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VALORISATION OF CITRUS PROCESSING WASTE: A REVIEW

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Abstract

This study analyses the quantitative and qualitative characteristics of citrus peel waste and discusses the systems for its valorisation. Citrus peel waste (CPW) is the main residue of the citrus processing industries and is characterised by a seasonal production (which often requires biomass storage) as well as high water content and concentration of essential oils. The disposal of CPW has considerable constraints due to both economic and environmental factors. Currently this residue is mainly used as food for animals, thanks to its nutritional capacity. If enough agricultural land is available close to the processing industries, the use of CPW as organic soil conditioner or as substrate for compost production is also possible, thus improving the organic matter content of the soil. Recently, the possibility of its valorisation for biomethane or bioethanol production has been evaluated by several studies, but currently more research is needed to overcome the toxic effects of the essential oils on the microbial community. Considering the high added value of the compounds that can be recovered from CPW, it has promising potential uses: in the food industry (for production of pectin, dietary fibres, etc.), and in the cosmetic and pharmaceutic industries (extraction of flavonoids, flavouring agents and citric acid). However, in many cases, these uses are still not economically sustainable.

Keywords: *agronomic utilization; animal food; citrus peel waste; essential oil; cosmetic and pharmaceutic compounds; storage.*

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1. INTRODUCTION

The citrus processing industry plays an important role in the agro-industrial sector. The orange is the most widely-cultivated fruit worldwide and accounts for about 50-60% of total citrus production; however also other species (e.g. lemon, lime, mandarin, grapefruit) have industrial importance (Satari and Karimi, 2018). Brazil, China, India, Mexico, Spain, and the USA produce over two-thirds of the world's citrus fruits (Paggiola et al., 2016; Satari and Karimi, 2018). In 2016 more than 124 million Mg (Mg is the SI unit equivalent to tonne) of citrus were produced (Figure 1a), of which about 50-60% was consumed as fresh fruit and the remaining 40-50% was destined for industrial processing (Figure 1b) (FAOSTAT, 2017; Satari and Karimi, 2018; Sharma et al., 2017; 2018).

Figures 1a and 1b

After processing (operated by different technologies with variable levels of automation), the citrus industry produces wastewater and solid/semisolid residues (citrus peel waste, henceforth "CPW"). The CPW production ranges from about 50% to 70% w/w of processed fruits, depending on adopted technology and fruit cultivar, and its annual world production is probably close to 10 million Mg. CPW shows a low pH and high concentrations of organic compounds; among these latter, the presence of essential oils (EO, of which D-limonene is the primary constituent) is the main problem for biological management options, due to their anti-microbial properties. The large amounts produced and the peculiar characteristics of citrus processing residues involve considerable constraints for their management due both to economic and environmental factors (Calabrò et al., 2016). As a matter of fact, traditional CPW disposal strategies (e.g., incineration or landfilling) are nowadays insufficient and problematic in terms of environmental impacts and energy efficiency (Satari and Karimi, 2018; Wei et al., 2017). Disposal of CPW requires high costs and unauthorised disposal can potentially cause soil (due to the EO toxicity on soil microflora) and water bodies pollution; in some cases the destruction of the aquatic ecosystem is possible (Zema et al., 2018), particularly when the body of water is insufficient to properly dilute the waste (Sharma et al., 2017).

To minimize management costs and prevent environmental damage, several uses of the residues from the citrus processing industry have been evaluated in recent decades. All the treatment/valorisation options for CPW depend on a large number of factors, which affect economic viability. CPW can be used directly or after simplified treatments as animal feed or soil conditioner (for a long time the most common destination) or further processed in biorefinery industries (currently still hampered by economic constraints).

Since the financial burden of residue treatment covers a significant amount of the annual budget of the citrus processing industry, its competitiveness may be considerably enhanced by the economically sound management systems of citrus residues (Zema, 2017). Furthermore, also the environmental constraints have to be properly considered regarding land and water conservation. Thus, the optimal solution has to combine the most efficient and environmentally sustainable technology for treatment/valorisation and the specific economic constraints, linked to the local market conditions. Over the years, researchers worldwide have been focusing on developing different processing methods for complete exploitation of CPW (De Gregorio et al., 2002; Lo Curto et al., 1992; Satari and Karimi, 2018; Sharma et al., 2017; Tripodo et al., 2004); however, more awareness and research are needed in order to change traditional attitudes, which consider citrus processing residues as a waste to be disposed of in landfills rather than a valuable resource for reusing in the bioeconomy (by a direct use or after further processing in biorefineries) thanks to its numerous applications in various fields. If the great potential in CPW valorisation by green economy schemes is realized, the negative impacts of citrus processing industries on the environment may be lessened.

After an analysis of the quantitative and qualitative characteristics of CPW, this paper proposes an overview of the possible uses and management systems of citrus residues; their pros and cons are discussed, considering the factors influencing the treatment and utilisation of citrus residues. Starting from this, an analysis of the most recent valorisation alternatives proposed in the scientific literature is carried out, in order to provide company managers and other stakeholders an insight into the most suitable solution for the economic and environmental sustainability of the citrus residue management chain.

2. CITRUS PROCESSING SYSTEMS

2.1 Citrus processing products

The main product of the citrus processing industry is juice, used in many beverages (e.g. soft drinks) or as ingredient in many foods. Other products include marmalades, jellies, potpourris, candied peel, jams, flavouring agents for beverages and health drinks, oils and essences, used as food-grade products (Figure 2) (Kimball, 1999; Sharma et al., 2017; 2018). As will be discussed later (see section 4.2.2), other food-grade products are extracted from citrus processing residues (mainly fibres and pectins) (Figure 3).

Figure 2

Figure 3

2.2 Processing technologies

Citrus processing consists mainly of receiving fruit from citrus groves and temporary storage, fruit washing, grading and sorting, juice extraction and finishing, heat treatment, and product packaging and storage (Figure 2).

Fruits are usually received mixed with limited quantities of leaves and stems that may disturb the conveying equipment. To avoid this, they are treated in a trash or leaf remover, such as a slanted tilted belt that allows fruits to move downstream, while impurities fall into a container. The spread roller conveyer is another device used to remove impurities, consisting of roll bars allowing smaller pieces to fall into a grid mesh, but retaining the larger fruits. Rotating brushes under a water spray are commonly used for fruit washing (in the case of wax coated fruits or excessive dirt or microbiological contamination) immediately prior to processing. Then, washed fruits are graded by hand or automated devices and then, if necessary, sorted; during this phase, fruit samples are collected for quality checking.

Processing technologies can be classified as “juice and EO extraction” or “sequential product extraction”. The processing choice depends on many factors such as citrus cultivar or desired product. The juice extractors of the "FMC" (Food Machinery Company) or "Brown" types (from the name of the producing companies this latter also known as reamer*)* are the most widely-used technologies, since they produce high-quality citrus juices.

The FMC juice extractor consists of upper and lower cups (from three to eight per processing machine): the upper cup, moving down, squeezes the fruit placed inside the lower cup; the squeezed juice is collected in the strainer tube and then conveyed to the juice-processing equipment. The peel slides through slots in the upper cup and falls into a screw conveyer plant. Simultaneously, EO sacs in the flavedo are burst thanks to a bending/scraping motion. Water is sprayed to wash the peel and oil, producing a slurry. It flows through a small screw conveyer to the oil recovery equipment. The citrus fruit is separated into oil emulsion, juice and peel as well as the remaining core material (Kimball, 1999).

Several models of Brown juice extractors are available, having the same technology, but different working capacity. Some models cut the fruit in two halves and then use a "reamer" (from which derives the alternative name of this extractor) to ream out the inner part; then, juice is poured and peel is discarded into a peel screw conveyer. Subsequently, juice is conveyed to a primary and secondary finisher to remove pulp prior to evaporation or heat treatment. These latter models produce juice with lower content of peel oil and higher quality. Other models do not ream the peel halves, but smash them between canted spinner disks. Because of this scraping action, the quality of the produced juice is lower; thus, this model is advisable for extracting juice from tangerines, tangelos and lemons, where juice quality is less important. After processing by Brown juice extractors, the fruit residues must be treated in a separate oil extractor (the so-called "Brown Oil Extractor"). This extractor uses rotating shafts with needles which cut the peel to release the oil, then dries the de-oiled fruits after lifting them from a washing tank.

In both extraction methods (that is, by FMC and Brown devices) the oil recovered is contained in an "oil slurry", which must be sent to a finisher to remove the residual soil material and centrifuged to produce an oil emulsion, from which, after a further centrifugation, oil is recovered and treated enzymatically or frozen.

After extraction, the juice is finished by separating pulp and other impurities using a screw press (FMC extraction system) or a paddle wheel (Brown system) to force the juice and pulp against a screen; the pulp is retained, while the juice passes through the holes in the screen.

The pulp discarded by juice extractors and finishers, which contains up to 80% juice (Kimball, 1999), is subjected to washing and several refinishing cycles to recover juice (e.g. by high-speed clarifiers and decanters), pectin and other solid fractions (such as juice sacs, the coarse membrane material of squeezed citrus). The solid fractions are added back to the juice after evaporation to increase appeal and palatability.

Citrus juice undergoes heat treatments (pasteurisation and evaporation). Pasteurisation is a stabilisation treatment, which deactivates the natural enzymes (peactinase) of juice and prevents microbiological degradation (such as turbidity loss and fermentation). This treatment generally consists of a sequence of plate or shell-in-tube heat exchangers (80-95 °C) and refrigerators (these latter to chill the juice), both of which function with circulating water. The pasteurised juice can be directly packed in an aseptic room (Not From Concentrate, NFC, juice) or subsequently concentrated. Evaporation reduces storage volumes and transportation costs and prolongs the microbiological shelf life of the juice (beside the other advantages common to pasteurisation), but simultaneously reduces the oxidative shelf life and removes delicate flavour components (Kimball, 1999). The most common plant is the Thermally Accelerated Short Time Evaporator (TASTE), where water evaporates from juice (absorbing heat from condensate, used as a heat source), while flowing into tubular heat exchangers accelerating (thermal acceleration) to supersonic velocities. For this treatment, plate heat exchangers are also used, consisting of vacuum vessels functioning as TASTE exchangers. After evaporation, the citrus juice is frozen and sent to markets. Heat treatment reduces the natural citrus flavour and aroma, which remain in the condensate as essential oil. Systems based on fractionation columns are thus used to recover oil from condensate; small fractions of the recovered oil are often added back to the juice concentrate to restore the flavour and aroma of the fresh citrus. Freeze concentration (carried out in chilling heat exchangers) is also an alternative to evaporation, since it allows energy savings and prevents flavour loss from citrus juice.

Finally, the concentrated or fresh juice, produced and finished as above, is stored in tanks until the marketing phase. Finally, the product is packed, possibly labelled, palletised and sold to other industries, traders and/or final consumers. Packaging can be in bulk (e.g. truck tankers, barrels, plastic bins) or retail containers (e.g. cartons, bottles, cans).

