Value-added Products from Fruit and Vegetable Wastes: A Review

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ABSTRACT

Fruit and vegetable wastes (FVW) are some of the most abundant agro-industrial wastes. This residual biomass can be used to obtain biofuels such as bioethanol, biomethane, biohydrogen and biobutanol. Additionally, FVW can also be employed as a raw material for recovering bioactive compounds (antioxidants, enzymes or antibiotics) and to produce organic acids of industrial interest (citric acid, lactic acid, acetic acid). However, the use of these wastes as a substrate to obtain the mentioned value-added products usually requires several steps, including different pre-treatments, microbial biotransformation and separation and purification processes. The aim of this work is to provide an overview of the different products that can be obtained from FVW, as well as the technologies that can be employed in the revalorization procedures.

Keywords: Bioactive compounds, Biofuels, Fermentation, Fruit wastes, Hydrolysis, Organic acids, Separation, Vegetable wastes, Waste valorization

1. INTRODUCTION

From agricultural production to final household consumption, one third of the world's food produced for human consumption becomes waste every year[1]. Underutilization of food leads to economic losses in terms of resources used in its production and, in addition, its management as waste entails environmental problems such as CO_2 and other greenhouse gas emissions. Therefore, the generation and accumulation of these organic wastes is not only a widespread and harmful environmental problem, but it is also important from an economic point of view in terms of collection, transport and final disposal costs. It has been estimated that the global production of municipal organic wastes will reach more than 1000 million tons per year by 2025[2]. Specifically, in Europe approximately 50% of the food produced is being discarded [1,3].

Additionally, today there is growing concern about environmental pollution, as well as the increasingly probable depletion of fossil fuels in the future[4]. Biofuels, which are defined as fuels, liquid or gaseous, that have been derived from biomass, may offer a good alternative and help to address this issue. Bioethanol, biobutanol, biomethane, biohydrogen and biodiesel are some examples of biofuels that have multiple uses, including transport, heating, and electricity generation[5]. Crops such as sugarcane, starch and corn are used as raw materials to produce first-generation biofuels. However, it is well known that the

use of food-based crops as a substrate for biofuel generation entails both economic and ethical problems[6]. Thus, in recent decades, agro-food wastes have been increasingly used as raw materials for the production of second-generation biofuels due to their availability and sustainability.

Among the most important agro-food wastes generated in the processing industry, supermarkets and households are fruits and vegetables, whose wastes in some cases exceed 25% of the purchased product[1]. Due to their high carbohydrate content, these residues are of interest as substrates for obtaining biofuels. Many studies have been carried out employing these wastes as substrates to obtain bioethanol[7,8]. In addition, several studies have also been published on their use for producing biohydrogen, biomethane and biobutanol[9-14].

From a medical perspective, the consumption of fruits and vegetables has been associated with a reduction in the risk of cardiovascular disease and cancer due to their content in bioactive compounds such as antioxidants, enzymes or antimicrobial compounds. Among the bioactive compounds present in fruits and vegetables are phytochemicals, specifically phenolic compounds, whose antioxidant activity is considered one of the main causes of their beneficious health effects[15]. For this reason, in recent years, new techniques for the identification, extraction and quantification of these compounds have been established[16,17] and their beneficial properties have led to their extraction from fruit and vegetable residues as a valorization alternative of great interest. Numerous examples of the extraction of phenolic compounds from fruit and vegetable wastes (FVW) have been reported in the literature[18-23], and there is also a growing interest in obtaining organic acids from fruit and vegetable residues. These acids represent one of the most important groups of biological products and have a wide variety of applications in the pharmaceutical (anticancer, antimutagenic), food (acidulant) or detergent/surfactant industries[24,25]. Apple pulp, banana peel, potato peel, grape stems or lettuce wastes are some of the numerous FVWs used to obtain these high added value organic compounds reported in the literature[24,26,27].

Although several reviews on bioethanol production have been published, few include other biofuels such as biohydrogen, biomethane and biobutanol. This review is focused specifically on the revalorization of vegetable and fruit residues, employing them as substrates not only to obtain biofuels, but also as a source of different compounds of interest. In addition, a discussion on the main techniques and procedures used to obtain these products is provided. The final objective of this work is to give a general overview of all the possible uses for these abundant organic wastes in order to decrease the amount of them that go to landfill and at the same time to produce value added products from cheap sources.

2. FRUIT AND VEGETABLE WASTES AS SUBSTRATES TO OBTAIN DIFFERENT PRODUCTS

From the perspective of waste valorization, fruit and vegetable residues are of great interest for many reasons. Large quantities of fruit peels, the main by-product of industrial fruit processing, are discarded as waste[28,29]. For example, approximately 36 million tons of banana peels and more than 15 million tons of citrus waste are generated worldwide every year[30]. Vegetable processing also generates significant amounts of waste. This is the case of onions, one of the major crops in Europe, generating more than 6 million tons of residues globally[31]. These wastes, when generated both at supermarkets and at industrial level, are very homogeneous in terms of their characteristics and composition, allowing them to be used

directly, without the need for a classification stage.

Pre-treatment of these FVWs allow them to be used as substrates in fermentative bioprocesses to obtain bioethanol, biobutanol, biomethane, biohydrogen or organic acids, due to their high carbohydrate content (20--30% dry weight (dw) in citrus pulp, 50--60% dw in apple pomace or 60--70% dw in potato peel)[32,33]. Another way to valorize these residues, and one of great interest at present, is by employing them as a substrate to extract bioactive compounds by means of diverse separation techniques.

Tables 1 and 2 provide a summary of FVWs and their products.

Regarding the topicality of the investigation, the search for different residues (banana, potato…) employing as keywords "waste biofuel" and "bioactive compounds" in the Scopus database between 2010 (January) and 2020 (May) inclusive, showed that, in the case of "biofuel", the most frequently used fruit and vegetable residues were cassava, potato, orange and coffee, from which mostly bioethanol was obtained. With respect to "bioactive compounds", olives, oranges and tomatoes are the wastes most commonly used to obtain phenolic compounds.

2.1. BIOFUELS

In recent years, much work has focused on obtaining bioethanol from biomass with a high lignocellulose content, as it is a very abundant material and, at the same time, a sustainable resource. However, the use of this lignocellulosic biomass for the production of bioethanol requires a specific pre-treatment, since this raw material consists of a complex structure of carbohydrates that cannot be directly fermented[4,53]. For this reason, these substrates must be hydrolyzed into simple sugars before bioethanol is obtained by fermentation. FVWs have been employed as a substrate for obtaining biofuels in several research studies. Among the main fruit wastes commonly used for bioethanol production are banana, citrus fruit, apple or pineapple.

Banana waste is considered a suitable substrate to produce bioethanol since it has a low lignin content[34,66]. According to the Food and Agriculture Organization (FAO), banana is the most frequently cultivated fruit in the world and about 30% of the world's crop of bananas comes from India, where more than 20% of banana production goes to waste[67]. In Australia and Malaysia, banana waste is estimated at 30% of total production, while in South and Central America it may be as high as 50%[68-70]. Besides, Happi et al.[71] indicated that, although banana peel is a residue, it has a high carbohydrate content, mainly starch, in addition to soluble sugars (glucose, fructose and sucrose), proteins and fibers. Therefore, this residue can be used as a renewable substrate in the production of bioethanol.

Citrus fruit is the most important fruit tree crop in the world, with an annual production of around 120 million tons[72]. Citrus waste (skin, seeds and pulp) reaches a yearly world total of 20 million tons and approximately 600 000 tons are generated in Spain. Citrus fruit employed at industrial scale consists mainly (98%) of lemons, mandarins, grapefruit and oranges[30]. Like banana peels, citrus peels are a very suitable material for ethanol production because of their low lignin content and high concentrations of fermentable sugars such as glucose, fructose or sucrose[73]. One aspect to be taken into account when using citrus peels in the production of bioethanol is the presence of D-limonene (0.8--1.6% wet weight). The citrus residues contain essential oils whose main component is limonene (95%) which turns out to be an inhibitor of the yeasts used in the fermentation process. Therefore, its elimination is necessary as a preliminary step for

biofuel production[36,74].

It is estimated that about 80% of citrus residues generated worldwide are orange peel. Oranges are one of the most often consumed citrus fruits, with a significant level of sales in the market. However, their peel, which represents 45--60% of the weight of fruit, is frequently discarded and used only as feed for cattle[75]. In Spain, of the 600 000 tons of citrus peel wastes, approximately 30% comes from mandarins[76]. As is true of other citrus fruits, mandarin residues are suitable for producing bioethanol. However, this is a topic that has received less investigation[76], whereas several studies have focused on its use as a fermentation medium for the production of multi-enzyme preparations or as a source of functional fibers[30,77].

Lemon is, after orange and mandarin, the third most important citrus species in terms of its cultivation, with an annual production of over 4 million tons. Several researchers have highlighted the potential use of lemon waste as a raw material for bioethanol production. For example, Boluda-Agilar and López-Gómez[38] reported a production of more than 60 L of ethanol per ton of lemon peels.

Grapefruit is another major citrus crop; around one million tons of this fruit are processed annually, of which about half is converted into waste. Grapefruit residues (husk, seeds and membrane residues) contain glucose, sucrose and fructose, which can be directly fermented by *Saccharomyces cerevisiae* to produce ethanol. In addition, galacturonic acid present in these residues can be employed as a substrate to produce ethanol by fermentation with *Escherichia coli* K011[40].

