methods, and develop more efficient methods for mass production and commercialization (Dave and Routray [2018\)](#page-14-14).

The situation of valorizing residues in artisanal fisheries also can reach other applications. For instance, the production of seafood generates great amounts of seashells. Regarding that and in order to reduce the dependency on virgin materials for construction, efforts have been made to incorporate by-products and wastes from different industries as alternatives in concrete. Hence, an opportunity has been visualized from the fishery industry. Seashell waste, such as oyster shells, mussel shells, and scallop shells, among others, is available in huge quantities in certain regions and is usually dumped or landfilled without any reuse value. Over seven million tonnes of mollusk discards are produced every year worldwide, being mainly shells, which can be reused due to their high content of calcium carbonate (approximately 95%).<sup>2</sup> For example, in Europe, France has an important fishing and shellfish farming industry that produces nearly 200,000 tonnes of shells from shellfish breeding and nearly 50,000 tonnes of shellfish per year from fishing (Nguyen et al. [2013](#page-16-12)). The use of seashell waste as a partial replacement for conventional materials in concrete and other related cement-based products is a possibility. The characteristics of different types of seashell waste, as well as the effects of incorporating the seashells on the fresh and hardened properties of concrete, have been studied (Moa et al. [2018](#page-15-12)). The results of this study show that despite the reduction in the workability and strength, it is suggested that seashell waste could still be utilized as a partial aggregate at a replacement level of up to 20% for adequate workability and strength of concrete for nonstructural purposes.

<span id="page-7-0"></span><sup>2</sup> <https://www.popsci.com/oyster-shells-alternate-uses>

Chitin and chitosan are other examples of products obtained from marine waste from crustacean shells such as shrimp, crabs, lobsters, and krill. In the study of Kumari et al. [\(2015](#page-15-13)), chitin from marine sources is converted to chitosan and characterized through different methodologies. On the other hand, there is the case of compounds from the fishery waste industry used in applications like packaging (Leceta et al. [2015\)](#page-15-14). That investigation was focused on the manufacture of sustainable films by using chitosan derived from wastes of fishery industry. Since chitosan is a hydrophilic polymer, moisture sorption behavior was analyzed in order to provide novel knowledge related to the best use conditions for chitosan as packaging films. The results revealed that chitosan films show a great potential to be used as packaging films for food products with intermediate moisture sorption. The main importance of these findings are the suitable design of chitosan-based sustainable food packaging films, valorization of waste product, maintenance of food quality, and, thus, reduction of food waste and environmental impact caused by conventional packaging systems.

# **3 Approaches to Optimize the Valorization of Wastes with Conventional and New Technologies**

Agro-industrial wastes are often underutilized and pose a major disposal problem to the concerned parties. Food processing wastes are promising sources of valuable compounds such as dietary fiber, antioxidants, essential fatty acids, antimicrobials, and minerals because of their favorable technological, nutritional, and functional properties (Schieber et al. [2001](#page-16-13)). However, the higher-value products may be developed through various modification methods and technologies. Here, the conventional and new technologies used for valorization or extracting processes from food waste or by-products will be analyzed.

#### *3.1 Solvent Extraction*

In solvent extraction, the solvent acts as a physical carrier to transfer the target molecules between different phases of solid, liquid, and vapor (Galanakis [2012\)](#page-14-9). Various compounds can be isolated using solvent extraction, which are tocopherols, flavonoids, and related compounds such as coumarins, cinnamic acid derivatives, and chalcones, phenolic diterpenes, and phenolic acids (Oreopoulou and Tzia [2007\)](#page-16-14). Nonpolar solvents (hexane, petroleum ether) can be used for the recovery of tocopherols and certain phenolic terpenes. Ethyl ether and ethyl acetate are very efficient for the recovery of flavonoid aglycons, low molecular weight phenolics, and phenolic acids. Solvents of higher polarity (ethanol or ethanol water mixtures) additionally can extract flavonoid glycosides and higher molecular weight phenolics,

resulting in higher yields of total extracted polyphenols. Organic solvents, such as acetone and ethyl acetate, are used for the extraction of carotenoids, and acetone results in the highest yield compared to ethanol, petroleum ether, and hexane (Calvo [2005\)](#page-14-15). From the regulatory point of view, solvents permitted for use in the preparation of food ingredients in the European Union are ethanol, ethyl acetate, and acetone (Marriott [2010](#page-15-15)). Pectin extraction is accomplished by the use of mineral acids, usually hydrochloric or nitric acid (Oreopoulou and Tzia [2007\)](#page-16-14). The extract is separated from the solid residue, and pectin is precipitated by the addition of ethanol or AlCl solution. Extraction of defatted soy flake with aqueous alcohol improves the flavor and color of soy protein isolate as well as markedly improved its foaming and gelling properties by removing phospholipids and other alcohol-soluble materials. Hence, it is clear that solvent extraction is a versatile way to selectively extract several types of compounds from vegetable and animal sources but is also a scalable technology and, in terms of costs, depends on the selected solvent and the downstream purification processes.