3. CITRUS PEEL WASTE PRODUCTION AND STORAGE

Citrus fruit consists of the peel or rind (the flavedo, that is the exterior peel, yellow/orange in many species, approximately 10% of the total fruit weight and the albedo, that is the interior white spongy peel, about 17%), the pulp or rag (about 71%) and seeds (about 2%) (Bampidis and Robinson, 2006; Mahato et al., 2018; Sharma et al., 2018). These constituents vary among the citrus varieties (Table 1).

Table 1

Chemical characterisation shows that about 87% of the citrus fruit is water, while the remaining 13% consists of several constituents (10% minerals, 5% essential oils, 3% fats, 9% proteins, 11% fibres, 16% citric acids, 21% pectins, 10% glucosides, and 15% pentosans) (ARS, 1956; Mahato et al., 2018; Oikeh et al., 2013; Rieger, 2018; Sharma et al., 2018, 2017). Pulp and juice are the edible parts, while segment walls, peel, pith residues and seeds are not edible and are found in CPW (Mahato et al., 2018). CPW ranges from 49% to 69% (w/w) of the citrus fruit processed, depending on citrus cultivar (Pascual and Carmona, 1980), juice extraction system (Marín et al., 2002b)and amount of processing water (retained by residues). Specifically, CPW is composed of about 40–55% peels, 30–35% internal tissues and less than 10% seeds (Sharma et al., 2018). CPW also contains variable concentrations of EO, which depend mainly on the citrus species and on processing techniques (Pascual and Carmona, 1980).

3.1 Physico-chemical characterization

Physico-chemical composition of CPW depends on cultivar, fruit cultivation method, harvesting time and ripening stage (Kale and Adsule, 1995), and the different methods or techniques employed for juice extraction (Marín et al., 2002b; Sharma et al., 2017). CPW contains insoluble carbohydrates (cellulose, pectin), other sugars (glucose, fructose, sucrose, galactose), acids (mostly citric and malic acids, but also tartaric, benzoic, oxalic and succinic acids), lipids (oleic, linoleic, linolenic, palmitic, stearic acids, glycerol and phytosterol), mineral elements (nitrogen, calcium and potassium), volatile compounds (alcohols, aldehydes, ketones, ester, hydrocarbons), flavonoids (flavanones, flavones, anthocyanins), limonoids (limonin, isolimonin), EO (mainly D-limonene, up to 95% in oranges), enzymes (pectinesterase, phosphatase, peroxidase), pigments and carotenoids (carotene, xanthophylls, lutein), polyphenolics (phenolic acid), nitrogen constituents (ammonia nitrogen and nitrates) and vitamins (ascorbic acid, complex B vitamins) (Bampidis and Robinson, 2006; Boukroufa et al., 2015; Braddock, 1999; Di Giacomo and Calvarano, 1987; Satari and Karimi, 2018; Sharma et al., 2018, 2017). Typical characterization for CPW is reported in Table 2 ~~1~~.

Table 2

As already mentioned, CPW is characterized by a high acidity with a pH from 3.5 to 5.8 (Bampidis and Robinson, 2006; Tamburino et al., 2007), high water retention capacity (4.33 L/kg$_{dm}$) and an osmotic pressure of 79 mOsm/L$_{water}$ (Giger-Reverdin, 2000) (due to the hygroscopicity of pectins). Water content varies from 90% for wet CPW (w/w) to 80% for pressed biomass and down to 8-10% for dried biomass (Tamburino and Zema, 2009; Satari and Karimi, 2018). The high water content of fresh CPW makes it difficult to dry through common conventional methods or industrial drying devices (Sharma et al., 2017). The high content of water and soluble sugars makes CPW highly perishable and easily fermentable, which causes many economic and environmental problems (Laufenberg et al., 2003; Montgomery, 2004); additionally, the high content of organic matter (95% of total solids, Satari and Karimi, 2018) restricts its direct disposal as this might affect the natural and beneficial microbial flora of the soil (Sharma et al., 2017).

Bulk density, which depends on the possible storage techniques, varies approximately from 900 kg m^{-3} for wet peel to 200-300 kg m^{-3} for dried biomass, while for pressed and compacted peel it is about 1000 kg m^{-3}.

CPW can be used wet or after pressing and, possibly, drying processes, in order to reduce weight and consequently storage and transport costs. If CPW is pressed or exposed to the sun, water content is reduced from about 80% to 10%.

3.2 Factors conditioning CPW valorisation: temporal production, storage, and transport costs

CPW production shows a noticeable temporal variability, linked to the amounts of citrus fruit processed, characterized by inter-annual and seasonal (intra-annual) variations.

Inter-annual variability depends on both crop yields and fresh fruit market demand.

Concerning the intra-annual variability, seasonal and weekly variations of citrus production are recorded. Since, in the Mediterranean area, more than 70% of citrus production is concentrated between February and April, citrus processing plants mainly operate in this period. Figure 4 ~~2~~ shows a typical monthly distribution of citrus transformation in a processing company with a potential capacity of 40,000 Mg year^{-1}.

Figure 4

Due to the seasonal nature of citrus production, the large intra-annual variability requires the temporal transfer of a share of CPW for almost all the available valorisation options, which thus requires its storage. Storage allows also conservation of CPW, available techniques are discussed below (see section 3.3).

CPW also requires the spatial transfer from the producer to the end-user (generally cattle farms). The transfer cost mainly depends on the amount of CPW that has to be delivered. However, these costs are also affected by other factors, such as: (i) road characteristics and distance between sites; (ii) technical characteristics and size of means of transport (Tamburino et al., 2007), also if large-sized trucks provide lower expenditures per unit of CPW transported, they require better roads not always available in the production areas; (iii) bulk density of wet CPW (0.9 Mg m^{-3}); (iv) unproductive times to load up CPW and fill the administrative transportation forms required by laws.

For a given citrus processing plant with certain characteristics (in terms of silos, means of transportation, management systems) transport costs strongly vary (generally from less than 0.5 up to over 5 € Mg^{-1}, in Italy, Tamburino and Zema, 2009), depending on several factors. Transport cost decreases with increasing dry matter content per unit of volume transported (by pressing or drying process), thus making possible transportation over longer distances, consequently widening the utilization market. The transport cost (on average 2.75 € Mg^{-1}) of wet peel (average dry matter content equal to 14.5%) is about 21.51 € per Mg of dry matter; the transport cost of dried peel (average dry matter content of 91.5%) is 3.40 € per Mg of dry matter, thus about six times lower (adapted from Tamburino et al., 2007, updating to the current market conditions of Southern Italy, one of the larger citrus producing areas in the Mediterranean).

3.3 Storage techniques

CPW can be conserved either by acidification of ensiled biomass or by drying. CPW, when used as forage, is usually stored by ensiling it in vertical tanks (generally made of concrete) or in horizontal ones (seldom directly into the soil, often wrapping CPW with plastic sheets). Storage of CPW is possible also without covers protecting biomass from air and soil contact, in this case the extermal part of the pile is spoiled due to the contact with soil and to aerobic degradiation. During ensiling, biomass is subject to acidic fermentation (pH down to 3.5) in absence of oxygen, due to lactic bacteria converting sugars and carbohydrates into lactic acid, hydrogen and CO_2. This process prevents the growth of other micro-organisms and enzymatic activity, thus hampering further biomass spoilage and assuring its conservation. Acidic fermentation of CPW during ensilage is enhanced by its high carbohydrate content, bulk density (which limits air permeability) and lack of proteins. Natural acidification prevents the growth of butyric and proteolytic bacteria that cause unpleasant odours in biomass and low desirability for animals due to fermentation. Moreover, acidic fermentation and the associated water evaporation and drainage during the ensiling process reduces the water content (Gohl, 1978), but also leads to loss of soluble volatile solid substances (such as sugars, organic acids and mineral salts) (Caparra et al., 2007b).

Megias et al. (1993) in orange peel waste (henceforth "OPW") subject to ensiling in microsilos (50 L) for 100 days found a rapid pH decrease down to 3; while the lactic acid concentrations increased from 2 to 5.7% of dry matter in just the first few days of the experiment, the remaining volatile fatty acids were constant throughout the experiment. After the early increase, dry matter (21.6%) and other nutritive parameters remained practically constant. Ashbell and Lisker (1987) ensiled OPW with 17.1% and 20.5% of dry matter in 400- and 280-litre barrels for 142 and 131 days and did not detect any differences in the chemical and microbiological components of ensiled peels, neither in the case of seepage kept inside the containers nor when allowed to drain out. Calabrò and Panzera (2017) evaluated the reduction of both total and volatile solids after 7, 14, 21 and 37 days of ensiling of OPW; the initial solid content (17% referred to wet material) decreased by about 1.2, 17.1, 10.6 and 21.7%, respectively, while the volatile solids showed a reduction of 0.68% after 7 days, 1.5% after 14 days and 1.6% after 30 days. For longer ensiling periods, pH also decreased from 3.5 for wet OPW down to 3.06 for an ensilage of 37 days. Similar results were also found in a successive study (Calabrò et al., 2018b).

Conservation of CPW occurs also with a drying process that reduces water content to 8-10%. From the liquid phase citrus molasses are recovered, while pressed and dried pulp is often milled by hammer mills. During drying, water evaporates, biomass porosity is reduced and bulk density decreases to 200-300 kg m^{-3} (Tamburino and Zema, 2009). This process makes the biomass more homogeneous and reduces attacks by microorganisms. Dried CPW must be stored in dry places at air humidity lower than 50-52%; otherwise, moisture adsorption by the dried biomass risks starting fermentation processes with heat production, which can lead to the spontaneous combustion of CPW with or without flame (Kimball, 1999).

CPW can be dried naturally (in the open air) or artificially (by fuel-drying). Because of its high cost, the *fuel-drying process* (after liming and pressing phases) is not economically viable, especially for traditional low-efficiency drying plants; molasses are often added to facilitate the drying process (Kimball, 1999). Sometime, dryers directly fed by the same biomass are used. The fluidised-bed drying technique, used mainly for granular materials, can be also applied for fuel-drying the CPW; fluidised bed dryers are characterised by a proper residence time distribution which approaches perfect mixing (Reay and Baker, 1985).

CPW drying in the open air by solar heat, cheaper than fuel-drying process, is common particularly when dried biomass is used as animal feed. CPW is spread on the ground; then an external crust develops, which expands from the outer layer slowly into the inner biomass. In the first phase of the process, biomass volume usually decreases due to the water losses on external surface and cracks develop due to strains that increase exchange surface. Then, when CPW water content is under 50-60%, steam flows through pores from inside the biomass and CPW is subject to further water losse~~s~~ without substantial volume reduction~~s~~ (Tamburino and Zimbone, 1997; Tamburino et al., 2001). Also, in this case natural acidification assures biomass conservation, even though during solar-drying process biomass losses are observed due to animals (such as insects, rodents and birds). In Mediterranean areas, characterised by a dry and sunny climate, solar-drying of CPW is a usual practice.

Treatment duration and losses of biomass during solar-drying can be reduced by proper mechanical handling operations (periodical removal of the external crust and shuffling of the wet biomass by excavators for exposition to sun). Dried clods are used as animal feed and the biomass in contact with the ground is used as conditioner (Bampidis and Robinson, 2006; Caparra et al., 2007b).