Apple, with an annual production of 86 million tons[67], is another fruit of interest for ethanol production, in which apple waste, especially pulp, is used as the raw material. Apple pulp is the main by-product of the cider and apple juice industry and it is estimated that about 20 kg of pulp is obtained for every 100 kg of processed apples[78]. Its high content of simple sugars (glucose, fructose and sucrose) and polysaccharides makes it an ideal substrate for bioethanol production. In South American countries, these residues are used as feed for livestock, although to a limited extent, due to their low protein and vitamin content[79]. Many researchers have looked for new uses for apple pulp, such as obtaining high added value products like enzymes or organic acids.

The industrial processing of pineapple also generates important quantities of waste, more than 40% of which corresponds to peel and core. Pineapple residues, like most fruits, are rich in simple and complex sugars which can be converted into ethanol by fermentation [80].

Consumption of coffee is high around the world and more than 50% of the weight of coffee fruit corresponds to un-used components that are discarded, generating around 15 million tons of waste annually[62,81]. Coffee mucilage, a residue of the coffee processing industry, contains mainly glucose and galactose[62]. Choi et al.[82] demonstrated that coffee waste is an appropriate feedstock for producing bioethanol (15 g/100 g coffee waste) under simultaneous saccharification and fermentation conditions using *S. cerevisiae* as the fermentative microorganism. Nguyen et al.[83], after a pre-treatment with 60% ethanol (1:5, w/v) and enzymatic hydrolysis of coffee residues, performed a fermentation with *S. cerevisiae* and *Pichia stipitis* and obtained 8 g of bioethanol from 100 g of pre-treated coffee waste.

According to The International Cocoa Organization, 16 million tons of residual cocoa biomass are produced every year and in recent years, interest in using by-products from the cocoa industry has increased[84]. It has been estimated that in 2017 the export of cocoa residues such as shells, husks or skins, mainly from Sierra Leone and The Netherlands, exceeded US$ 200 million. Countries such as Spain or Malaysia are the main

importers and use these cocoa residues for products such as animal feed or fertilizers[85]. Several authors have indicated the high carbohydrate content of cocoa pod husk, the main waste of cocoa production (32--47%), and the production of bioethanol as a way to valorize this residue[64,65,86].

Potato, carrot, cassava and onion wastes are also vegetable residues commonly investigated as substrates for the production of bioethanol. During the industrial processing of potato, between 20 and 50% of the raw product is discarded as residue[87]. Potato waste has a high carbohydrate content (69% w/w on a dry weight basis) of which approximately 75 % corresponds to starch[33], making it a potential raw material to be used as substrate for fermentation. Chohan et al.[88] used potato peel as feedstock to produce bioethanol by means of *S. cerevisiae* under simultaneous saccharification and fermentation conditions, obtaining a maximum bioethanol concentration of 22.5 g/L. Pre-treating potato peel with acid and enzymes resulted in about 90% bioethanol yield[89].

Large quantities of carrots are annually discarded in the world, amounting to roughly 30% of the carrot harvest. These residues cause major environmental problems because only approximately 20% of them are reused as animal feed. With a content of 68% (w/w on dry weight basis) of carbohydrates, mainly sucrose, fructose and glucose, carrot wastes are a potential substrate to obtain significant amounts of bioethanol (50--80 L for each ton of discarded carrots)[47,90,91].

Cassava is one of the most promising species for bioethanol production in China and several countries of Central and South America. Over 14 million tons of cassava waste are produced annually[4,59,92]. Studies based on the use of cassava wastes to obtain bioethanol have been reported[4,93,94]. Cassava waste presents a high carbohydrate content (7% w/w on dry weight basis) and it has been reported that using cassava wastes to obtain bioethanol is a more efficient process than employing other crops like potato or sugar cane[60,92,95,96].

More than 500 000 tons of onion wastes are produced annually in the European Union. These residues are rich in carbohydrates (76% w/w dry weight), and therefore, some authors[97-99] have used them as feedstock to produce bioethanol. Kim et al.[100] obtained approximately 20 g of bioethanol from 100 g of onion wastes by fermentation with *S. cerevisiae*.

Another biofuel that is important due to its high energy content (122 kJ/g) is biohydrogen. This is a very promising energy resource, since producing hydrogen by biological methods requires lower energy consumption than thermo-chemical and electrochemical methods. In addition, during the combustion of biohydrogen, water vapor and energy are released instead of greenhouse gases[9,11,101]. Carbohydrate-rich raw materials with low amounts of nitrogen and requiring minimal pre-treatment are suitable for biohydrogen production[101,102]. In this sense, FVW is a very useful resource for obtaining this biogas because of its biodegradability, low total solids content and high volatile solids content[103,104]. In addition, using fruit and vegetable wastes as a raw material for biohydrogen production is a sustainable and environmentally friendly way to manage these residues[105]. Mixtures of fruits and vegetables such as pepper, onion, potato, eggplant, carrot, cabbage, cucumber, citrus, pear, apple and grape have been used as substrates to produce biohydrogen by dry fermentation under thermophilic and mesophilic conditions[9-11].

Biomethane is a renewable biofuel similar to fossil gas present in nature. Its increasingly widespread use represents a significant reduction in the quantity of oil employed, as well as in the emissions of harmful gases into the atmosphere[13]. Additionally, another advantage in comparison to fossil gas is that using

organic wastes as the raw material to obtain biomethane helps to reduce pollution from organic waste themselves[106]. Regarding biomethane production, anaerobic digestion is one of the most efficient techniques because of the increase in nutrient recovery and the reduction in greenhouse gas emissions[107,108].

Some studies on the revalorization of banana residues highlight the potential use of this waste as a substrate to produce methane (40--64% CH_4 content in biogas)[13]. Saha et al.[109] used a mixture of orange, banana, grape and pineapple wastes, obtaining about 350 mL of methane from 80 g of residue after 86 days of digestion. In addition, Zhao et al.[110] obtained approximately 290 mL of methane/g volatile solids (VS) from fruit and vegetable wastes including lettuce, tomato, carrot and apple residues after a 24 day-anaerobic digestion.

Biobutanol is also an alternative biofuel to be considered due to its low vapor pressure, its non-corrosive capacity, and its high energy level. The butanol industry generated about $6 billion globally in 2018, although this value is estimated to have tripled in 2020. It has certain advantages over ethanol, such as higher energy content and lower flammability. In addition, it has been used in chemical industries as a reagent in synthesis processes[111,112].

The high content of soluble sugars and carbohydrates make apple residues an appropriate starting material for obtaining butanol, as has been highlighted by Jin et al.[111]. These authors were able to obtain 17 g butanol/100 g dry apple pomace by acetone/butanol/ethanol (ABE) fermentation. In addition, Sanguanchaipaiwong and Leksawasdi[14] described pineapple waste juice as an ideal raw material to obtain butanol, as it does not need pre-treatment. Although high concentrations of butanol are not achieved (3.14 g/L), the absence of pre-treatment is a practical and economic advantage. It is estimated that vegetables generate more than 30% (w/w) of residues during harvesting, processing and marketing. In this sense, India is the main producer of peas, with an annual production of 3.6 million tons that generate more than one million tons of waste[113]. Nimbalkar et al.[51] have pointed out that the high holocellulose content of pea pod waste means that these residues can be used as a potential raw material for butanol production.

Table 3 summarizes work on fruit and vegetable substrates used to obtain different biofuels, as well as the techniques employed for this purpose, the microorganisms involved and process yields.

2.2. BIOACTIVE COMPOUNDS

Bioactive compounds are substances that can play a key role in reducing the risk of certain diseases[120]. As a result of these health-enhancing activities, research and studies on bioactive compounds have increased considerably in recent years. Different studies indicate that the intake of certain bioactive compounds can reduce the risk of cardiovascular disease, cancer or degenerative disease. Therefore, the antioxidant activity of bioactive compounds, sequestering free radicals, is of great importance in reducing their harmful effects[22,121].

Fruit and vegetable wastes contain bioactive fractions that usually include carbohydrates, proteins, lipids and secondary metabolites[122]. For example, certain polysaccharides present in fruit and vegetable residues act as anticancer and anti-inflammatory agents[123]. Furthermore, fruit and vegetable seeds are rich in proteins whose hydrolysis favors the release of bioactive peptides with pharmacological activity[124]. In addition, carotenoids, sterols or fatty acids are some examples of the bioactive lipids present in fruit and

vegetable wastes such as citrus, mango or tomato seeds[122]. For these reasons, the use of theses wastes as a source of bioactive polysaccharides has generated increasing interest in recent years. Finally, several authors have investigated the use of fruit and vegetable residues as a substrate for obtaining secondary metabolites, among which stand out polyphenols, alkaloids or volatile acids[120,125,126].

Within the family of bioactive compounds, antimicrobial compounds, antioxidant compounds and enzymes are important groups.

2.2.1. Antimicrobial compounds

Antimicrobial compounds are defined as natural substances capable of inhibiting the growth of microorganisms and altering their metabolism. There is an increasing interest in the study of organic compounds that inhibit the growth of microorganisms responsible for food deterioration and foodborne illness [127]. In addition, the increasing antibiotic resistance of different bacteria has led to a search for new compounds that can be employed instead of conventional antibiotics[128].

It has been published that fruit and vegetable peels are an important source of compounds with antimicrobial, antioxidant and anti-inflammatory function. For example, citrus peels contain essential acids, alkaloids, sesquiterpenes or hypericin, whose presence is directly related to the antimicrobial activity of these fruits against various bacteria. Specifically, the antimicrobial capacity of orange is effective against strains of *E. coli*, *S. aureus* and *Pseudomonas fluorescens*, whereas lemon compounds affect the growth of *Pseudomonas*, *Salmonella* and *Micrococcus*[129,130].