#### *3.2 Supercritical Fluid Extraction (SFE)*

Supercritical fluid extraction involves the use of gas above its critical temperature and pressure (Galanakis [2012](#page-14-9)). Supercritical fluid is defined as a state where the liquid and gas are indistinguishable from each other above its critical point or a state where the fluid is compressible and has a similar density and solvating power to liquid. Supercritical fluid extraction has several advantages over the conventional methods, including faster processing times, high selectivities (i.e., high quality extract), and high extraction yields (Farías-Campomanes et al. [2013;](#page-14-16) Herrero et al. [2006\)](#page-15-16); however, energy cost to operate at high pressure is elevated. Carbon dioxide is the most commonly used fluid in SFE due to its low critical point (304.2 K/7.4 MPa), favorable environmental characteristics, and low costs.  $CO<sub>2</sub>$  can be easily separated by depressurization and, thus, can be recovered and reused (Farías-Campomanes et al. [2013\)](#page-14-16). Numerous vegetable matrices have been used as natural sources for compressed fluid extraction. Legumes, spices, aromatic plants, and even fruit beverages, such as natural orange juice (Señoráns et al. [2001\)](#page-16-15), have been processed to obtain natural antioxidant compounds.

Several applications have been developed using SFE in the recovery of valueadded components from grape residues, including oil from seeds, tannins from seeds, and polyphenols from both skins and seeds (Farías-Campomanes et al. [2013\)](#page-14-16). The recovery of catechin and other phenolic compounds was found to be higher during isolation of phenolic compounds from grape seeds using supercritical carbon dioxide (Murga et al. [2002;](#page-15-17) Louli et al. [2004](#page-15-18)). The use of supercritical fluid extraction after ethyl acetate extraction of wine industry by-products caused higher antioxidant activity, allowing odorless and clearer extracts.

Some authors analyzed the economic feasibility of obtaining different bioactive molecules from plant matrices. In the case of oil extraction from pre-pressed seeds,

it was possible to determine that the lowest cost of manufacture (COM) is in the order of 4.08 USD/kg of oil recovered from pre-pressed seeds (by-products of the oil extraction process by cold pressing). Considering the cost of raw materials, inputs such as  $CO<sub>2</sub>$  and co-solvent, energy costs, manpower, among others, it allows establishing the feasibility of using this type of process for the valuation of vegetable matrices (del Valle et al. [2014](#page-14-17)). Prado et al. ([2012\)](#page-16-16) reported that the production cost for grape seeds depended on the operating conditions, taking into account that by increasing the scale of the process it becomes economically viable. COM values ranging from 290.17 US \$/kg extract for a scale process of 5 L and operational time of 60 min, up to 11.93 US \$/kg for a scale process of 500 L and 300 min of operation. It is even possible to estimate the global cost of obtaining extracts using SFE, using rapid estimation models that allow establishing that the recovery process is economically feasible (Rosa and Meireles [2005](#page-16-17)). The case of lycopene recovery from tomato processing waste have also been reported, determining that COM value is close to 1.8 M $\epsilon$ /kg lycopene when using supercritical  $CO_2$ , while this value can be improved when it uses supercritical ethane given the higher the extraction speed, therefore the shorter the process cycle, and the higher the productivity, therefore the lower the COM (Silva et al. [2014\)](#page-16-18); for its part, the recovery of oil from depleted coffee beans through supercritical fluid technology reports annual productivities up to 454 tonnes/year (extraction conditions 2 h, 300 bar, 50  $\degree$  C, 30 kg CO<sub>2</sub>/ kg raw material h) with COM of 2.4 M€ and net economic income of 56.6 M€ (Melo et al. [2014\)](#page-15-19). It is important to consider that the cost of manufacture will depend basically on the raw material to be used, if there is a use of co-solvent or not, and on the scale of the extraction process and therefore of the productivity process (Veggi et al. [2014](#page-17-5)), determining, for example, variations of the COM between 1300 and 833 USD/kg crude extract rich in polyphenols from bean when  $CO<sub>2</sub>$  was used and considering the lower value for the greater scale of process. The data provided allows establishing the variability in the cost of manufacturing extracts from different plant matrices and therefore the potential use of AIW. This cost is associated with different variables, especially the scale and operational conditions of the process; in addition, the costs are associated with the molecule to be recovered (a crude extract or a specific compound) and are increasing with the purity required for the final product; however, it is still technically and economically feasible to take advantage of different plant matrices, with high net returns.

#### *3.3 Subcritical Water Extraction (SWE)*

Subcritical water extraction (SWE), an extraction which uses hot water under pressure, has recently emerged as a useful and environmentally friendly tool to replace the traditional extraction methods. Basically, the instrumentation consists of a water reservoir coupled to a high-pressure pump to introduce the solvent into the system, where the extraction cell is placed and extraction takes place and a restrictor or valve to maintain the pressure. Extracts are collected in a vial at the end of the extraction system. Subcritical water extraction has been widely used to extract different compounds from several vegetable matrices such as rosemary (Arvanitoyannis and Kassaveti [2008;](#page-13-4) Herrero et al. [2006\)](#page-15-16).