Often CPW is crushed into coarse pieces and then into small pieces; subsequently, the biomass is mixed with lime, which makes the drying process easier (because of the lack of hygroscopicity), since this mixing neutralises the free acids binding with pectins and releasing water (Sharma et al., 2017).

In some cases, after fruit processing, CPW is simply pressed or treated with lime and pressed (an operation commonly known as “liming”) to reduce moisture content by 10%; pressing and liming often precede fuel-drying, in order to reduce energy consumption and limit cost of reuse or disposal. Liming at doses up to 0.5% (w/w) and subsequent shredding (by hammer mills) limits hygroscopicity of pectins (which precipitate, reacting with calcium) and increases water removal efficiency. Liquid percolating from pressing is subject to concentration for molasses production, a dark dense fluid with a high sugar content (60-75%) used as animal feed (Gohl, 1978; Kimball, 1999). Shredding, liming and pressing of CPW provides a more appealing and uniform texture and composition for animals (Bampidis and Robinson, 2006; Gohl, 1978; Kimball, 1999). Dried CPW is often subject to pelletisation, in order to reduce volume and limit transport costs. Dried CPW can be also used as component of concentrated fodder (Cevolani, 2016).

4. CITRUS PEEL WASTE VALORISATION SYSTEMS

Traditional methods of CPW disposal (e.g., incineration or landfilling) are nowadays insufficient and problematic in terms of environmental impacts and energy efficiency (Wei et al., 2017). Applications using the whole citrus peel without differentiating individual constituents (such as animal feed, organic fertilizer, base for compost) represent the most common and simplest way to process the raw material (Siles Lòpez et al., 2010). More recently, conversion processes in biorefineries have been proposed for most profitable and environmentally sound uses, leading to the production of a number of products. In the following, both uses (direct use and uses in biorefinery) will be discussed.

4.1 Direct use

4.1.1 Agronomic utilization

Agronomic utilisation of CPW can be carried out either by direct land spreading or after composting. However, the well-known antimicrobial activities of the abundant amounts of EOs and other bioactive molecules in CPW (e.g., Aggarwal et al., 2002; Andiloro et al., 2013; Zema et al., 2016, 2012) may be very harmful for soil micro-organisms. Murdock and Allen (1960) reported that EO present in the OPW is toxic to yeasts; inhibitory effects have been detected on the growth of several useful bacteria, yeast and moulds (e.g., *Bacillus subtilis, Saccharomyces cerevisiae, Aspergillus awamorii*) (Sharma et al., 2017; Subba et al., 1967). In addition, the soil application of non-stabilized organic matter can cause oxygen depletion of soil and odours emission from the treated fields. This suggests the need to spread the biomass well before seeding operations of herbaceous crops, and without incorporating biomass into the soil. Moreover, supplying soil with untreated CPW may induce percolation with possible groundwater pollution.

Hence, proper land spreading protocols, or composting, or adequate processing of the bioactive compounds must be adopted prior to agronomic utilisation of CPW.

4.1.1.1 Organic soil conditioner

Agronomic utilization of CPW by direct land spreading is a suitable practice to increase organic matter content of soil and consequently to improve its fertility. The addition of organic matter improves soil resistance to raindrop impacts and water infiltration capacity, thus reducing water runoff and soil erosion. The presence of organic matter also leads to a high water retention capacity, greater porosity, air permeability and better efficiency in nutrient utilization in the soil.

Furthermore, when spread on soil, CPW releases the macro-elements contained in the biomass. Table 3 shows the average content of nitrogen (N), phosphorous (P_2O_5) and potassium (K_2O) in wet and solar-dried CPW. However, additional supply with mineral fertilizers is generally necessary to achieve the nutrient content required by crops.

Table 3

The feasibility of agronomic utilization of CPW as a soil conditioner depends on many factors. Its cheapness is often offset by the distance between the production and the spreading site (when biomass transport is required over considerable distances), the mechanization level of distribution operations and the availability of large areas for its application; furthermore, to increase CPW suitability as an amendment for the selected soil, it is suggested that the biomass be applied on arable lands in dormancy years and on loamy soils, with easy access for transport (also in winter). Bombino et al. (2010) tested the hydrological effects of spreading of solar-dried CPW over steep lands (with bare soils or covered by vegetation) and found that biomass addition noticeably reduces surface runoff and soil loss, furthermore encouraging the establishment and development of vegetation.

In the past, in Italy up to 30-40% of the total production of CPW has been used as soil conditioner on fallow lands in rotation with durum wheat. In the 8-11 months between land spreading (January-March) and sowing (November-December) CPW udergoes the following processes:

- drying (with the development of a porous biomass, strongly cracked and pervious to water and air);
- spreading of CPW piles on land;

- aerobic fermentation after early rainfalls in autumn;
- incorporation into soil and sowing.

Despite the good results (high yield of wheat production in the 3-4 years after soil application without use of other fertilizers), the use of CPW as a soil conditioner was profitable only in proximity to orange processing plants (Tamburino et al., 2007).

4.1.1.2 Compost production

As with other vegetal matrices, CPW can be used to produce compost of good quality. Compost of CPW, as with the biomass derived from other organic residues, is considered to be a partial or integral substitute for non-renewable resources (i.e. peat, Bernal-Vicente et al., 2008; Tittarelli et al., 2003).

The biochemical process linked to composting of CPW starts from a short latency phase followed by a rapid increase of temperature for about 2 months and a final phase of gradual cooling for another month. Composting transforms organic matter into stable compounds, which can be handled, stored, transported and applied to land without adverse effects in the environment (van Heerden et al., 2002). Proper composting effectively destroys pathogens and weed seeds though the metabolic heat generated by microorganisms during the process (Crawford, 1985).

Citrus compost is characterized by a high level of ligno-cellulosic compounds, high C/N ratio and pH (Bernal-Vicente et al., 2008; Chef et al., 1983; Cotxarrera et al., 2002; Hoitink and Boehm, 1999; Rose et al., 2003; Serra-Wittling et al., 1996). Siles Lòpez et al. (2010) recommended adjusting the waste’s C/N ratio, pH, and water content to 24:1, 6.3, and 60%, respectively, while, according to Golueke (2017), the optimal pH and C/N values for a rapid and complete humification of an organic substrate should be between 6.0-7.5 and 25-35, respectively. To adjust the low pH (4.1) of CPW, van Heerden et al. (2002) used calcium hydroxide, generally applied for composting acidic substrates, because of its exothermic reaction that promotes thermophilic microbial activity (inherent to composting) (Poincelot, 1974). During humification phyto-toxicity and C/N ratio of CPW decrease; this latter parameter generally does not induce immobilization of mineral nitrogen in soil (Casale et al., 1995).

However, the excessive moisture of wet CPW makes it difficult to compost by the methods commonly used for urban solid waste, because it requires a previous mixing with ligno-cellulosic support (either pruning residues or other similar organic substrates) or straw with additional costs. Co-composting of CPW with the organic fraction of municipal solid waste (OFMSW) has also been demonstrated to be a suitable practice (Siles et al., 2016). A blend of approximately 17% of OPW and 83% of OFMSW is optimal for co-composting and reduces odour emissions by 37% compared to OFMSW composting. A higher percentage of CPW (up to 50%) decreases the pH of the mixture (less than 5.0), and stops the biological stabilization of organic matter, because of the inhibition of aerobic microorganism activity and the reduction of oxygen consumption (Siles et al., 2016). Thus, a longer composting time would be required to obtain a stable amendment.

Composting of organic residues from the citrus processing industry has been widely investigated in recent years, also as a way to offset the environmental issues linked to the increasing amount of citrus fruits processed yearly and requiring CPW disposal (Bernal-Vicente et al., 2008; Calabretta et al., 2004; Tittarelli et al., 2002). Some researches (Intrigliolo et al., 2005) have shown the positive agronomic effects of compost produced by CPW. Bernal-Vicente et al. (2008) investigated the effects of two types of citrus composts and their water extracts, as partial substitutes for peat in growing media for melon seedlings in greenhouse nurseries; these Authors demonstrated higher plant growth compared to the control soil, where peat was used, thus demonstrating that citrus compost could reduce peat and agrochemical costs, due to its nutriactive and biocontrol effects. Kato-Noguchi and

Tamaka (2006) found an allelopathic potential (suppression of germination, growth, survival and reproduction of a plant by the production of one or more biochemicals) of *Citrus junos* fruit waste after juice extraction on the growth of the roots and shoots of alfalfa (*Medicago sativa L.*), cress (*Lepidium sativum L.*), crabgrass (*Digitaria sanguinalis L.*), lettuce (*Lactuca sativa L.*), timothy-grass (*Phleum pratense L.*), and ryegrass (*Lolium multiflorum Lam.*). This inhibitory activity was attributed to the abscisic acid-b-d-glucopyranosyl ester, which is highly concentrated in CPW. Pulp and peel residues from orange processing were used as organic soil fertilizer to improve the production of lettuce (Guerrero et al., 1995). Pulp application made nutrients more available when compared to peel, with a significant increase in crop production due to the fast mineralization of organic matter contained in the orange pulp.

4.1.2 Animal food

The most widespread utilization of CPW in many areas of the Mediterranean basin, such as Southern Italy, is animal feed, which accounts for up to 70-80% of production (although this percentage is variable from one processing plant to another, and on an annual basis) (Tamburino et al., 2007). CPW (wet, ensiled or dried) is used to partially replace the feed of the conventional animal diet, such as cereals. The amount of CPW to be gradually introduced in the diet depends on cattle breed and physiological condition (Tamburino and Zema, 2009).

4.1.2.1 Wet feed

Wet CPW can be used only in the short period of the citrus processing season and for livestock close to processing plants. As mentioned above, the cost of transport impacts negatively on the economic advantages of using the wet residue as animal feed, due its high water content. Moreover, the low cost of CPW for cattle breeders can be further limited by farm management operations (e.g. need for storage tanks, automated fodder systems, management of innovative animal diets). The most advanced farms, which can completely exploit the peel's nutritional capacity, are able to pay higher prices compared to the less developed farms (e.g. many sheep and caprine farms, often managed by traditional techniques). Consequently, in most cases, only transportation over short distances can be remunerative; in such cases CPW is generally laid on pasture land and eaten by animals from January to November. Furthermore, the breeders' lack of knowledge about peel's nutritional capacities negatively affects CPW prices, in particular for OPW. Some breeders, in fact, pay 5 or 10 times less for OPW than for lemon, even though their nutritional capacity is similar. These factors, together with the temporal and spatial availability of wet or ensiled CPW, determine a wide range of variability (0.55-16.50 € Mg^{-1}) for OPW price (at the current market conditions of Southern Italy, Tamburino and Zema, 2009, updated).

Figure 5 shows, for a 40,000 Mg $year^{-1}$ citrus processing industry in Sicily (Southern Italy), the monthly sales of wet OPW to cattle breeders in a processing season. Data has been split into four profit classes: on average, about 73% of OPW sale to breeders yields a profit (difference between sale price and transport cost) to the producer (Tamburino et al., 2007).