Mokbel and Hashinaga[35] investigated the antioxidant and antibacterial capacities of banana peels, as well as the substances responsible for these properties. Malic and succinic acids present in the banana residues were effective against Gram-negative bacteria, such as *E. coli* and *Salmonella*, and also against Gram-positive bacteria, such as *S. aureus* and *Bacillus*. On the contrary, palmitic acid hardly affected the different species used in the tests.

Mango waste, especially shell extracts and seeds, have been found to have antibacterial properties. Extracts of mango seeds employing methanol, ethanol, hexane and phosphate have been studied for their possible antimicrobial effects. The methanol extract was found to be effective against *E. coli*, *Salmonella typhimurium*, *Aspergillus niger*, *Candida albicans*, *Shigella flexneri*, *S. aureus*, *Streptococcus pyogenes* and *Yersinia enterocolitica* among others[44,131]. The antimicrobial activity of the methanol extract was higher against Gram-positive than Gram-negative bacteria because the complex structure of the Gram-negative wall prevents or hinders the entrance of antimicrobial compounds. The ethanol extract had antibacterial activity against strains of *Listeria monocytogenes*, *Nocardia*, *S. aureus*, *Citrobacter*, *Enterobacter aerogenes*, *E. coli*, *Aeromonas hydrophila*, *Bacillus cereus* and *Bacillus licheniformis*[44,132]. Engels et al.[133] studied the inhibitory effect of the hexane extract, obtaining minimum inhibitory concentration (MIC) values <0.2 g/L for *S. aureus*, while Mirghani et al.[134] described the effect of the phosphate extract against *S. aureus*, *Bacillus subtilis* and *E. coli*. Table 4 summarizes the effects of different extracts obtained from different fruit and vegetable wastes on diverse bacterial strains.

These results suggest that fruit peels could be used for obtaining new antibiotics. Nevertheless, comprehensive studies are still needed to determine the effectiveness of these residues against a wide range of bacteria, fungi and yeasts[39].

With respect to vegetables, extracts from potato peel using different solvents have shown antimicrobial activity against several bacteria and fungi. For instance, chloroform, hexane, acetone and methanol extracts were effective against Gram-positive bacteria, such as *Staphylococcus subflava*, Gram-negative bacteria, including *Klebsiella pneumoniae*, *Enterobacter aerogenes* or *Proteus mirabilis* and fungi such as *Candida albicans*, *Candida glabrata* or *Cryptococcus luteolus* among others. Potato peel extracts showed better antifungal activity than antibacterial activity[135].

Szabo et al.[136] found that phenolic extracts from tomato wastes, using methanol as solvent, had antibacterial activity against Gram-positive and Gram-negative bacteria such as *S. aureus*, *B. subtilis*, *Pseudomonas aeruginosa* or *E. coli.* These tomato extracts were highly effective against *S. aureus* with MIC values about 0.625 mg tomato waste/mL. Furthermore, the authors observed that Gram-positive bacteria were more sensitive to the extracts than Gram-negative bacteria.

Several studies about the antimicrobial activity of pumpkin wastes have been published. Pumpkin extracts with methanol as solvent showed positive activity against bacteria such as *Bacillus cereus, B. subtilis, Enterobacter aerogenes, S. aureus* or *Providencia stuartii* and fungi such as *Candida albicans, Rhodotorula rubra, Rhizopus oligosporus* or *Cryptococcus meningitis*[137-139].

The ethanol extract of pumpkin seeds had antimicrobial activity against *S. aureus*, *B. subtilis*, *P. aeruginosa*, *E. coli* or *A. niger*[140]. The water extract of pumpkin peels has been effective against *E. coli*, *Pseudomonas* sp. and *Vibrio cholerae*[141].

2.2.2. Antioxidant compounds

Antioxidant compounds play an important role in the immune system by protecting the body from the oxygen free radicals responsible for oxidative stress, which are closely linked to many chronic problems and degenerative diseases[142]. Their main functions also include the scavenging of reactive species of cellular metabolism, preventing damage to lipids, proteins, nucleic acids and, ultimately, preventing cell damage[143]. Within the antioxidants, phenolic compounds, carotenoids, vitamin C and vitamin E are important compounds.

2.2.2.1. Phenolic compounds

Phenolic compounds, or polyphenols, are the main group of secondary metabolites present in fruits such as apple, citrus fruits, grapes, pineapple and pomegranate and vegetables such as olive, lettuce and tomato. Recent research has demonstrated that phenolic compounds play an important role in protecting the immune system, as well as in preventing diseases such as cancer, atherosclerosis, or cardiovascular disease, mainly because of their antioxidant properties[144]. Phenolic acids and flavonoids are the most frequent polyphenols in nature (30 and 60%, respectively)[144,145].

Chemical characterizations of the composition of citrus peels have proved that they are important sources of polyphenols[146,147]. Lime, for example, is rich in flavonoids and phenolic acids[148]. The flavonoids contained in citrus fruits are important enzymatic modulators, inhibit cell proliferation and show anti-allergic and anti-inflammatory properties[149]. Numerous studies have analyzed the beneficial effect of citrus peel against different diseases. For example, flavonoids present in orange peels have beneficial properties against liver disease and several cancers or an anti-inflammatory effect, whereas other citrus peels such as

lemon peel or mandarin peel have shown antidiarrheal and antidiabetic activity and anti-obesity effects [150]-[154].

An increase in global pomegranate consumption has been reported in recent years, due to its beneficial effects on health originated by its high content in phenolic compounds, mainly flavonoids, phenolic acids and ellagitannin[46]. Pomegranate residues such as peel are a promising raw material for the extraction of natural antioxidants, for which demand has increased in recent years. Alexandre et al.[155] reported antioxidant activity values of 346 mg Trolox equivalent (TE)/g dry weight of pomegranate peel extracts obtained by a combination of high-pressure extraction and enzymatic extraction. Verotta et al.[25] highlighted the bioactive role of ellagic acid from pomegranate wastes due to its anti-mutagenic, anti-cancer and anti-inflammatory properties.

Red fruits such as blueberries or strawberries are also rich in phenolic compounds with antioxidant and antimicrobial properties, particularly anthocyanins, phenolic acids, ferulic acid and caffeic acid[156-158]. Given their high content in polyphenols, blueberry residues such as blueberry pomace could have potential value for improving gut health. Cheng et al.[159] demonstrated that by inhibiting the growth of bacteria such as *E. coli* and *Enterococcus* and increasing the abundance of beneficial bacteria such as *Lactobacillus* and *Bifidobacterium* in the intestinal tract, blueberry pomace exerts a beneficial effect on fecal microbiota. Vázquez-González et al.[160] analyzed the presence of phenolic compounds in strawberry and raspberry wastes and obtained a maximum phenolic activity of 1.3 and 0.7 mg TE/g fresh weight for strawberry and raspberry residues, respectively.

Pineapple residues are not usually used as animal feed due to their high fiber and carbohydrate content and low protein content. Although most research on the revaluation of pineapple wastes is based on the extraction of bromelain, a proteolytic enzyme, some authors have also studied the extraction of antioxidants. For example, Correia et al.[42] evaluated the ability of *Rhizopus oligosporus* to produce phenolic compounds from pineapple wastes with soy flour as a nitrogen source. Likewise, Sepúlveda et al.[161] investigated the extraction of phenolic compounds from pineapple residues (core and skin) by an auto-hydrolysis process, obtaining a maximum amount of total polyphenols of 1.75 g/L.

Olive fruit is a source rich in phenolic acids and alcohols, flavonoids and oleuropein derivatives[57]. It has been reported that the extraction of phenolic compounds from olive residues is profitable in economic and environmental terms[162]. Wang et al.[162] studied the extraction of total phenolics from olive pomace by ultrasound-assisted enzyme-catalyzed hydrolysis, obtaining a maximum phenolic content of 64 mg/g from the ethyl acetate extract fraction. Rubio-Senent et al.[57], who determined the phenolic composition of ethyl acetate extract obtained from hydrolyzed alperujo, found that hydroxytyrosol was the most abundant phenolic alcohol (30 mg/mL fraction).

Among vegetables, lettuce has been reported as a source of polyphenols (caffeic acid, flavonols and vitamins C and E). Some authors have indicated that lettuce residues, i.e., discarded outer leaves, have higher levels of phenolic compounds than the edible portions. In this sense, Viacava et al.[163] observed that the content of phenolic compounds in lettuce leaves depends on the leaf position. Therefore, the higher levels of polyphenols corresponded to the most photosynthetic lettuce leaves (11 mg gallic acid/g dry weight). The results showed that the main phenolic compounds in lettuce wastes were the phenolic acids: chlorogenic, isochlorogenic and chicoric.

Potato, with an annual production of almost 400 million tons in the world, generates significant amounts of waste that is rich in bioactive compounds, not only antioxidants but also food fibers and minerals[61]. Among the phenolic components in potato peel reported in the literature, caffeic and chlorogenic acid are principally responsible for its antioxidant activity[164,165]. Riciputi et al.[166] reported values of chlorogenic acid of 4 mg/g dry weight, representing 50--60% of the total phenolic compounds in potato wastes. Several authors have used response surface methodology to optimize the extraction of phenolic compounds from potato peel with ethanol as solvent. Amado et al.[167] evaluated different extraction conditions (temperature, time and ethanol concentration) and observed that the higher the temperature and concentration of ethanol, the greater the recovery of total phenols from potato peel.

One of the most widespread crops in Europe is onion, with a production of almost 6 million tons[168]. Onion residues, generated from inedible portions, are richer in polyphenols than edible parts and have a particular composition. Quercetin is the most abundant flavonoid in onion residues (9 mg/g) and appears in the form quercetin 4'-*O*-β-glucopyranoside, quercetin 3,4'-*O*-β-glucopyranoside and quercetin 3,7,4'-*O*-β-triglucopyranoside. These compounds can be extracted from onion skins using methanol and water as solvent agents and it has been reported that quercetin is between two and three times more active as an antioxidant agent than other compounds extracted from onion residues, such as cysteine[21,48,169].