Although at present there are no economic analyzes in the literature regarding the feasibility of the extraction process with subcritical water, different authors point out that it is an economically viable technology, given the fact that traditional organic solvents are replaced by water, the extraction product would not require desolventization, among other things (Zakaria and Kamal [2016](#page-17-6); Gbashi et al. [2016;](#page-15-20) Tian et al. [2017\)](#page-17-7). On the other hand, it is also necessary to consider that in general it has been reported that different green technologies, such as extraction by supercritical fluids (as seen in the previous point), microwave-assisted extraction, or electric pulse, among others, are economically feasible to be applied for the recovery of extracts with bioactive molecules (Bromberger et al. [2018](#page-14-18)).

#### *3.4 Solid-State Fermentation (SSF)*

Solid-state fermentation (SSF) is gaining wide interest these days for the production of organic acids such as citric, lactic, and oxalic acids, enzymes, and other biotechnological products, which could be extracted from AIW, which are generally considered the best substrates for this fermentation processes, especially for enzyme production (Dhillon et al. [2013\)](#page-14-19). The presence of lignin and cellulose/hemicellulose acts as natural inducers, and most of these residues are rich in sugar, promoting better fungal growth and thus making the process more economical especially for the cellulo- and ligninolytic enzymes. Other potential applications of AIW through SFF technology are the production of fructooligosaccharides, bioactive compounds, and bio-insecticides, among others (Mussatto et al. [2012](#page-16-19)). For example, apple pomace undergone solid fermentation to produce organic acids, heteropolysaccharide (i.e., xanthan, chitosan), flavor and aroma compounds, bioethanol, enzymes, edible mushroom (Pleurotus ostreatus), antioxidants, and nutritional enrichment among others. Several factors making apple pomace suitable as a raw material for biotechnological products are the high content of polysaccharides (mainly cellulose, starch, and hemicelluloses); presence of mono-, di-, and oligosaccharides, citric acid, and malic acid, which can be metabolized by microorganisms; and richness in vitamins and other mineral ions which could limit the cost of nutrient supplementation for fermentation media (Dhillon et al. [2013](#page-14-19)). Also there is great potential for coffee pulp and coffee husk used as substrates to microbial aroma production by solid-state fermentation using two different strains of *C. fimbriata* (Murthy and Naidu [2012\)](#page-16-20).

## *3.5 Extrusion*

Extrusion combines a number of unit operations, i.e., mixing, cooking, shearing, puffing, final shaping, and drying in one energy-efficient rapid continuous process (Harper et al. [1989](#page-15-21)), and can be used to produce a wide variety of starchy foods including snacks, ready-to-eat (RTE) cereals, confectioneries, and extruded crisp breads (Suknark et al. [1997\)](#page-17-8). This process of high-temperature short-time extrusion brings gelatinization of starch, denaturation of protein, modification of lipid, and inactivation of enzymes, microbes, and many antinutritional factors (Bhattacharya and Prakash [1994\)](#page-14-20). Extruded foods are able to provide nutritious products, by means of combine quality ingredients and nutrients to produce processed foods that are formulated to contain specific amounts of each required nutrient (Cheftel [1986\)](#page-14-21). The fruit wastes, defatted hazelnut flour, and durum clear flour can be used in combination with cereal flours for production of nutritionally balanced convenient extruded snack foods due to their valuable characteristics.

#### **4 Conclusion: Biorefinery Concept from AIW**

The use of AIW for its use as a source of bioactive compounds can be associated with two different concepts, the biorefinery and the circular economy. The processes based on agro-industrial wastes can consider different steps and technologies that allow the recovery of bioactive compounds of interest in a better way. As shown in Fig. [2](#page-13-5), it is possible to consider a first stage of wet milling that allows reducing the particle size, facilitating both the development of later extractive processes and the release of different compounds through the syneresis process. Depending on the raw material, it is possible to remove soluble molecules (low molecular weight) such as minerals or sugars of low molecular weight, among others. In this aspect, also AIW can be an important source of macromolecules such as fibers (soluble and insoluble) and proteins, so that a fractionation of these molecules would allow a better use of waste as a raw material. In the case of proteins, these can be solubilized by the addition of an alkaline solution that is then removed by centrifugation or pressing, which allows obtaining a solid residue rich in fibers, which can contain molecules as antioxidants. In this way, the solid can be treated by different technologies for the recovery of these compounds, for example, direct extraction for the recovery of antioxidants, leaving an expended solid fraction rich in fibers; the application of SFF as a technology for the generation of enzymes or other compounds; or the application of different treatments prior to the extraction itself (such as an enzymatic treatment, or physicochemical treatments), obtaining a final residue rich in fiber that can be used by the food industry or a solid with a better metabolism capacity of the raw material and that can be used in the generation of bioenergy.

<span id="page-13-5"></span>

**Fig. 2** AIW processing under the biorefinery concept

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