Citrus pulp is characterized by a high nutritive potential because the high amount of pectin and the low content of lignin increases the digestibility of the food (Marino et al., 2013). Sweet orange pulp has been observed to be a source of calories and proteins comparable to maize (Oluremi et al., 2006). However, the bitter taste, due to the presence of EO and the acidity (especially for lemon) reduce its palatability for animals (Cevolani, 2016). On the contrary, ensiled CPW has a pleasant odour, and it can be mixed with grass, hay, sugarcane bagasse or cereal straw in order to increase dry matter content, and it can be readily eaten by cattle (Mahato et al., 2018). Feeding ensiled citrus pulp to pigs has been shown to improve meat quality, without affecting their growth (Cerisuelo et al., 2010).

Figure 5

4.1.2.2 Dried feed

Dried CPW is more palatable for animals compared to wet or ensiled peel and provides a significant nutritional capacity, as widely demonstrated over the last 50 years (Bampidis and Robinson, 2006; Caparra et al., 2007b; Chapman et al., 1972; Gohl, 1978).

In general, about 5-10% of CPW production used for animal feed is fuel-dried, but, as mentioned above, the fuel-drying process is not economically advantageous (especially for traditional low-efficiency drying plants). Some investigations have confirmed the possibility of exploiting solar energy to dry CPW in rural areas of the semi-arid zones, thus making the reuse of CPW in agriculture and livestock easier (Tamburino and Zimbone, 1997; Tamburino et al., 2001). For instance, in many areas of the Mediterranean basin, California and Australia, a significant share (about 40-50%) of CPW production is eaten by animals after solar-drying from May to September (mostly in sheep and caprine zoo-technics).

When peel is left in piles or rows over agricultural land near the processing plant, the upper part of the pile (which is cleaner) can be utilized as animal feed; however, the lower part (the dirtier), which may be degraded by contact with the ground, is given to less profitable uses, such as organic soil conditioner or fuel (Bampidis and Robinson, 2006; Tamburino and Zimbone, 1997; Caparra et al., 2007b). This practice, however, cannot be used human settlements due to its bad odour. Suitable techniques for biomass handling can reduce drying times, increase bulk density, and lower mould growth and organic matter losses (Tamburino and Zimbone, 1997; Tamburino et al., 2001): for instance, it is advisable to remove the surface crust by excavators or forklifts.

Rarely, dried CPW, used as supplementary animal feed, is frozen for inhibiting microbial growth of animal feed during storage without disrupting rumen fermentation (Nam et al., 2009).

4.1.2.3 Effects on animal health and nutrition

From the nutritional point of view, CPW is characterized by a high energy value. Because of its high carbohydrate and fibre content, it is easy to digest; indeed, forage units (FU) per kg of dry matter is about 95-98 for OPW and 90-95 for lemon peel (Lanza and Messina, 1979a). Conversely, the protein content of CPW has a low digestibility (Caparra et al., 2007b) and, thus, in the case of animal diets mainly based on CPW, it is necessary to integrate the protein portion (beside vitamins and minerals). Due to its particular properties, CPW is better used as feed for ruminants bred for meat and milk production, since it can partially or totally replace the cereal portion. CPW in swine diets should not be higher than 20-25% (Lanza and Messina, 1979b). Dried peel from sweet orange processing is a useful additive for broiler feed, as it promotes feed intake and weight gain of the animals (Ebrahimi et al., 2014). Feeding cattle with a high amount of dried pulp does not affect food palatability or milk production (Cevolani, 2016). Dried CPW is also added as a supplement to the cereal diet of lactating dairy cows, since it is highly digestible and high-energy compared to cereals, the energy not being based on starch but on soluble carbohydrates and digestible fibre. Conversely, dried CPW is not recommended for pigs or poultry, because of the fibre content and presence of limonin (Mahato et al., 2018).

Many experiences of feeding animals with CPW have been carried out, mainly in Mediterranean areas. For instance, CPW was supplied in diets of fattening lambs resulting in good colour and quality of meat; CPW improved ruminant digestion, increasing the secretion of acid solution in the stomach (Marino et al., 2013). Caparra et al. (2007a), evaluating the influence of an ensiled mixture made of OPW (60%), crude olive cake (35%) and wheat straw

(5%) on ewe diets, found a significant variation in fatty acid composition compared to animals fed with pasture graze.

In order to reduce the water content of CPW from juice centrifugation and facilitate its pressing, which enhances its subsequent use as animal feed, Tripodo et al. (2004) tried an enzymatic treatment. This produced an animal feed with excellent digestibility *in vitro* and a protein content that, although not being noticeably high, is comparable with many other agro-industrial by-products currently used as components of animal feed. A meal made of sun-dried OPW, as a replacement for maize in the diet of rabbits, had a positive effect on their growth performance, shown by body weight gain and water intake (Hon et al., 2009). However, it is best not to exceed 20% and 40% of sun dried peel in the dietary of broilers and rabbits (Oluremi et al., 2007), respectively.

CPW has even been supplied to fish: juvenile orange koi carps, fed with diets containing up to 20% OPW, showed better pigmentation than fishes fed with ordinary diets, but had worse weight gain, specific growth rate, food conversion and utilization ratios; this suggests that the inclusion of raw OPW in the fish's diet is not recommended (Ipinjolu, 2000).

Oluremi et al. (2007), analysing different meals based on CPW, found the presence of tannins (0.433-0.523%), saponins (0.030-0.043%), phytates (0.062-0.082%), oxalates (0.033-0.048%) and flavonoids (0.025-0.045%). In ruminants, dietary condensed tannins of 2-3% have imparted beneficial effects, because they reduce the wasteful protein degradation in the rumen by the formation of a protein tannin complex (Barry and Blaney, 1987). Saponins are bitter, and reduce both the palatability of the feed and growth in swine and poultry; however, they increase excretion of cholesterol reducing its concentration (Malinow et al., 1981). The saponin content of the peel meals have no negative effects on cattle health because concentration is below 3%, the value reported by Kumar (1991) to be harmful for cattle. The level of phytate is lower than that reported in maize, sorghum, potato and other crops (Concon, 1988) and is safe for livestock consumption (Oluremi et al, 2007). Phytate and oxalate complexing the essential minerals render them poorly available to monogastric animals. Flavonoids, thanks to their anti-oxidant property (Kumar, 1991), can inhibit enzymes in mammals (Hollman et al., 1997). However, the high pectin amount in CPW acts an astringent and anti-diarrheal in young animals (Cevolani, 2016).

Beneficial effects of EO on animal health have been widely studied. Generally, EO of CPW has positive effects on animal health because of its anti-bacterial and anti-fungal activities (Nam et al., 2006). According to these Authors, citrus EO inhibits the growth of *Escherichia coli* (with a recovery after 24 hours of incubation) and *Salmonela enteritidis* (with inhibition for no less than 72 h) at 0.112 g kg^{-1}. However, high dosages of D-limonene are toxic to pigs and poultry (Serres, 1999). Afzalani et al. (2015) showed that a basal diet at a dose of 400 ppm of EO extracted from OPW is a suitable feed additive to manipulate rumen microbial fermentation and to improve blood metabolites in fattening Bali cattle. Sweet OPW extract was added to drinking water to improve the immune response and disease resistance of broiler feeding, indicating that it can be a useful additive to broiler diets (Pourhossein et al., 2015). Callaway et al. (2011a) successfully used CPW and dried OPW as additives to a typical sheep diet to affect *Escherichia coli* population in vivo. The same authors demonstrated that the inclusion of OPW in diets reduced *Salmonella Typhimurium* populations in the gut of experimentally inoculated sheep (Callaway et al., 2011b).

4.2 Biorefinery valorisation approaches

A biorefinery is a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from waste biomass (Martín et al., 2010). Since CPW contains many high-value-added compounds (such as soluble sugars, cellulose, hemi-cellulose, pectin, proteins, EO), using a biorefinery can valorise this agricultural waste: the production of multiple products has the advantage of maximizing the value derived from the biomass feedstock, while producing a lower amount of waste to be treated (Siles Lòpez et al., 2010). A biorefinery approach contributes to the growth of the bioeconomy and mitigates the negative environmental effects linked to agro-industry (Satari and Karimi, 2018).

A summary of the main proposed biorefinery schemes/strategies for CPW are reported in Mamma and Christakopoulos (2014).

In the scheme proposed by Siles Lòpez et al. (2010), the first step consists of EO removal followed by ethanol and methane production. Other high-value products - such as pectin, industrial enzymes, and single cell proteins - are also extracted before the final use of the residual lignin as an energy source.

The scheme proposed by Pourbafrani et al. (2010) focused on ethanol, biogas and limonene production. Depending on the market and process profitability, pectin is also recovered by solvent as a by-product (about 78% of its total content). After limonene extraction from hydrolysates CPW, the residual sugars are converted into ethanol, while the remaining liquid and solid materials of the hydrolyzed CPW can be subjected to anaerobic digestion to obtain biogas.

Balu et al. (2012) have developed a microwave assisted approach to transform OPW not only into a range of valuable products - chemicals (D-limonene and a-terpineol) and polysaccharides (pectin), - but also into a novel form of mesoporous cellulose.

Boukroufa et al. (2015) have proposed extracting EOs, polyphenols and pectin from OPW by integrating green processes such as microwaves and ultrasound assisted extraction, combining environmentally sustainable and high yielding processes.

Satari et al. (2017) proposed a novel process (SPEP, "Simultaneous Pectin Extraction and Pretreatment", able to enhance both pectin extraction and sugar production from CPW with dilute nitric acid at a low/moderate temperature. Satari and Karimi (2018) reported three different ways for CPW valorisation: direct use of native/modified CPW (for producing nanoporous materials, biosorbent for heavy metals and biofertilizer), biochemical processes, and green extraction techniques.

4.2.1 Energy production

The high carbohydrate and low lignin contents of CPW (Table 2) also make it a promising lignocellulosic feedstock for second-generation liquid or gaseous fuels (e.g., bioethanol by hydrolysis/fermentation and biogas/biomethane by anaerobic digestion) (Ruiz et al., 2016; Satari and Karimi, 2018). Moreover, since CPW has a high calorific value (about 17 MJ kg^{-1} when dried), it can be used directly for energy production (heat or electricity) through combustion (Siles et al., 2016). Different food processing wastes, including CPW (Torquato et al., 2016), were suitable substrates for hydrogen production by dark-fermentation, photo-fermentation and/or combined-fermentation processes (Van Dyk et al., 2013). To the knowledge of the authors these processes have not been applied until now for the valorisation of CPW but are mentioned since they too can offer a promising way to valorise this waste.
However, since pre-treatments are usually necessary before the most promising CPW energy conversion processes (in order to limit the inhibiting effects of EOs on the biochemical processes), an integrated biorefinery approach is suggested by Negro et al. (2016), in order to recover limonene, biogas and bioethanol at the same time.

4.2.1.1 Fuel from dried CPW

Within an increasing trend for energy production from crop and agro-food industry residues, solar-dried CPW has been proposed as a fuel for combined heat and power or only electrical energy power stations. This practice is mainly adopted where the power stations are close to where the biomass is produced, in order to reduce transport and storage costs (Botta et al., 2003).