2.2.2.2. Carotenoids

Carotenoids are tetraterpenoids with double conjugated bonds and cyclic or acyclic groups that confer light absorbing and free radical elimination properties. They are classified into two groups: carotenes which are carotenoids without any oxygen molecule, such as β-carotenes and lycopene, and xanthophylls, which are carotenoids with oxygen molecules, among which lutein and zeaxanthin can be cited[142].

Carotenes possess the "provitamin A" activity that plays a very important role in human health. A vitamin A deficiency can trigger visual problems, increase risk of anemia and generate reproductive problems[170]. The xanthophyllic group lacks pro-vitamin A activity. However, this group has outstanding antioxidant and biochemical properties, for example, against age-related macular degeneration[171].

One of the most prominent carotenes is lycopene, the main carotenoid in tomatoes. It is an acyclic carotenoid with double conjugate bonds without cyclic β-ionone structure and, therefore, lacks pro-vitamin A activity[172]. Many studies have shown that lycopene is a more potent scavenger of reactive oxygen species than other antioxidant compounds[52,173,174]. Shi et al.[175] suggested that this is due to the high number of conjugated double bonds (11), as well as to the linearity of the β-ionone ring. More than 80 % of the total carotenoids present in the tomato corresponds to lycopene, although the content varies depending on the season and variety of the vegetable[176]. Tomato also contains β-carotene, lutein and flavonoids. Several studies have therefore suggested that tomato consumption is linked to a reduction in the risk of cardiovascular disease and cancer of the prostate, lung or stomach[172,177]. Tomato residues, which include seeds and peels, are rich in lycopene (0.5--0.8 mg/g on dry basis) and β-carotene (about 0.096 mg/g on dry basis)[178,179]. Lycopene is mainly found in the chromoplast of vegetable cells, and it is present in a complex form with proteins, so thermal or mechanical processes with organic solvents are necessary for its extraction from tomato peel[180]. In work carried out by Jurić et al.[181] tomato peel was used as feedstock to recover lycopene. For this purpose, tomato waste was mixed and centrifuged and it was found that the

lycopene content in the pellets decreased when residues were treated with higher-shear mixing (1.9 mg/g on wet basis) compared to the samples without treatment (4 mg/g on wet basis). In the supernatant obtained from centrifugation, 2 mg/g of lycopene (wet basis) were recovered. Coelho et al.[182] demonstrated that when the extraction temperature was higher, more carotenoids could be recovered from tomato wastes, obtaining a maximum of 0.2 mg eq. β-carotene/g fresh weight when working at 70°C.

Mango waste also has a high carotenoid content, between 0.02 and 0.035 mg/g of pulp[183,184]. Sánchez-Camargo et al.[20] have reported that the β-carotene contained in mango skins could be used as an alternative to synthetic antioxidants applied in the oil industry. Liang et al.[185] recovered a total carotenoid content of 0.08--0.1 mg/g (fresh weight) and 0.05--0.08 mg/g (fresh weight) from mango peel and mango pulp, respectively, with an ethanol/hexane mixture as extraction agent. In addition to β-carotene, α-carotene, lycopene, lutein, zeaxanthin and β-cryptoxanthin can be also recovered from mango waste.

2.2.2.3. Vitamin C

Vitamin C, or ascorbic acid, is an antioxidant that occurs in humans in the form of the ascorbate anion. It has beneficial properties for the skin, teeth and the immune system[186]. Fruits such as strawberry, lemon or orange and vegetables such as broccoli, cabbage and spinach are the main sources of vitamin C[187,188]. Lado et al.[189] evaluated the extraction and quantification of vitamin C from different citrus wastes (orange peel, mandarin peel and grapefruit peel) using metaphosphoric acid as the extraction agent. Maximum values of ascorbic acid of 2.5, 2.5 and 2 mg ascorbic acid (AsA)/g (fresh weight) for orange peel, grapefruit peel and mandarin peel, respectively, were recovered. Nilnakara et al.[190] determined the content of ascorbic acid in fresh and blanched cabbage wastes (outer leaves of cabbage). The results showed a lower content of vitamin C in blanched cabbage leaves (3.45 mg/g dry matter) than in fresh cabbage residues (5.33 mg/g dry matter). The authors explained that this difference might be due to the high solubility of vitamin C in water and its low stability at high temperatures (during blanching, wastes were subjected to hot water at 93°C).

2.2.2.4. Vitamin E

Vitamin E comprises a group of eight compounds, namely tocopherols and tocotrienols, which have a hydrophobic isoprenoid tail. Both, tocopherols and tocotrienols, can be found in nature in the α-, β-, γ- and δ-forms. The most abundant are α- and γ-tocopherol, present in leaves and seeds, respectively, while tocotrienols are less frequent[191]. Due to its antioxidant properties, vitamin E protects human cells against free radicals. Vitamin E is present in plant-based foods, especially those with green leaves such as broccoli or spinach. Several authors have obtained vitamin E and its compounds from different fruit and vegetable wastes. One of the richest natural sources of vitamin E are grapes, with a content of 2.3--10.0 mg/g in seed oil[192-194]. Tangolar et al.[195] evaluated the content of tocopherol in grape residues (seed, pomace, bagasse and stalk). The highest amount of α- (0.089 mg/g dry weight), δ- (0.088 mg/g dry weight) and γ-tocopherol (0.008 mg/g dry weight) was obtained from the grape bagasse fraction, whereas the highest value of β-tocopherol was detected in grape stalk (0.001 mg/g dry weight). The maximum total tocopherol content (0.1 mg/g dry weight) was recovered from grape stalk. Durante et al.[196] studied the presence of toco-chromanols (tocopherols and tocotrienols) and their antioxidant activity in pomegranate, tomato and grape seeds. The maximum toco-chromanol content was detected in tomato seeds, 0.16 mg/g (dry basis) of which

90% was γ-tocopherol and 10% was α-tocopherol and the maximum antioxidant activity was obtained in grape residues (0.18 mg TE/g). From pomegranate and grape residues, α- and γ-tocotrienol were also obtained.

2.2.3. Enzymes

Enzymes are biological catalysts responsible for metabolic processes[197]. They have applications in different fields such as the food, cosmetic, pharmaceutical or textile industry[198]. Examples of enzymes are amylases, pectinases, cellulases, lipases and proteases.

a) Amylases: these degrade starch into low molecular weight sugars such as glucose or fructose. They are classified as endo- and exo-amylases depending on the link they attack. The exo-amylases specifically break the α-1-4 bond, whereas some endo-amylases attack equally the α-1-4 and α-1-6 bonds, obtaining glucose and maltose[199,200]. Ethanol production from starch and the manufacture of alcoholic beverages and sweeteners are some applications of these enzymes [201].

b) Pectinases: these hydrolyze pectin and are classified into depolymerizing and demethoxylating enzymes. In the food industry, they play a significant role in the processing of fruit juices in combination with cellulases and in the extraction of vegetable oils[202-204].

c) Cellulases: these are a complex of three enzymes (endo- and exo-glucanases and cellobiase) that degrade cellulose into glucose monomers[205].

d) Lipases: these hydrolyze triglycerides to fatty acids and glycerol and also present phospholipase, cholesterol esterase or amidase activities. In recent years, their application has been extended to the production of biodiesel, biopolymers or flavoring agents[206].

e) Proteases: they are also known as peptidases, attack the peptide bonds of amino acids and are also classified as endo- and exo-peptidases depending on the bond they hydrolyze. They are used in the food industry to coagulate milk, brew beer or obtain new ingredients[200,207].

Enzymes are considered as bioactive compounds of high added value that can be obtained from the biotransformation of FVWs[208].

Large quantities of pulp waste are generated during the processing of citrus fruit juices. De Gregorio et al. [208] isolated two strains of fungi, *A. niger* and *Trichoderma viride*, and used them to produce pectinases employing lemon pulp as substrate. The pectinases obtained were found to have an activity similar to that of commercial enzymes and could therefore be used, for example, in the juice processing industry. Oberoi et al.[209] used dried kinnow pulp as a substrate for cellulase production with *Trichoderma reesei* under solid state fermentation (SSF) conditions.

Mango residues have been employed to produce amylases. Kumar et al.[210] studied α-amylase production by *Fusarium solani* in submerged fermentation using mango kernel. In addition, banana peels can be used as feedstock to produce amylases. Radha et al.[211] employed banana waste as a substrate to produce α-amylase by solid submerged fermentation and SSF conditions using *A. niger*. SSF was found to be much more effective in obtaining enzymes than submerged fermentation.

One of the alternatives for the valorization of pineapple residues is the production of bromelain. It is a protease with wide application in the food industry, such as softening meat, brewing beer or designing new dietary supplements[212]. In addition, it stands out for its anti-inflammatory and anti-diarrheal capacity[213].

Waste from the oil processing industry was employed as feedstock to obtain lipases by SSF using *Yarrowia lipolytica*[214]. The authors used both solid and liquid olive residues and observed that, with an adequate alkaline treatment of the substrate, lipase production increased more than ten times without prior treatment. Different researchers have suggested that the presence of polysaccharides, such as cellulose, hemicellulose and lignin in potato residues make these wastes suitable for the growing of certain enzyme-producing microorganisms. Elayaraja et al.[215] used potato processing wastes (peel) as the nutritional support for production of α-amylase by *Bacillus firmus*. Mukherjee et al.[216] studied an alkaline protease produced by *B. subtilis* using potato peel under SSF conditions and they reached about 400 U/g (dry substrate). Schalchli et al.[217] studied the production of lignolytic enzymes (manganese peroxidase and manganese-independent peroxidase) using potato peel and discarded tubers by means of *Anthracopyllum discolor*. They reported that the production of manganese enzymes, mainly manganese peroxidase, was higher in potato peel (193 U/L) than in discarded potatoes (110 U/L). Table 5 shows different enzymes obtained from several fruit and vegetable wastes.

2.3 ORGANIC ACIDS

The organic acids with most extensive industrial use are citric acid, acetic acid and lactic acid, although there are many others such as succinic, ellagic or ferulic acid which are also of industrial interest. Commercially, these acids are produced by different strains of bacteria, fungi and yeasts. Examples of the microorganisms employed are *Bacillus* sp., *Lactobacillus* sp., *Aspergillus* sp. and *Penicillium* sp.[218,219]. Fruit and vegetable wastes have proved to be an important source of organic acids and several studies have used these residues from the food industry as a substrate to obtain different organic acids[220-222].

Citric acid is a tricarboxylic acid widely employed in food (70%) and pharmaceutical (12%) industries as an acidifying agent[26,223]. Industrially it is usually obtained by submerged fermentation or by SSF of sucrose using microorganisms like *A. niger*[224]. Kareem and Rahman[26] used banana peel waste as a substrate to produce 82 mg citric acid/g (dry weight) using *A. niger*. Dhillon et al.[27] demonstrated that the addition of 3% (v/v) ethanol and 4% (v/v) methanol favored the production of citric acid from apple pulp under SSF using *A. niger*, obtaining approximately 18 mg/mL of acid.

Lactic acid is one of the most frequently occurring organic acids in nature. It is a chemical precursor widely applied in the food, pharmaceutical and textile industries. Lactic acid is also used to produce biodegradable polylactic acid plastic and as a preservative and acidulant in food[218,225]. Various FVWs had been used as feedstock to obtain lactic acid. For example, Jawad et al.[226] obtained lactic acid (17.48 mg/mL) from fermented mango peels with a consortium of indigenous microorganisms. Liang et al.[227] studied lactic acid production using mixed cultures from four different residues: two varieties of potato, banana and orange. The results showed that, after one day of incubation, an increase in lactic acid levels was observed in potato and banana residues, whereas lactic acid was not detected in orange peels until the second day. The highest acid concentrations were obtained from potato residues (6.7 and 4.8 mg/mL), followed by orange (3.4 mg/mL) and banana peels (3 mg/mL).

Acetic acid is another important organic acid recognized for giving vinegar its sour taste. It can be obtained either by aerobic or anaerobic fermentation by means of the genera *Acetobacterium* or *Clostridium*, respectively[218]. Raji et al.[228] obtained acetic acid from pineapple residues by two-stage fermentation with

S. cerevisiae to produce ethanol, and then, *Acetobacter aceti* converted the alcohol into acetic acid, 4.77 g acetic acid/100 g being achieved under optimal conditions. Papaya peel is another alternative substrate to obtain acetic acid as demonstrated by Vikas and Mridul[229]. In this case, the production of acetic acid by fermentation was carried out by the conversion of ethanol (previously obtained by mango peel fermentation) to hydrated acetaldehyde. This was followed by dehydrogenation of acetaldehyde to acetic acid by aldehyde dehydrogenase produced by *A. aceti.*

Ellagic acid is one of the most valuable bioactive compounds obtained from pomegranate residues. This compound exhibits anti-mutagenic activity, anti-inflammatory properties and it can prevent cardiovascular disease. Verotta et al.[25] carried out extractions of ellagic acid at room temperature from fermented pomegranate residues using methanol as solvent, obtaining process yields >40 % (w/w). In order to demonstrate the liberation of ellagic acid from fermented pomegranate wastes in physiological environments, the feedstock was subjected to simulated gastrointestinal conditions and they observed that in only 2 h more than 80% of the ellagic acid was released.

Ferulic acid is a monomer of phenolic acids present in the grain of barley and in the cell walls of plants. Vegetable and fruit residues such as fruit leaves, grape stems or nut shells have been used as the raw material for the production of this acid [230]. In this study, raw residues were subjected to acid and alkaline hydrolysis and the content of ferulic acid was quantified. Values in the range of 0.06--0.1 mg/mL of ferulic acid were obtained from grape stems and fruit leaves.

Succinic acid is usually obtained from petroleum by chemical synthesis. However, the environmental problems resulting from this practice have led to a search for biological alternatives for its production. Thus, mixtures of hydrolysates of fruit and vegetable wastes such as apples, pears, oranges, cabbages, potatoes, taros and lettuces have been used as feedstock to produce this acid (2.3 g/L) by *Yarrowia lipolytica* fermentation[24]. Table 6 summarizes organic acids reported in the literature that were obtained from fruit and vegetable wastes.

3. PROCESSING OF FRUIT AND VEGETABLE WASTE

3.1. PRETREATMENT

On many occasions the complex structure of FVW material requires a pre-treatment stage before the process for obtaining the added value products previously indicated. The FVWs contain variable amounts of lignocellulose and for this reason, an effective pre-treatment to eliminate lignin, depolymerize hemicelluloses, reduce the crystallinity of cellulose, as well as to minimize the formation of inhibitors is frequently needed if the subsequent step is fermentation[231,232]. The importance of a suitable pre-treatment of FVW in the production of added-value products is key in most cases. This is demonstrated by Abubackar et al.[9] who carried out two parallel biohydrogen production tests from banana peels. In one case the substrate was hydrothermally pre-treated and in the other case the wastes were not subjected to treatment. It was observed that in the first test twice the amount of biohydrogen was obtained (41% v/v) compared with untreated banana peels (21% v/v).

The choice of the pre-treatment method mainly depends on the waste, the subsequent process and the desired product[233]. Mechanical, thermal, chemical and enzymatic processes have been used for the pre-treatment of different FVWs.

3.1.1. Mechanical pretreatment

The aim of mechanical pre-treatment is to reduce the particle size and increase the specific surface area of the material that will subsequently be subjected to another treatment[233]. After a crushing process, the average size of the waste is usually between 10 and 30 mm, whereas it is reduced by 0.2 to 2 mm after grinding. The most common techniques used as mechanical pre-treatment are wet and dry milling, vibratory ball milling and compression milling. Milling with vibrating balls has been found to be a much more effective technique for breaking the crystallinity of cellulose than milling with ordinary balls[232]. The selection of the mechanical treatment depends mainly on the initial and final particle size and the moisture content of the residue[232,234]. Several examples of these pre-treatment techniques have been reported in the literature. For instance, Agrawal et al.[235] milled fruit and vegetable dried waste to reach a final particle diameter between 1 and 2 mm as a pre-treatment before applying the dark fermentation process. Likewise, Jiang et al.[236] evaluated the effect of a ball-milling pre-treatment on the physical properties, bioactive compounds and structural characteristics of onion skins. The pre-treatment was carried out at 300 rpm for different times (0, 6, 12, 18 and 24 h) and the results showed that ball-milling for 18 h improved the total extracted phenolic content and also the antioxidant activity.

3.1.2. Thermal pretreatment

3.1.2.1. Steam explosion

This pre-treatment, which is also known as autohydrolysis, consists of the application of steam at high pressure and temperature to the raw material in a pressure reactor. After a given reaction time, the biomass is rapidly depressurized and cooled, causing explosive decompression. Usually, the material is subjected to temperatures of 160--260 °C and pressures of 0.70-5 MPa for several minutes before it is exposed to atmospheric pressure[74,232].

Steam explosion is commonly employed in combination with an enzymatic treatment, since it favors enzymatic accessibility and eliminates inhibitory compounds such as D-limonene. Widmer et al.[118] reported a 67% decrease in limonene content after subjecting orange peel to steam explosion pre-treatment at 160°C. In a similar way, Boluda-Aguilar et al.[76] studied the effect of a steam pre-treatment in mandarin peel waste and the amount of D-limonene in the waste was reduced from 0.3-0.4% to 0.02-0.05% (v/v). In addition, the enzymatic load required for subsequent treatments was lower in the substrates pre-treated by steam explosion. Some authors have reported that the addition of acids or CO_2 to the process increases the yield of subsequent enzymatic hydrolysis and extractions, as well as reducing the formation of inhibitory compounds[237,238].

Among the advantages of this technique, it is important to mention the low environmental costs and energy consumption in comparison with other thermal and mechanical pre-treatments.

3.1.2.2. Hydrothermal hydrolysis

Hydrothermal hydrolysis is used as a pre-treatment to break down complex carbohydrates into simple sugars. This pre-treatment leads to an increase in the amounts of fermentable sugars that can be obtained. Hamelinck et al.[239] have estimated that, in absence of pre-treatment, these yields of lignocellulosic biomass

are usually below 20%.

This pre-treatment consists of mixing the starting material with water and thereafter, the mixture is subjected to elevated temperatures and pressures under inert atmospheres[240-242]. These parameters and the relationship between the mass of the material and the volume of water are key factors influencing the degree of degradation achieved. Many different conditions can be found in the literature, though the most common conditions used are 121°C, 1 atm and a time of several minutes. For example, Arumugam and Manikandan[28] employed 1 atm and 121°C for 15 min to treat a mixture of banana and mango wastes (10% w/w in water), Díaz et al.[53] treated tomato, potato and green pepper wastes (5% w/v) at 1.5 atm and 110°C for 5 min, and Razaghi et al.[243] carried out thermal hydrolysis of a mixture of broccoli, banana, orange, pumpkin, apple, carrot and tomato, without adding water, under 1 atm and 121°C for 30 min.