Thermal treatment methods (such as incineration and pyrolysis) cannot be directly applied to CPW. Despite being technically feasible, these energy conversion methods would not be efficient from an energy or economic point of view, requiring ~~a~~ expensive, prior drying, given the high water content of the biomass (Siles et al., 2007; Negro et al., 2016). However, the moisture content of the feedstock subject to thermal treatments should be under 10%, in order to reduce its presence in the oil produced (Bridgwater, 2011). Aboagye et al. (2017) carried out CPW pyrolysis to evaluate OPW as a potential oil producing feedstock using fast pyrolysis technology in Ghana and found promising results. The environmental impact of the combustion of CPW was evaluated by Siles et al. (2016), who observed that the direct oxidation of nitrogen contained in OPW (structural NO_x) produce large concentrations of NO_2 (around 4.5 g NO_2/m^3_{STP}), which is one of the main disadvantages of this process. Pelletized and dried CPW has been used as a fuel for direct combustion in domestic stoves and this increased the pellet value (Tamburino and Zema, 2009).

4.2.1.2 Ethanol production

In recent decades, the possibility of converting CPW into ethanol has been evaluated: pectin, cellulose and hemi-cellulosic polysaccharides can be hydrolysed into simpler sugars and fermented into alcohol. Ethanol is an efficient fuel and can be used to enhance octane content as well as to replace lead as an anti-knocking agent. Although 20% ethanol can be blended with petrol in conventional cars, it can induce oxidative corrosion in iron components of the engine: therefore, anhydrous ethanol is required for blending with petrol (Kimball, 1999).

To summarise, the process of ethanol production consists of a preliminary pretreatment and of a subsequent hydrolysis of pectin, cellulose and hemi-cellulose of CPW into simple sugars. Finally, alcoholic fermentation (using saccharomycetes) converts sugars into ethanol (John et al., 2017) and produces carbon dioxide by glycolysis, piruvate-decarbossilasys and alcoholdehydrogenasys.

Although the free sugars can easily be water-extracted (Satari et al., 2016), pretreatment is usually required for an efficient release of fermentable sugars from carbohydrate polymers to produce gaseous fuels and fermentative products (Satari et al., 2017). Several pre-treatment techniques such as ammonia fibre explosion, liquid hot water, organosolv extraction, alkaline hydrolysis, oxidative delignification and biological method can be applied for different lignocellulosic biomasses (Calabrò et al., 2018a, 2018b; Calabrò and Panzera, 2017), in order to help in the solubilization of hemicellulose and modification of lignin; other pre-treatments for citrus waste include steam explosion and acid hydrolysis (John et al., 2017). However, these two latter pre-treatments are quite expensive.

The pretreatment methods for the hydrolysis of CPW are simpler than that required for usual lignocelluloses (because of the low lignin content of citrus peel) and have mainly focused on hydrothermal processing, primarily aimed at removing and/or lowering limonene and other chemicals that show inhibitory effects for energy valorisation (Satari and Karimi, 2018). As a matter of fact, the major limiting factor for the process is the content of EO, which prevents alcoholic fermentation due to its toxicity for many micro-organisms. EO reduction down to a concentration of 0.08-0.12% (Kimball, 1999; Wilkins et al., 2007b) should be performed in order to avoid micro-organism inhibition. Moreover, the EO/D-limonene inhibitory concentration was found to be variable, since it depends on micro-organism strain. A minimum inhibitory EO concentration of 0.01% (v/v) was reported for ethanolic fermentation of OPW by *Pichia kudriavzevii* KVMP10 bacterium (Koutinas et al., 2016); for the *Zymomonas mobilis* (at 37 °C) these inhibitory concentrations were 0.05%, 0.10%, and 0.20%, after 24, 48, and 72 hours, respectively, while no inhibition was observed after 96 h (Wilkins, 2009). *Mucor indicus*, a filamentous ethanol-producing fungus, and *Rhizopus sp.*, isolated from tempeh, showed a maximum tolerance of 2% of D-limonene in semi-synthetic media under aerobic and anaerobic conditions (Lennartsson et al., 2012); ethanol production by *S. cerevisiae* was inhibited between 0.33% and 0.14% (v/v) of D-limonene (Wilkins et al., 2007b).

Oberoi et al. (2011) did not observe inhibition of ethanolic production with a D-limonene concentration of 0.09% (v/w) in dried, milled and hydrothermally pre-treated *Citrus reticulate* peel, while Wilkins et al. (2006) found inhibition at a D-limonene concentration of 0.28% (v/v). Wilkins et al. (2007a) studied the influence of EO in ethanol production from Valencia OPW at 37 °C using two ethanologenic yeasts (*Saccharomyces cerevisiae* and *Kluyveromyces marxianus*), identifying a final ethanol yield of 35.1 g L^{-1} and the minimum inhibitory EO concentration of 0.05%. The inhibitory concentration for lemon EO was above 0.025% (Boluda-Aguilar and López-Gómez, 2013). These Authors applied steam explosion to reduce EO concentration; the subsequent simultaneous saccharification and fermentation (SSF) produced more than 60 L of ethanol per Mg of wet lemon peel waste. Steam explosion treatment was used also by Wilkins et al. (2007b) to volatilize EO from CPW that was subsequently subject to SSF by *S. cerevisiae* at 37 °C. The treatment removed more than 90% of the initial D-limonene. The maximum ethanol concentration (39 g L^{-1}) was achieved at 0.08% (v/w) of D-limonene. In order to separate D-limonene from CPW, Choi et al. (2015) proposed a removal column coupled with an immobilized cell reactor (ICR): yeast fermentation resulted in ethanol concentrations (14.4–29.5 g L^{-1}) and yields (90.2-93.1%) 12-fold greater than those in ICR fermentation alone.

Hydrolysis of the lignocellulosic materials using enzymatic processes is commonly used to produce monomeric sugars for subsequent biofuels extraction (Zhu et al., 2011). The combination of both cellulase and pectinase was reported to be more effective to hydrolyse OPW compared to the individual use of these enzymes (Grohmann and Baldwin, 1992).

Enzymatic hydrolysis and fermentation can be traditionally performed by separate or integrated processes (i.e., simultaneous saccharification and fermentation; non-isothermal simultaneous saccharification and fermentation; simultaneous saccharification, filtration, and fermentation; and simultaneous saccharification and co-fermentation) (Satari and Karimi, 2018).

Suitable technologies to reduce the cost of ethanol production from CPW in the short term were explored also by Widmer (2006), Widmer et al. (2010) and Rahmani and Hodges (2007). The use of acid or base adjustment prior to limonene removal by thermal pre-treatment (at 160 °C) did not improve ethanol yield (Widmer et al., 2010).

In some areas, such as Florida, ethanol is commonly produced from citrus molasses. Despite the higher sugar content of CPW, molasses are technically easier to convert into ethanol due to their lower concentration of EO (Braddock, 1999; Kimball, 1999). However, the cost of ethanol extraction from citrus molasses is higher compared to other crops (e.g. corn).

4.2.1.3 Biogas production

Biogas, generally a mixture of methane (50-70%) and carbon dioxide (30-50%), is the main product of the anaerobic digestion of organic substrates. Agro-industrial waste is a suitable substrate for biogas production and often contains mineral ions that enhance methane yield (Bozym et al., 2015). The increasing development of biogas production from organic waste and residues also suggests the future utilization of CPW, whose methane potential is even higher than other crop residues (Calabrò et al., 2018b; Gunaseelan, 2004; Plöchl and Heiermann, 2006). An energy analysis showed that in a citrus processing plant handling 600 Mg per day of fruits, the biogas produced from the waste streams is enough to meet the electricity and fuel demand and the excess electricity generated from biogas may also be sold (Koppar and Pullammanappallil, 2013).

Methane yield of CPW depends on many factors, such as pH, temperature, nutrient availability for microorganisms and, secondarily, on citrus cultivar. However, as with alcoholic fermentation, anaerobic digestion of CPW is mainly limited by the presence of EO in the substrate. Lane (1984) reports an inhibiting concentration of EO over 2.5 mg L^{-1}; Ruiz and Flotats (2016) found the inhibitory effect of D-limonene over concentrations of 200 mg kg^{-1}, mainly due to cymene. In their review, Ruiz and Flotats (2014) reported the following inhibition limits for the anaerobic digestion of CPW (used alone or as co-substrate): 24 mg L^{-1} d^{-1} (Srilatha et al., 1995) and 34 mg L^{-1} d^{-1} (Forgács et al., 2012) for D-limonene and 50 mg L^{-1} d^{-1} (Mizuki et al., 1990), 75-95 mg L^{-1} d^{-1} (Lane, 1984) and 192 mg L^{-1} d^{-1} (Akao et al., 1992) for EO. The effect of increasing concentration of orange EO (up to 2 g L^{-1}) was studied by Calabrò et al. (2016), who reported methane yields up to 0.37 Nm^3 kg^{-1} of volatile solids (VS) in mesophilic and 0.30 Nm^3 kg_{VS}^{-1} in thermophilic conditions; moreover, the same Authors observed that D-limonene is quantitatively transformed in *p*-cymene, but other removal mechanisms could be present, such as volatilization. Gunaseelan (2004), estimating biochemical methane potential of peel of different fruits (including citrus) in batch tests of 100 days at 35 °C, found that methane yields and rates were variable among the species and fruit parts. Methane yields from sweet OPW and pressings were 0.46 and 0.50 m^3 kg^{-1} of added VS, respectively; peels, pressing, whole rotten fruit and seeds of loose skinned mandarins yielded 0.49, 0.43, 0.49 and 0.73 m^3 $kg_{VSadded}^{-1}$, respectively; lemon pressing yielded 0.47 m^3 $kg_{VSadded}^{-1}$. More than 90% of methane yield was achieved between 40 and 50 days of fermentation. These methane yields are consistent with the values (0.43-0.64 m^3 kg_{VS}^{-1}) reported by other Authors (Gunaseelan, 2004, Kaparaju and Rintala, 2006; Koppar and Pullammanappallil, 2013; Plöchl and Heiermann, 2006) for anaerobic digestion of wet CPW. In the mesophilic semi-continuous anaerobic digestion of citrus waste, reported methane yield ranges from 0.21 to 0.29 m^3 kg_{VS}^{-1} (Lane, 1984; Srilatha et al., 1995; Ruiz and Flotats, 2014), while higher values (0.3–0.6 m^3 kg_{VS}^{-1}) were reported in thermophilic conditions (Kaparaju and Rintala, 2006; Martín et al., 2010; Ruiz and Flotats, 2014). Chanakya et al. (2009) found a methane yield of only 0.110 m^3 kg^{-1} of Total Solids (TS) from mesophilic digestion of OPW, attributed to the inhibiting effect of Volatile Fatty Acids (VFA). Thermophilic anaerobic digestion of orange pulp and peel was evaluated also by Kaparaju and Rintala (2006), who reported methane yields of 0.49 m^3 $kg_{VSadded}^{-1}$ in batch tests and 0.6 m^3 $kg_{VSadded}^{-1}$ in semi-continuous digestion (Organic Loading Rate, OLR, of 2.8 kg_{VS} $m^{-3}d^{-1}$ and Hydraulic Retention Time, HRT, of 26 days). Operating at OLR of 4.2 kg_{VS} $m^{-3}d^{-1}$ and 40 days of HRT, a methane yield of 0.5 m^3 $kg_{VSadded}^{-1}$ was obtained, but a further increase in OLR to 5.6 kg_{VS} $m^{-3}d^{-1}$ resulted in an unstable and unproductive process, directly shown by a complete block of methanogenesis, drop in methane content, reduced pH and increase in volatile fatty acid concentrations. Zema et al. (2018) evaluated the methane production through semi-continuous anaerobic digestion of industrial OPW under mesophilic and termophilic conditions and increasing OLR and EO supply rates (EOsr) until complete process inhibition. Under mesophilic conditions, the highest daily specific methane yield was achieved at OLR of 1.0 g_{VS} L^{-1} d^{-1} and EOsr of 47.6 mg L^{-1} d^{-1}. Partial inhibition of anaerobic digestion was detected at OLR and EOsr of 1.98 g_{VS} L^{-1} d^{-1} and 88.1 mg L^{-1} d^{-1}, respectively and the process irreversibly stopped when OLR and EOsr reached 2.5 g_{VS} L^{-1} d^{-1} and 111.2 mg L^{-1} d^{-1}, respectively. Under thermophilic conditions, the cumulative methane production (0.12 m^3 $kg_{VSadded}^{-1}$) was about 25% of that under mesophilic conditions (0.46 m^3 $kg_{VSadded}^{-1}$). The thermophilic digestion was completely inhibited at lower OLR (1.98 g_{VS} L^{-1} d^{-1}) and EOsr (88.1 mg L^{-1} d^{-1}) compared to mesophilic conditions.