One aspect to be taken into consideration is the possible appearance of fermentation inhibitor compounds such as furan compounds or acetic acid. These inhibitor compounds are formed due to the severe conditions used for the hydrolysis. Higher temperatures and longer treatment times usually increase the formation of these compounds[244].

3.1.3. Chemical pretreatment

3.1.3.1. Acid hydrolysis

Acid hydrolysis is one of the most common processes employed in the pre-treatment of lignocellulosic materials. It consists of the use of acid to transform polysaccharides into monosaccharides. Different acids (sulfuric, hydrochloric, phosphoric, etc.) can be used in two different ways, at high concentration working at room temperature or at low concentrations working at high temperature. As with hydrothermal hydrolysis, a disadvantage of this method is that it can generate inhibitory by-products such as furfural, hydroxymethylfurfural, acetic acid, formic acid or levulinic acid. The production of these inhibitors is determined by the type of feedstock used but also by the process conditions, mainly acid concentration and temperature[239,245]. Sulfuric acid is one of the acids most frequently used in these processes, with a concentration of 5% and a ratio of substrate/acid of 2:1 (w/v)[53,232]. Gupta et al.[246] and Razaghi et al.[243] used HCl instead of H_2SO_4 to prevent the formation of furfural and hydroxymethylfurfural.

A variation of this technique, known as dilute acid pre-treatment (DAP), has been reported as a promising method to avoid secondary reactions during the acid hydrolysis. DAP consists of two stages employing sulfuric acid: a first step at mild conditions (0.7% H_2SO_4 and 190°C) to degrade the hemicellulose, and a second step at higher temperature (0.4% H_2SO_4 and 215°C) to degrade the cellulose[247,248].

3.1.3.2. Basic Hydrolysis

Basic hydrolysis pre-treatment, also known as alkali hydrolysis, is similar to acid hydrolysis, but, in this case, the starting material is treated with a base, usually sodium, potassium, calcium or ammonium hydroxide and the processing time is shorter in comparison with acid hydrolysis. One of the alkalis most commonly employed is NaOH. The treatment of lignocellulosic materials with NaOH produces an increase in the area of the internal surface, a decrease in the degree of polymerization, a decrease in crystallinity, separation of structural bonds between lignin and carbohydrates and alteration of the lignin structure. In addition, this method can allow higher fermentation efficiency because of the low formation of toxins and

inhibitor compounds, which is an advantage over other pre-treatments such as acid hydrolysis[232,249-251]. However, Gupta et al.[246] carried out acid and basic hydrolysis of banana residues in parallel to check the effectiveness of these treatments in terms of fermentable sugars. The results showed that acid hydrolysis is more effective for sugar extraction when comparing the two methods, obtaining more than 8 g/L of sugar content from acid pre-treatment and about 7 g/L of sugar content from alkali hydrolysis.

3.1.3.3. Other operations

The removal of lignin, or delignification, is sometimes carried out as a pre-treatment of lignocellulosic material. Lignin is an aromatic biopolymer interspersed with cellulose and hemicellulose, conferring rigidity and a high degree of compactness to the cell wall. It can be removed by chemical pre-treatments that break the lignocellulosic matrix and facilitate hydrolysis of cellulose and hemicellulose.

The removal of lignin can be carried out by NaOH, Na_2CO_3 or ammonia, although delignification with NaOH is the most common. The process consists of immersing the residue in a solution for a specified time. In the case of NaOH and Na_2CO_3, this time usually varies between 5 and 60 min, eliminating between 40 and 80% of lignin present in the residue[252]. Kim et al.[252] performed a longer delignification by subjecting palm fruit residues to a 10 N NaOH solution for 4 h at room temperature. Other authors used a combination of 0.1 N NaOH for 15 min and subsequent addition of $CaSO_4$ for 3 h[53].

In ammonium treatment, the most commonly used conditions consist of subjecting the material to a 5--30% ammonium solution for at least 5 min[249].

3.1.4. Enzymatic pretreatment

Enzymatic pre-treatment consists of the use of highly specific enzymes to break down polysaccharides. The products of this hydrolysis are usually reducing sugars, including glucose. The catalytic enzymes are specific for the reaction, so the hydrolysis yields obtained are usually higher and the formation of inhibitory products is avoided. Moreover, enzymes may be more economical than acid hydrothermal hydrolysis and do not cause corrosion of materials.

The main enzymes used in this process are cellulases, pectinases and β-glucosidases, although some authors also used xylanases[4,41,82]. The cellulase-producing microorganisms include bacteria from different genera such as *Clostridium*, *Bacillus*, *Acetovibrio* and *Streptomyces* and also fungi like *Penicillium* and *Trichoderma*, among others[232]. Enzymatic pre-treatment can be combined with other processes. For example, Arumugam and Manikandan[28] carried out a two-stage enzymatic hydrolysis of banana and mango wastes consisting of the addition of the enzyme α-amylase to the pre-treated acid hydrolysates and subsequent heating to 93°C. After 1 h of heating, the mixture was cooled and the enzyme glucoamylase obtained from *A. niger* was added. After enzymatic hydrolysis a maximum amount of reducing sugar of 64% (w/w) was recovered. Table 7 summarizes different enzymes used as enzymatic pre-treatments for different fruit and vegetable wastes published in the literature.

3.2 FERMENTATIVE PROCESS

After the hydrolysis of FWVs into pentoses and hexoses, fermentation can be carried out to obtain biofuels, organic acids or bioactive compounds. Fermentations can be carried out in batch, fed-batch, or continuous

mode. The operation mode will depend on different factors such as the type of raw material, the stability of the microorganisms used and the productivity of the fermentation process[5].

The fermentation processes use bacteria and fungi that produce enzymes capable of degrading the matter. Most of the work published on the production of bioethanol from fruit residues uses *S. cerevisiae* as the fermenting microorganism[34,82,114,253]. However, different strains of bacteria and yeasts have also been employed. *Zymomonas mobilis* deserves special attention, as several studies have reported its advantages over *S. cerevisiae* for the fermentation of fruit and vegetable residues, i.e., lower biomass production, higher ethanol production (up to 12% w/v) and lower process maintenance[254,255]. As demonstrated by Sarkar et al. [115], under determined conditions, *Citrobacter* sp. can produce ethanol (3 g/L) without pre-treating the fruit waste substrate, which is an important advantage regarding the waste processing procedure.

A mixture of probiotic bacteria (*Bacillus amyloliquefaciens* and *Lactobacillus brevis*) and yeast (*Starmerella bombicola*) have been used to obtain products with antibacterial and antioxidant capacity from blueberry waste by liquid fermentation[157]. Results showed that all probiotic-based fermented extracts presented higher antibacterial and antioxidant activity than the control. Additionally, Moreira et al. [256] carried out a fermentation of coffee residues by *Rhodotorula mucilaginosa* to obtain carotenoids.

Solid state fermentation has been used to obtain phenolic compounds, carotenoids or organic acids from fruit and vegetable wastes such as pineapple waste, orange peel, grape stems, carrot peel or vine leaves by employing bacteria (*Streptomyces setonii*) and fungi (*A. niger*, *Blakeslea trispora* or *Rhizopus oligosporus*)[42,223,236,257].

Acetone, butanol and ethanol (ABE) fermentation has been used to obtain biobutanol. It consists of the generation ABE by *Clostridia* sp. from pentoses and hexoses released during the hydrolysis process[258]. *Clostridium beijerinckii* stood out as an important producer of butanol by fermentation. Nevertheless, different species can be employed, for example, *Clostridium acetobutylicum*, which has been used by Khedkar et al.[259] to produce butanol from dry pineapple residues pre-treated by acid hydrolysis, obtaining a concentration of 5.23 g/L of total ABE. Similar values of total ABE (4-6 g/L) were obtained by Nimbalkar et al.[51] using *C. acetobutylicum* to ferment pea residues with a similar procedure.

For the production of biohydrogen, a dark fermentation process is necessary. It is an anaerobic digestion process that can employ diverse organic residues as substrate[260]. In this fermentation, *Clostridium* sp. and *E. coli* have been identified as the main hydrogen-producing microorganisms[5]. There are several examples in the literature of this technology used to obtain biohydrogen from FVW mixtures[9-11]. Keskin et al.[11] studied the production of biohydrogen from a mixture of radish, pepper, onion, pumpkin, carrot, cucumber, cabbage, grape, pomegranate, pear, apple, lemon, peach and orange wastes. They designed a fermentation reactor consisting of a percolation tank and a dry fermenter and conducted three tests with different percolation frequencies: once a day, once every two days, and twice a day. The results showed that on increasing the percolation frequency, the dry fermenter production increased too.

Several authors have modified or incorporated fermentation variables to achieve optimal conditions and thus obtain better results in terms of quality and quantity. For instance, Gupta et al.[246], to optimize the time period for maximum fermentation of banana waste for the production of bioethanol, added 0.3% yeast extract to the banana residue. Tan et al.[34] carried out fermentation of banana residues adding external nitrogen sources (yeast extract, peptone and ammonium sulfate). It was found that the highest bioethanol

concentrations (42.5 g/L) were obtained by supplementing the fermentation medium with 15 g/L of yeast extract.

To increase fermentation efficiency, Choi et al.[117] vacuum evaporated solutions with low concentrations of fermentable sugar obtained from the hydrolysis of tangerine residues in order to increase the sugar concentration.

Some studies have indicated that a simultaneous saccharification and fermentation process is more advantageous in contrast to carrying out these steps separately, because the yields obtained are higher, only one tank is required, and the operation time is shorter[88,261]. The increase in yield is mainly due to the fact that glucose is rapidly transformed into bioethanol, avoiding its inhibitory effect on hydrolytic enzymes, which increases glucose yield and increases the availability of substrate for alcoholic fermentation. However, simultaneous saccharification and fermentation requires the optimization of parameters such as temperature, pH and enzymatic concentrations, since the optimal temperature and pH, as well as the fermentation strains are different in the two processes. Oberoi et al.[66] proved that this combined process not only increased ethanol production from banana residues in terms of concentration (28.2 g/L) but also was economically advantageous by reducing the number of unit transactions.

3.3. SEPARATION PROCESS

After the different steps carried out to obtain added-value products from FVWs, diverse separation processes can be employed, and some of the most usual are summarized below.

3.3.1. Distillation

In the process of obtaining alcohols, distillation is necessary after the fermentation stage. On heating the ethanol/water mixture, the alcohol is separated due to its higher volatility, and an ethanol-rich steam is obtained, which is usually successively distilled to obtain high-quality ethanol. For example, Sarkar et al.[115] carried out a fractional distillation, with a simple column, of a fermentation broth from fruit wastes to obtain a yield of 0.3 g of ethanol from 1 g of fruit residues. Borah and Mishra[262] distilled fermented apple pomace and banana waste on a laboratory scale, obtaining concentrated bioethanol (48%).

The traditional distillation method is the most commonly used in the literature but has some disadvantages with respect to time and energy. Therefore, in recent years, new distillation alternatives have been developed. Gavahian et al.[263] carried out an innovative distillation technique known as Ohmic-assisted hydro-distillation (OAHD) that consists of the passage of an electric current through the material to be distilled, thus generating heat within the product[264]. The results showed that, in terms of energy consumption, OAHD achieved a reduction of more than 30% in the energy required during the process, as compared to traditional distillation.

One aspect to be considered in the production of ethanol by distillation is the energy cost of the process. Figure 1 shows the energy cost of the distillation process against the initial ethanol concentration present in the sample to be distilled. It clearly shows that, as the initial ethanol concentration increases, the energy cost decreases, to reach values of around 5 MJ/L for an ethanol concentration of above 40 g/L. For this reason, a relatively high sugar concentration in the sample to be distilled is recommended, since low concentrations imply lower concentrations of ethanol which affects the economic and energy efficiency of

the process[265].

3.3.2. Pervaporation

Pervaporation consists of the passage of a liquid mixture through a membrane so that the components of the mixture selectively permeate through the membrane, producing a selective elimination of organic compounds from aqueous solutions[114]. This separation technique has been studied for ethanol and butanol extraction[266-268], since it has certain advantages compared to distillation, i.e., reduction in process costs, high energy efficiency and environmental friendliness[269].

Bello et al.[114] used pervaporation as a method of extraction of ethanol from treated banana wastes. Results showed that the passage of ethanol/water mixtures through the membrane depended on the process temperature. In addition, a further increase in flow was detected when the vapor pressure of the permeate was similar to the vapor pressure of the ethanol. The authors concluded that this could be an appropriate technique to separate bioethanol obtained from fruit residues. Jitesh et al.[267] studied pervaporation as a separation method to remove inhibiting compounds that are generated during ABE fermentation. They used different pervaporation membranes such as styrene butadiene rubber (SBR), poly-dimethyl siloxane (PDMS) and ethylene propylene diene rubber (EPDR) and observed that PDMS was the most efficient for removing the inhibitors.

3.3.3. Extraction with organic solvents

Extraction with organic solvents is one of the most common methods for obtaining bioactive compounds with antimicrobial or antioxidant activity. This method consists of mixing the substrate with organic solvents, which are usually evaporated thereafter by distillation or other suitable techniques.

The organic solvents used in this technique are diverse. For example, Obied et al. [270] used methanol for extracting biophenols from olive residues. The experiment consisted of mixing olive residue with 80 % (v/v) methanol for 30 min at room temperature and once filtered, the solvent was eliminated in a rotary evaporator. In another study, Verotta et al.[25] obtained methanol extracts from pomegranate waste that contained ellagic acid. Stajčić et al. [52] carried out an extraction of carotenoids from tomato waste with hexane for 10 min at room temperature. Rubio-Senent et al.[57] also used hexane, not as an extraction agent, but to remove the lipid fraction from olive residue, and then, phenolic compounds were extracted continuously from the wastes with ethyl acetate at 77°C for 8 h. In addition, it is very common to use different solvents combined in the same extraction procedure. Saleem and Saeed[39] studied the antimicrobial capacity of extractions from orange, lemon and banana peels, employing as extractive agents water, methanol, ethyl acetate and ethanol (10 g of each waste with 100 mL of each solvent). Kallel et al.[271] obtained extracts with antimicrobial activity from garlic residues with pure methanol and ethanol or diluting them in water (50 % v/v).

3.3.4. Extraction at high pressure

High pressure extraction (HPE) consists of several steps. Firstly, the raw material is subjected to high pressures (100--1000 MPa) at room temperature and mixed with extraction solvents. Then, there is an intermediate stage during which the pressure is maintained in the tank for a certain time. Finally, a pressure

relief stage takes place[272].

One of its main advantages is the absence of heat during the process, which avoids negative effects on the bioactive compounds, preserving their activity. In addition, this procedure provides higher yields than other extraction techniques[272]. A variety of products have been obtained by HPE, such as phenolic compounds from orange, lemon, mandarin and lime peels[273-275], flavonoids from orange wastes[276] and lycopene from tomato wastes[277]. Alexandre et al.[155] observed that extracts directly obtained from pomegranate peel by HPE showed antimicrobial activity against bacterial genera such as *Bacillus* and *Pseudomonas*.

3.3.5. Enzymatic extraction

Enzymatic extraction is based on the use of enzymes that degrade the cell wall, thus making intracellular materials more accessible for extraction. The most commonly used enzymes are pectinases and glucanases. This technique is usually employed for the extraction of antioxidants such as carotenoids.

It has been seen that the extraction of carotenoids from tomato residues with organic solvents generates low yields and for this reason, several authors have used enzymatic extraction with pectinases and glucanases as a previous step to break the cell wall, and so facilitate the subsequent extraction. After the enzymatic treatment, ethyl acetate, acetone or hexane were used as solvents and the results showed higher yields compared with those obtained from untreated substrates[173,174,278]. Additionally, Strati et al.[279] proved that enzymatic pre-treatment of tomato waste prior to extraction with organic solvents increased the extraction yields, not only for carotenoid, but also for lycopene.

4. ECONOMIC ASPECTS AND FUTURE PERSPECTIVES

4.1. Economic analysis

In addition to the technical studies, several attempts have been made to evaluate from an economic point of view the production of biofuels from plant-derived residues.

One key aspect for the production of bioethanol is the energetic cost of the distillation process, which depends on the concentration of ethanol achieved after fermentation. Galbe et al.[280] reported an abrupt reduction in the specific energetic cost of the distillation process when the initial ethanol concentration increased to values of around 20 g/L. This means that the energetic cost of obtaining 1 L of concentrated ethanol (94%) from a broth with 12 g/L of ethanol is approximately two times the cost of obtaining it from a concentration of 20 g/L. For this reason, the initial concentration of fermentable sugars in the broth should be at least about 50 g/L.

Another fundamental aspect is the size of the industrial plant. Concentrations of fermentable sugars of 68 g/L could be obtained by thermal hydrolysis at 135°C from a mixture of fruit wastes (orange, apple, banana, kiwi fruit and pear) (data not published). An economic assessment of a hypothetical process to obtain bioethanol from these wastes was carried out. This analysis showed that a continuous supply of fruit wastes of at least 100 t per month would be necessary for the profitability of the process.

In other work, Hernández et al.[281] carried out an economic assessment of two simulated biorefinery schemes employing olive stones as substrate. The first scenario was designed to obtain xylitol, ethanol, poly(3-hydroxybutyrate) and furfural, whereas, in the second case, the production of these compounds was integrated with a cogeneration system for bioenergy production from the solid residues. Regarding the

profit margin, values of 53 and 6% for the first and the second biorefinery scheme were found, respectively. The additional capital cost of the cogeneration system was responsible for this great difference. In addition, Mussato et al.[282] conducted an economic analysis to study the possible production of xylitol, lactic acid, phenolic acids and activated carbon from brewer's spent grain. Four scenarios with different levels of heat and mass integration were considered and the highest economic margin (62%) was achieved with full mass and full energy integration.

Regarding bioactive compounds, the purification step is usually associated with important costs [281]. Laufenberg et al. [283] remarked that to make the bioconversion of vegetable wastes economically profitable, high value-added products should be produced. Biofuels produced by biotechnological means achieve moderate prices in the market, whereas selling prices for bioactive compounds, such as bioflavors obtained by fermentation process from vegetable wastes are notably higher[284].

4.2. Future prospects

This review aims to highlight the main revalorization possibilities of fruit and vegetable residues in order to minimize the environmental and economic problems derived from the generation of these wastes. Exploitation of these residues as a source of biofuels and high value-added products is a promising field that demands multidisciplinary research from food engineering, food chemistry and biotechnology areas. Additionally, economical aspects should be taken into account with the aim of ensuring suitable progress in this field.

Overall, the utilization of fruit and vegetable wastes as a potential source of bioactive compounds and biofuels relies on three future approaches: (a) implementation of cost-effective and efficient methods for obtaining value-added products, (b) optimization of techniques that adequately pre-treat the wastes to be employed as substrate for fermentative processes, and (c) development of novel applications of bioactive compounds in food and pharmaceutical products.