The convenience of mesophilic or thermophilic temperatures in CPW anaerobic digestion depends on several factors (summarised in Table 4). The choice of temperature must be considered in each specific case. Although thermophilic conditions allow a higher methane production rate and faster organic matter degradation, mesophilic digestion seems to result in a more stable process.

A method to limit the process inhibition due to EO consists of co-digesting CPW with other substrates, thus diluting the toxic compounds. Serrano et al. (2014) mixed sewage sludge and OPW (70:30 of wet weight, respectively), observing a methane yield of 0.165 m^3 kg_{VS}^{-1}, a biodegradability of 76% and a maximum OLR of 1.6 kg_{VS} $m^{-3}d^{-1}$; increasing OLR, the methane production rate decreased, showing process inhibition. The anaerobic co-digestion of OPW with residual glycerol, a low-price by-product from biodiesel production, was investigated by Martín et al. (2013), who demonstrated that the biomethanisation process is more efficient under mesophilic conditions. In that case the methane yield was 0.330 m^3 $kg_{VS\ added}^{-1}$ with mean OLR 1.91 kg_{VS} m^{-3} d^{-1}; however, inhibition was observed at OLR higher than 2.10 kg_{VS} $m^{-3}d^{-1}$ due to the accumulation of volatile acids in the digesters, with a consequent pH decrease. A similar OLR limit (about 1.9 kg_{VS} m^{-3} d^{-1}) observed by Lane (1980). OPW (50%) in co-digestion with kitchen waste (50%) had a methane potential of about 0.395 m^3 kg_{VS}^{-1} in mesophilic conditions (35°C) in 30 day batch tests (Calabrò et al., 2016).

In addition to co-digestion, many other treatments (such as distillation, aeration, solid state fermentation, biological removal, steam explosion, solvent extraction) have been investigated, in order to reduce EO concentration in the substrate prior to anaerobic digestion (Ruiz and Flotats, 2014). Lane (1984) working on anaerobic digestion of comminuted peel diluted with water at 10% TS (w/v), found an OLR limit of 3.3 kg_{VS} m^{-3} d^{-1} (corresponding to an EO concentration of 95 mg L^{-1} d^{-1}) after EO extraction by distillation and of 2.8 kg_{VS} m^{-3} d^{-1} (EO of 75 mg L^{-1} d^{-1}) after EO recovery in a juice extraction factory. Mizuki et al. (1990), in anaerobic digestion of CPW at 37 °C with a HRT of 10 days, obtained the highest production (up to 50 mL g_{TS}^{-1}) with an OLR of 0.9 g_{VS} L^{-1} d^{-1} and a lower production with an OLR of 1.8 g_{VS} L^{-1} d^{-1} (EO feeding close to 0.07 mL L^{1} d^{-1}), while no inhibition was observed after removal of EO by steam distillation or aeration with an OLR of 1.8 g_{VS} L^{-1} d^{-1} (90-95 mL g_{VS}^{-1}). Martín et al. (2010), after removing D-limonene by steam distillation under 2 mg L^{-1}, observed higher methane yields (0.332 m^3 kg_{VS}^{-1} added) under thermophilic (67 °C) conditions compared to mesophilic ones (37 °C, 0.230 m^3 $kg_{VSadded}^{-1}$) at an optimal OLR between 1.20-3.67 kg_{COD} m^{-3} d^{-1}. Siles et al. (2016), using steam distillation to reduce the concentration of D-limonene (with removal efficiency around 70% after one hour), reported a methane yield of 0.280 m^3 kg_{COD}^{-1} added under thermophilic conditions at the maximum OLR of 3.67 kg_{COD} m^{-1} d^{-1} without acidification and process inhibition. Srilatha et al. (1995), studying the anaerobic digestion (at 30 °C) of pre-treated OPW by solid-state fermentation (82.4% of limonene removal, down to 24 mg L^{-1} d^{-1}), found an OLR limit of 2.5 kg_{VS} m^{-3} d^{-1} and a methane yield of 0.3 m^3 $kg_{VSadded}^{-1}$. Ruiz et al (2016) evaluated the efficiency of three pre-treatment methods (biological removal by fungi or recovery steam distillation and ethanol extraction) of limonene and their influence on biochemical methane production, resulting in limonene concentration decreases of 22%, 44% and 100%, respectively; by-products of limonene biodegradation by fungi exhibited an inhibitory effect, reducing interest in this biological pre-treatment. In many cases, the methane yields and rate of the treated OPW increased significantly after the pre-treatments. Calabrò et al. (2018b) evaluated the influence of different pretreatment methods (e.g. ensiling, aeration, thermal and alkaline treatments) on D-limonene removal of OPW and successive anaerobic digestion. The results demonstrated the ability of alkaline treatments, combined with either thermal or aeration treatment, to reduce D-limonene content up to 80%, due to the opening of oil sacs, which allowed D-limonene stripping. Aeration was found to be the least efficient method to remove D-limonene (removal efficiency less than 15%). A relatively high biomethane potential production of OPW (up to about 500 NmL CH_4 $g^{-1}VS$) was measured. Wikandari et al. (2015), investigating the efficiency of hexane, diethyl ether, dichloromethane or ethyl acetate to extract the limonene prior to anaerobic digestion process of OPW, showed a higher methane production in the case of pretreatment with hexane. Finally, Panuccio et al. (2016) showed that the digestate from anaerobic digestion of a blend of animal manure, maize silage, and CPW is an antioxidant-rich compound that can be used as fertilizer in agriculture (Satari and Karimi, 2018).

Overall, the biomethane production from CPW is an appealing option, which is currently feasible through co-digestion with other substrates. However, the problems related to the seasonal production of CPW and EO toxicity to micro-organisms have not been yet overcome: optimisation of storage techniques or new simplified pre-treatment techniques for D-limonene removal are probably the most promising options for a sustainable anaerobic digestion of CPW.

4.2.2 Added-value product extraction

A number of commercially important high value-added compounds can be potentially extracted from CPW to be used mainly in food, pharmaceutical and cosmetic industries and even directly sold for domestic usage (Sharma et al., 2018). However, to date, the most common process with industrial importance is EO/limonene extraction.

4.2.2.1 EO/limonene extraction and uses

4.2.2.1.1 Characteristics and uses

EO is mainly present at different depths in the peel and cuticles of the citrus fruit and is released when oil sacs are crushed during juice extraction (Mahato et al., 2017). EO refers to a variety of products extracted from citrus fruits during juice processing. Citrus EO is a mixture of terpenic hydrocarbons and oxygenated derivatives such as aldehydes, alcohols and esters (Arce et al., 2005). OPW typically contains 5.4 kg of oil per Mg of raw biomass, of which approximately 90-98% is D-limonene (Fisher and Phillips, 2006; Hull et al., 1953; Moufida and Marzouk, 2003; Ruiz and Flotats, 2014). Most of the EO is found in oil sacs in the flavedo and peel, although small amounts can be found also in other parts of the fruit, such as the juice cells themselves. The oil from the juice cells is not exactly the same as that of the fruit peel and is generally of better quality. Lemon and sweet orange EO differs from other citrus oils in their content of valencene, a sesquiterpene (0.3-2.0%) that is only found in small amounts in other oils (Espina et al., 2011; Kimball, 1999). Table 5 reports the EO composition of different citrus fruit varieties.

EO has been extensively used in many applications for a long time. In recent years, many diversified applications have been proposed: insect/pest control for long-term storage of food products or feedstuffs at high temperatures and in humid conditions (Nam et al., 2006), processed food preservation, antimicrobial packaging for food products, edible thin films and antimicrobial packaging films, nanoemulsions for preservation of vegetables and fruits, ingredients in soda/citrus concentrates, flavouring agents in carbonated drinks (including alcoholic and non-alcoholic beverages), candy, gelatin (Bousbia et al., 2009), meat, fish and seafood preservation (Mahato et al., 2017). Moreover, citrus EO - and its main component, D-limonene - is used in the cosmetic, pharmaceutic and chemical industries. EO is a flavouring agent used to reduce the unpleasant taste of medicines. In the cosmetic industry, it is used as a fragrant ingredient in many preparations (Arce et al., 2005; Bousbia et al., 2009), such as toilet soaps, detergents, creams, lotions and perfumes and other home care products (Sahraoui et al., 2011) or as a green solvent (Bertouche et al., 2012; Veillet et al., 2010). Citrus EO can also be used as an alternative to synthetic fungicides and antibacterial agents (M’hiri et al., 2017), since it has a strong antibacterial activity that destroys the cellular integrity of microbial cells and inhibits their respiration (Sharma et al., 2017).

Table 5

4.2.2.1.2 Extraction methods

EO extraction from CPW not only provides a valuable product for several uses, but also contributes, as mentioned above, to make CPW feasible for other uses such as bioethanol or biogas production. According to the literature, in these cases EO can be extracted from CPW by several methods, either with the aim of simple removal or of recovery (Ruiz et al., 2016). However, pre-treatments are generally required before EO extraction, in order to increase the process yield; thermo-chemical or thermo-physical processes (such as milling or steam explosion) are commonly used (Choi et al., 2015).

Removal techniques includes aeration and biological treatment. Reduction by aeration is mainly due to evaporation or oil stripping, rather than to microbial degradation, although limonene-degrading micro-organisms are present (Ruiz and Flotats, 2014; Calabrò et al., 2018b). Conversely, biological treatments reduce EO concentration of citrus fruits by micro-organism activity (Akao et al. 1992; Srilatha et al., 1995).