5. CONCLUSIONS

Due to social concerns about environmental problems arising from the accumulation of organic wastes at global level, there is an increasing interest in potential valorization alternatives. Agro-food wastes can be used as a substrate for the production of different products of interest, mainly biofuels, but also compounds of great importance from a biotechnological point of view, such as enzymes, antioxidants or antimicrobials with potential applications in the pharmaceutical, cosmetic or food industry. Difficulties originated by the complex structure of these wastes have led to the development of novel technologies for sample processing, separation and extraction of compounds of importance. Major investigations have been carried out at research level, with promising results. The challenge for the future is to change the scale, in order to achieve suitable procedures to obtain value-added products from agri-food wastes, not only from a technological, but also from an economic point of view.

The authors have declared no conflict of interest.

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Table 1. Fruit wastes and their products.

Waste	Main carbohydrate content	Bioethanol	Biohydrogen	Biomethane	Biobutanol	Bioactive compound	Reference
Banana	Sucrose	x		x		x	[13],[34],[35]
Orange	Fructose	x	x			x	[9],[19],[36]
Mandarin	Glucose	x	x				[11],[37]
Lemon	Glucose	x				x	[38],[39]
Grapefruit	Fructose	x					[40]
Apple	Glucose	x	x				[10],[41]
Pineapple	Fructose	x			x	x	[14],[42]
Pear	Fructose		x			x	[43]
Grape	Glucose		x			x	[11],[23]
Mango	Glucose					x	[44],[45]
Pomegranate	Fructose		x			x	[9],[46]

Table 2. Vegetable wastes and their products.

Waste	Main carbohydrate content	Bioethanol	Biohydrogen	Biomethane	Biobutanol	Bioactive compound	Reference
Pepper	Glucose		x				[9]-[11]
Carrot	Sucrose	x	x				[9],[47]
Pumpkin	Sucrose		x				[9]-[11]
Onion	Sucrose	x	x			x	[9],[48],[49]

Radish	Fructose		x			[10],[11],[50]
Pea	Sucrose			x		[51]
Tomato	Sucrose	x	x		x	[11],[52]-[54]
Lettuce	Fructose				x	[55],[56]
Olive	Glucose				x	[57],[58]
Cassava	Glucose	x				[59],[60]
Potato	Starch	x			x	[33],[61]
Coffee	Glucose	x			x	[62],[63]
Cocoa	Glucose	x				[64],[65]

Table 3. Fruit and vegetable wastes as feedstock for biofuels, methods, microorganisms and process yield.

Substrate	Product	Process	Microorganism	Yield	Reference
Apple	Bioethanol	Fermentation	*Saccharomyces cerevisiae*	19%	[41]
Banana	Bioethanol	Fermentation		24--65%	[34],[66],[114], [115]
		Simultaneous saccharification and fermentation (SSF)	*S. cerevisiae* *Enterobacter* sp. EtK3		
		Fermentation and pervaporation			
Cocoa	Bioethanol	Fermentation	*S. cerevisiae*	17%	[116]

Coffee	Bioethanol	Fermentation SSF	*S. cerevisiae* *Pichia stipitis*	47--93%	[62],[82],[83]
Grapefruit	Bioethanol	Fermentation	*S. cerevisiae*	91%	[37]
Lemon	Bioethanol	Fermentation	*S. cerevisiae*	60%	[38]
Mandarin	Bioethanol	Fermentation	*S. cerevisiae*	91%	[117]
Orange	Bioethanol	Fermentation SSF	*Zymomonas mobilis* *S. cerevisiae*	43--94%	[36],[118]
Pineapple	Bioethanol	Fermentation Consecutive saccharification/fermentation SSF	*S. cerevisiae* *Saccharomyces bayanus*	35--43%	[80]
Carrot	Bioethanol	Fermentation	*S. cerevisiae*	40--97%	[90],[91]
Cassava	Bioethanol	Fermentation SSF	*S. cerevisiae* *Z. mobilis*	39--79%	[119]
Potato	Bioethanol	Fermentation SSF	*S. cerevisiae*	32--92%	[33],[88]

Banana	Biomethane	Anaerobic fermentation	Microbial consortium (sludge)	250--285 mL/g VS	[12],[13]
Mixture of orange peel, banana peel, grape pulp, pineapple waste	Biomethane	Anaerobic fermentation	Microbial consortium (Anaerobic digester sludge)	350 mL/g VS	[109]
Mixture of pepper, onion, potato, eggplant, carrot, cabbage, cucumber, citrus, pear, apple, pomegranate, grape	Biohydrogen	Dark fermentation	*Clostridium butyricum*	21--68 mL H_2/g VS	[9]-[11]
		Dark fermentation and percolation			
Apple	Biobutanol	ABE fermentation	*Clostridium beijerinckii*	28--33%	[111]
Pea pod	Biobutanol	ABE fermentation	*Clostridium acetobutylicum*	24%	[51]
Pineapple	Biobutanol	ABE fermentation	*C. beijerinckii*	8%	[14]

Table 4. Food waste extracts with antimicrobial activity against (Gram-negative, Gram-positive) bacteria and fungi [35],[44],[129]-[134],[135]-[139]

Residue	Banana peel	Lemon peel	Orange (whole)	Mango kernel	Mango peel	Potato peel	Tomato seed and peel	Pumpkin waste
Extraction								

agent					
Ethyl acetate	*Escherichia coli* *Salmonella* *Staphylococcus aureus* *Bacillus*				
Water			*E. coli* *S. aureus* *Pseudomonas fluorescens*	*Bacillus cereus* *Bacillus subtilis* *Candida albicans* *Micrococcus flavus*	*E. coli* *Pseudomonas* sp. *Vibrio cholerae*
Ethanol		*Pseudomonas Salmonella, Micrococcus*	*Listeria monocytogenes* *Nocardia* *S. aureus* *Citrobacter* *Enterobacter aeruginosa* *E. coli* *Aeromonas hydrophyla* *B. cereus*	*S. aureus*	*S. aureus* *B. subtilis* *P. aeruginosa* *E. coli* *Aspergillus niger*

		Bacillus licheniformis				
Acetone	*Pseudomonas Salmonella, Micrococcus*		*S. aureus Proteus mirabilis*	*Enterobacter aerogenes Klebsiella pneumoniae Cryptococcus luteolus*		
Methanol	*Pseudomonas Salmonella, Micrococcus*	*E. coli A. niger, Salmonella, Candida albicans, Shigella flexneri, S. aureus, Yersinia*		*Staphylococcus subflavia C. albicans Candida glabrata*	*S. aureus B. subtilis P. aeruginosa E. coli*	*B. cereus B. subtilis E. aerogenes S. aureus Providencia stuartii Rhodotorula rubra Rhizopus oligosporus Cryptococcus meningitis*
Hexane		*S. aureus*		*K. pneumoniae C. glabrata*		
Phosphate		*S. aureus B. subtilis, E. coli*				
Chloroform				*S. subflavia*		

	K. pneumoniae
	C. albicans
	C. gabrata

Table 5. **Enzymes from fruit and vegetable wastes.**

Residue	Enzyme	Microorganism	Treatment	Activity	Reference
Lemon pulp	Pectinase	*Aspergillus niger*, *Trichoderma viride*	ND	9 U/g	[208]
Kinnow pulp	Cellulase	*T. reesei*	SSF	18 U/g	[209]
Mango kernel	Amylase	*Fusarium solani*	ND	0.9 U/g	[210]
Banana peel	Amylase	*A. niger*	SSF	>20 U/g	[211]
Olive	Lipase	*Yarrowia lipolytica*	SSF	850 IU/dm^3	[214]
Potato peel	Amylase	*Bacillus firmus*	Ammonium sulphate precipitation	676 U/g	[215]
	Alkaline protease	*Bacillus subtilis*	SSF	400 U/g	[216]
	Ligninolytic enzymes	*Anthracophyllum discolor*	ND	193 U/g	[217]
Apple pomace	Xylanase	*A. niger*	SSF	4870 U/g	[27]

ND, non-defined

Table 6. Organic acids obtained from fruit and vegetable waste, microorganism, treatment process and amounts produced.

Residue	Organic acid	Microorganism	Treatment	Amount	Reference
Banana peel	Citric acid	*Aspergillus niger*	ND	82 g/L	[26]
Apple pulp	Citric acid	*A. niger*	SSF	>18 g/L	[27]
Mango peel	Lactic acid	ND	Fermentation	17.5 g/L	[226]
Potato peel, banana, orange	Lactic acid	*Lactobacillus*	Fermentation	3--6.7 g/L	[227]
Pineapple	Acetic acid	*Saccharomyces cerevisiae*	Fermentation	4.7 g /100 g	[228]
Papaya peel	Acetic acid	*Acetobacter aceti*	Fermentation	ND	[229]
Grape stem	Ferulic acid	ND	Alkaline hydrolysis	0.06--0.1 g/L	[230]
Mixture of apple, pear, orange, cabbage, potato, taro and lettuce	Succinic acid	*Yarrowia lipolytica*	Fermentation	2.3g/L	[24]

ND, non-determined

Table 7. Fruit and vegetable wastes pretreated by enzymatic methods. [24],[33],[40],[41],[53],[66],[80],[117],[118].

Enzymes / **Residue**	Cellulase	Hemicellulase	Amylase	Xylanase	Pectinase	β-Glucosidase	β-Glucanase	Glucoamilase	Amiloglucosidase
Apple	x	x			x	x		x	
Banana	x								
Fruit mix	x		x	x	x				
Grapefruit	x				x	x			
Lemon	x				x	x			
Mandarin	x			x	x	x			
Orange	x	x			x	x		x	
Pear	x	x			x			x	
Pineapple	x	x							
Cabbage	x	x			x			x	
Lettuce	x	x			x			x	
Pepper	x		x				x		x
Potato	x	x	x		x		x	x	
Tomato	x		x				x		x

Figure 1. Energy requirements of the distillation process against the concentration of ethanol in the substrate (adapted from Galbe et al. (2011).