Recovery includes cold pressing (henceforth CP), centrifugation, steam distillation (SD), steam explosion (SE), liquid extraction with organic solvents (Ruiz et al., 2016; Ruiz and Flotats, 2014) and acid hydrolysis (Lohrasbi et al., 2010). CP, SD or solvent extraction with hexane or carbon dioxide are relatively simple and well-established processes of extraction of D-limonene from OPW (Hull et al., 1953), while centrifugation is used for the recovery of citrus EO from CPW press liquors (Lane, 1983).

The traditional way to extract EO is by cold-pressing CPW. By this technique, oils are removed mechanically from peel and utricles, yielding a water emulsion, which is then centrifuged to separate the EO (Bousbia et al., 2009; Mahato et al., 2017). The recovered EO is further distilled in order to separate the D-limonene from the other less volatile oxygenated flavour compounds. These concentrated oils can be added back to citrus juices to enhance flavour without increasing oil concentration (Kimball, 1999).

SD is commonly used on an industrial scale for D-limonene recovery, whose yields are usually around 50% of the total EO amount (Ruiz et al., 2016). During distillation, the CPW is exposed to boiling water or steam and releases the EO through evaporation (Bousbia et al., 2009). As steam and EO vapours are condensed, both are collected and separated in a vessel traditionally called the ‘‘Florentine flask” (Dugo and Di Giacomo, 2002; Guenther, 1948). In the case of lemon peel, distillation gives an oil yield of 0.21% of the total peel weight against 0.05% of cold pressing (Ferhat et al., 2007).

Distillation methods (such as hydro-distillation, vacuum distillation, as well as steam distillation at atmospheric pressure) are also widely used for the extraction of aroma producing compounds, because of the low temperature distillation. The different extraction methods determine the variable composition of aroma producing compounds in the EOs (Mahato et al., 2017).

Hydro-distillation (HD) is a traditional technique that is based upon the evaporation of a mixture of immiscible liquids at a lower boiling temperature than the boiling temperature of the single components; after separation of volatile and non-volatile compounds, the EOs are separated from the water by a simple decantation. The simplicity of the equipment and its high selectivity are positive aspects of this approach; however, like other traditional methods, HD requires long extraction times and this can cause the alteration of some thermo-labile compounds, such as terpenic compounds (Negro et al., 2016).

SE, able to remove high amounts of limonene (over 90%, Ruiz et al., 2016), disrupts the complex polymers of the matrix, resulting in a partial hydrolysis of the carbohydrates and in several changes to the basic fractions that make up the natural matrix (cellulose, hemicellulose and lignin) (Negro et al., 2016). The explosion of the EO sacs leads to the release of D-limonene, which is carried by the steam and recovered in a condenser. The advantage is the possibility of using a non-toxic solvent such as water, but the high process temperature increases energy demand (Negro et al., 2016) and this technique can be adopted only for large-scale facilities, due to high investment cost (Forgács et al., 2012). However, SE ~~steam explosion~~ is a potential pre-treatment of CPW able to increase enzyme accessibility to polysaccharides of cell walls, while removing D-limonene. This process applies pressurized steam to cellulosic biomass in a reactor. After a reaction time, some of the steam is vented to quickly reduce the pressure in the reactor, thus causing a rapid decompression of the water in the biomass and disruption of cell walls (Wilkins et al., 2007b).

Liquid-liquid (using ethanol) and solid-liquid extraction (using n-hexane) show a good efficiency in limonene extraction (Ruiz et al., 2016). Arce et al. (2005) studied the liquid-liquid extraction for a limonene + linalool + ethanol + water quaternary system at 298.15 K. The highest selectivity values were obtained for EO with low linalool content; moreover, these Authors showed that a high ethanol dose in the solvent and low EO/solvent ratio should be used to carry out the citrus EO deterpenation. By solid-liquid extraction limonene is leached at room temperature into a solvent that is put into contact with the CPW (Seader and Henley, 2006); this technique requires that the compounds to be extracted are present at low concentration, such as in OPW. Solid-liquid extraction using four solvents (hexane, diethyl ether, dichloromethane, and ethyl acetate) was used by Wikandari et al. (2015) to extract the limonene prior to anaerobic digestion process.

However, all these traditional methods for the extraction of citrus EOs have shown some disadvantages. In more detail, the elevated temperature and the prolonged extraction time required by steam distillation represent the main disadvantages, because chemical modification of the volatile molecules, as well as loss of sugars (that may be used for ethanol production) can occur (Choi et al., 2015); moreover, the EOs obtained by distillation deteriorate easily and develop off-flavours because of the instability of the terpene hydrocarbons, particularly D-limonene (Yamauchi and Saito, 1990). When using cold pressing, citrus EO is agitated vigorously with water and a gradual diminution in citral and terpene alcohol content occurs. The use of solvents to extract EOs from citrus involves environmental problems linked to waste disposal/treatment. All these techniques are expensive, since they require a high energy input. These shortcomings have led to consideration of the use of new techniques in EO and aroma extraction, which typically enhance the quantity of EO, preserve its quality and use less energy (Ferhat et al., 2007).

Due to increasing energy prices and the need to reduce CO_2 emissions from fossil fuels, new extraction techniques requiring a lower energy demand and which are solvent-free (thus reducing the energy input and eliminating the risk of environmental concerns) have been developed. The following green extraction techniques - e.g., Supercritical Fluid Extraction (SFE), Microwave-Assisted Extraction (MAE), Microwave-Accelerated Distillation (MAD), Microwave Steam Distillation (MSD), Microwave Hydro-Diffusion and Gravity (MHG), and Sonication-Assisted Extraction (SAE) - have been developed (Negro et al., 2016).

SFE is one of the most suitable methods for the extraction of volatile organic compounds from plant matrices, because the operating conditions of the process are maintained above the critical temperature and critical pressure of the solvent used (typically CO_2, which does not show any contamination problems, and is cheap, non-flammable, and chemically inert). Thanks to these operating conditions, SFE exhibits high diffusivity (similar to gases) and a high solvent power (similar to liquids) allowing a higher mass transfer and extraction rate. Other important advantages are the low solvent consumption, the absence of corresponding residues in the extract (purity of extracted limonene higher than 99.5% w/w, Mamma and Christakopoulos, 2014; Mira et al., 1999; Yasumoto et al., 2015) and higher extraction yield (compared to HD pretreatment, Atti-Santos et al., 2005). However, the equipment is costly and SFE performance decreases sensibly with the moisture content in the matrix, therefore, a pre-drying step is often required (Negro et al., 2016).

As regards methods using microwaves, this technology is based on the use of waves characterized by a frequency that ranges from 0.3 to 300 GHz and a wavelength that ranges from 1 cm to 1 m (Negro et al., 2016). This electromagnetic radiation can penetrate the matrix and heat polar substances. For these reasons, microwaves can assist the extraction of organic compounds by heating the moisture inside the cell, which collapses due to the increase in the internal pressure (Eskilsson and Bjorklund, 2000).

Fast MAD (also known as microwave ‘dry’ distillation, DryDist) is a new patented method for isolating EOs from natural products by combining microwave energy and natural distillation (Chemat et al., 2004, 2003). Ferhat et al. (2007) evaluated the effectiveness of MAD methods in the isolation of EOs from fresh CPW and compared it to traditional HD and cold pressing. The microwave methods offer important advantages over traditional alternatives, that is, shorter extraction times (30 min vs. 3 hours for HD and 1 h for CP), better yields (0.24% vs. 0.21% for HD and 0.05% for CP), lower environmental impact (since energy cost is appreciably higher for performing HD and for mechanical motors used in CP), cleaner features (as neither residue generation nor water/solvent used), increased antimicrobial activities, and more valuable EO quantity and quality (with high amounts of oxygenated compounds and better reproduction of the natural aroma of citrus compounds. Finally, the microwave methods yield EOs that can be analysed or used directly without any clean-up, solvent exchange or centrifugation steps (Ferhat et al., 2007).

MAE is a process of using microwave energy to heat solvents in contact with a sample in order to partition analytes from the sample matrix into the solvent (Eskilsson and Bjorklund, 2000). The main advantages of using MAE are primarily the reduction in extraction time when applying microwaves that heat the solution directly (instead of conventional heating that requires a finite period of time to heat the vessel before the heat is transferred to the solution) and secondarily the significant reduction in organic solvent consumption (Negro et al., 2016). Using MAE, Negro et al. (2017) extracted D-limonene from flavedo of OPW by applying an accelerated moderate temperature extraction; up to 0.48% (w/w wet basis) D-limonene was extracted at 130 °C for 60 min.

Aside from MAE, microwave-assisted hydro-distillation (MAHD) has been successfully applied to extract EOs from CPW, with the advantages of reducing costs, avoiding additive~~s~~ usage, and improving process yield (Bustamante et al., 2016).

MHG technique reduces the time required by HD method, without considerable changes in the volatile oil composition: an extraction time of 15 minutes with MHG provides yields comparable to those obtained after 180 minutes by means of HD (Bousbia et al., 2009). Boukroufa et al. (2015) optimized a technique - previously proposed by Bousbia et al. (2009) - using MHG without distillation or solvent extraction (which are the most energy- and solvent-consuming unit operations).

MSD is a highly efficient method, which not only greatly accelerates the extraction process, but also enables recovery of EOs without causing any changes in oil composition. The effectiveness of MSD over SD is attributed to the more rapid rupture of the cell wall under strong microwaves and release of the cell cytoplasm (Mahato et al., 2017). Sahraoui et al. (2011) studied MSD for the extraction of EO from OPW. Compared to conventional SD, MSD offers important advantages, such as shorter extraction times (6 minutes for complete extraction), savings of energy and comparable yields; moreover, MSD produces EO with better sensorial properties at optimized power (500 W), avoiding the loss of volatile compounds. Results from chemical and cytological approaches confirmed the effectiveness of this new technique.

Ultrasound waves, characterized by frequencies higher than 20 kHz, are used in SAE: these waves travel through the matrix, and molecules are submitted to compression and expansion cycles. The pressure cycles create bubbles, which can expand until the cellular wall collapses and organic compounds are released. Extraction with an organic solvent can be assisted through the use of ultrasound in a process called sonication (Negro et al., 2016).

However, while techniques used in green extraction methods, in alternative to the traditional methods, have proved to be potent, their use in an integrated biorefinery is rare (Satari and Karimi, 2018).

4.2.2.2 Food production additives

The consumption of fruits by humankind has well known health benefits, attributed to vitamins and minerals, as well as to some specific organic micro-nutrients, such as carotenoids, polyphenols, tocopherols and others (Fernández-López et al., 2004; Schieber et al., 2001). An important property of citrus fruit is its higher content of soluble dietary fibre (about 30%) (Gorinstein et al., 2001; Grigelmo-Miguel and Martín-Belloso, 1999).

Many of these healthy compounds of citrus fruits are also found in their processing residues. The food industry extracts the following products from citrus residues (Tables 6 ~~4~~ and 7 ~~5~~, Figure 3) (Goodrich and Braddock, 2006; Kimball, 1999):

- *concentrated base for beverage production*, produced after a debittering processes, containing sweeteners, citric acid, food colorants, natural flavours, turbidity agents, vitamins and natural preservatives, all of them representing marketable commodities;
- *pectins*, especially from the processing of lemon, for the production of marmalade, jelly, jam, and other food products (thickeners, stabilizers, emulsifying agents, etc.) or drugs and medicines (Kesterson e Braddock, 1976);
- *peels*, used for candied fruit production;
- *dietary fibres*;
- *EO*, whose main uses have been described above.

However, the processing cost generally makes these productions economically unsustainable and thus these options are still marginal at an industrial level.

Table 6

Table 7

Pectin is a complex carbohydrate (a polymer of α-galacturonic acid with a variable number of methyl ester groups, Liu et al., 2006), which is a significant component of the primary cell wall of plants. In CPW pectins naturally exist in complex and unsoluble forms (protopectins). Most of the pectins in CPW are found in juice sac material, with large amounts occurring in the albedo of the peel.

Pectin production is the first real, large scale, industrial utilization of lemon peel. It is not economically viable for OPW, due to the lower jellying capacity of derived pectins. Citrus pectins are used as thickeners, emulsifiers and stabilisers in many foods, because they lead to a desirable texture of food and beverages (Satari and Karimi, 2018) as well as in pharmaceutical and cosmetic products; however, 75% of the pectin produced is used in the manufacture of jams, jellies, marmalades and similar products. Furthermore, it is a suitable substrate to produce edible active films with vast applications in food packaging because of its biodegradability, biocompatibility, edibility, and chemical versatility (Espitia et al., 2014).

Pectins are extracted from CPW by the following operations: peel washing with water (in order to remove EO and soluble sugars); acidic hydrolysis; filtration; final precipitation by isopropyl or ethyl alcohol. In order to reduce the use of solvents in the extraction of pectins and other value-added products from CPW (thus avoiding inherent health or environmental hazards) (Sharma et al., 2017), pectin extraction is usually carried out using water as a solvent. More recently, other methods have been introduced to separate the pectin, such as ultrasonic extraction (Zhang et al., 2013), enzymatic extraction (Ptichkina et al., 2008), MAE (Fishman and Cooke, 2009), and subcritical water extraction (Ueno et al., 2008). Liu et al. (2006), using water as a solvent (up to the optimal ratio of 1:12.5) to recover pectin from flavedo and albedo of OPW with different extraction techniques, reported that the total pectin yield from the dried peel is 2.2%, which becomes higher by using the Soxhlet method.

Dietary fibres are valued for their nutraceutical properties and the presence of antioxidant compounds (Marín et al., 2007). Dietary fibres, including polysaccharides and lignin, delay adsorption of nutrients (Fernández-López et al., 2004; Ritz et al., 1991; Roberfroid, 1993) and gastric emptying (Low, 1990; Roberfroid, 1993); moreover, they decrease triacylglycerol concentrations (Fernández-López et al., 2004; Rivellese et al., 1980). The content of total dietary fibres is higher in peels (about 65%) than in peeled citrus fruit (Fernández-López et al., 2004; Gorinstein et al., 2001) (Table 6); in particular, albedo is the principal component in peels containing a good source of fibre (Mahato et al., 2018).

4.2.2.2 Production of cosmetics and pharmaceutics

Many products that can be extracted from CPW are used in cosmetic and pharmaceutic industries, such as the EO, pectins, flavonoids, carotenoids and citric acid.

The main uses of *EO* and *D-limonene* have been discussed above (see section 4.2.2.1).

Pectins are used in the pharmaceutical industry for gastrointestinal treatments, as well as a haemostatic agent or thickener for preparation of batters and capsules (Kesterson and Braddock, 1976; Kimball, 1999). Being a soluble fibre, pectin has a proven capacity to increase the growth rate of natural bacteria in the digestive apparatus, thus improving digestion (Goñi et al., 2015). Moreover, binding pectin to low-density lipoprotein reduces lipid absorption during digestion, making it a suitable dietary product (Karboune and Khodaei, 2016).

Flavonoids are phenolic compounds that are present in high amounts in CPW (Satari and Karimi, 2018) and show interesting biological activities (antioxidant, anticarcinogenic, anti-inflammatory, antioxidant, anti-aging, cardio-protective, chemo-protective). Flavonoids are secondary metabolites naturally occurring in plants and possessing significant biological properties, e.g. the protection of plants against ultraviolet radiation (Sharma et al., 2018). The most important flavonoids are naringin, neoeriocitrin, hesperidin, diosmin, rutin, naringenin, eriodictyol, hesperetin, apigening, luteolin, diosmetin, kaerapferon, quercetin, tangeretin (Benavente-García et al., 1997).

These compounds show a very complex pattern, since they can be found under different forms in citrus fruits (flavanones, flavones and anthocyanins) (Cook and Samman, 1996; Peterson and Dwyer, 1998; Tripoli et al., 2007). Tripoli et al. (2007) reports that some studies have shown that flavonoids are active as antiviral (against rhino- and poliomyelitis viruses, Middleton et al., 2000, as well as herpes simplex, poliovirus, para-influenzal and syncytial viruses, Kawaguchi et al., 2004) and antibacteric (against *Salmonella typhi* and *S. typhimurium*, Kawaguchi et al., 2004) compounds.

Since a significant antioxidant activity is known for fruits and vegetables with a high concentration of polyphenols and flavonoids (Jayaprakasha et al., 2008; Kedage et al., 2007; Kiselova et al., 2006; Klimczak et al., 2007), the correlation between the content of these compounds and antioxidant activity has been widely studied also for citrus fruits (also containing phenolic compounds). No correlation between total flavonoids and radical scavenging activity has been found (Anagnostopoulou et al., 2006; Ghasemi et al., 2009; Heinonen et al., 1998; Nickavar et al., 2007); only flavonoids with a certain structure and particular hydroxyl position in the molecule can act as proton donating and show radical scavenging activity (Ghasemi et al., 2009; Hou et al., 2003; Mensor et al., 2001). Table 8 ~~6~~ reports the radical scavenging activity related to total phenol and flavonoid content for 26 methanolic extracts from 13 citrus species. It is evident that the phenol and flavonoid content has a large range of variability, depending both on the citrus variety and part (that is, peel or tissue). The scavenging activity, measured by IC_{50} index (Table 8) and variable also among the different citrus varieties, is higher for citrus tissues than for extracts from peel.

Table 8

Because of their intrinsic biological properties and ability for lipid antiperoxidation effects, flavonoids represent an important class of bioactive compounds (Marín et al., 2002a); their crude extracts are often used in pharmaceutical formulations. Various studies have shown that flavonoids act as regulators of prostaglandin synthesis, which are natural and very active compounds against inflammatory states as well as in platelet aggregation and other physiological processes. Other flavonoids have antiallergic and anticancer properties. Hesperidin, nobiletin, naringin and especially tangeretin have been investigated for their capacity to block neoplastic metastasis at its start through which primary cancer develops to secondary and tertiary phases (Benavente-Garcia et al., 1997). Apart from their anti-oxidant and anti-inflammatory effects, nobiletin and tangeretin may represent beneficial drug candidates for the treatment and prevention of Alzheimer's and Parkinson's disease (Braidy et al., 2017).

The most important flavones are rutin and diosmin. Rutin, diosmin and hesperidin have an interesting pharmacological activity mostly for vascular syndromes and thrombotic diseases.

Anthocyanins, found in typical Italian pigmented orange cultivars (*Moro*, *Tarocco* and *Sanguinello*), have a high antioxidant activity. Anthocyanins, in particular, act as scavengers of free radicals, which are produced during oxidative cellular metabolism and may become extremely dangerous if accumulated: they can damage membrane cell lipids, proteins and DNA (Proteggente et al., 2003; Rapisarda et al., 1999; Terao, 1999; Yao et al., 2004).

The abundance of *carotenoids* in citrus fruits, with higher content in the peel than in the pulp (Tao et al., 2003), makes them an important source of dietary nutrients. Carotenoids are usually divided into two main classes: hydrocarbon carotenoids, known as carotenes (e.g., b-carotene, lycopene), and oxygenated carotenoids, known as xanthophylls (e.g., b-cryptoxanthin, lutein, violaxanthin) (Sharma et al., 2017). Carotenoids are responsible for the various colours of citrus ranging from yellow to red (Dugo et al., 2006) and are natural colourants, preferred over synthetic colouring materials for foods, instead of artificial colourants (Sharma et al., 2017).

Citric acid, an intermediate of the tricarboxylic acid cycle, is found in citrus fruits, as well as in a variety of acidic fruit juices (Torrado et al., 2011). OPW is also used as a substrate, in alternative to citrus fruit, for citric acid fermentation (Rivas et al., 2008). OPW is previously subject to auto-hydrolysis, in order to increase the content of soluble sugars to be used as a carbon source for citric acid fermentation. Without any additional nutrients, liquors obtained by this process are used for citric acid production from *Aspergillus Niger*, also in solid-state fermentation, which has been shown to be a very versatile method without additional nutrients or treatment apart from sterilization (Torrado et al., 2011). Addition of calcium carbonate prevents progressive acidification of the substrate. Moreover, the influence of the addition of methanol on citric acid formation was investigated. Some recent applications of citric acid in the detergent and cosmetic industry, or as the active ingredient in some bathroom and kitchen cleaning solutions are reported (Wang and Liu, 1996).

Overall, such uses will enhance the valorisation of progressively increasing amounts of citrus residues, given the high added value of these products and the development of extraction techniques (Goodrich and Braddock, 2006; Tamburino et al., 2007), thus allowing cost reduction.

5. CONCLUSIONS

The management of citrus processing waste, as for other residues of agro-food industries, involves noticeable economic (due to the high incidence of disposal costs on a company's profit) and environmental (in view of the increasing interest in the protection of natural resources) constraints. As a matter of fact, the large quantitative and qualitative variability of citrus waste production together with its particular physical and chemical properties (acidity, concentration of EO, scarcity of nutrients and presence of inhibiting and added-value compounds) require eco-compatible and economically viable management systems~~,~~ to be established using a circular economy and a biorefinery approach.

The most traditional use of CPW as food for animals (both wet or dried), thanks to its nutritional and beneficial properties, is advisable in areas with high livestock density, since the costs of its transportation to the farm may be too high. Some studies have shown the improvement in the organic matter and nutrient contents of soil by using CPW as organic conditioner or for compost production, also in this case preferably on agricultural lands in proximity to citrus processing industries.

The possibility of recovering energy from CPW has been explored by several researchers, who have measured the biomethane (in anaerobic digestion processes) and bioethanol (by alcoholic fermentation) yield under different environmental conditions and organic loading. However, the bioenergy conversion systems of CPW should be further improved by suitable techniques, minimising the toxic effects of EO on the microbial mass.

Several studies have highlighted the nutraceutic and beneficial characteristics of many compounds recovered from CPW. These suggest its utilisation in food, cosmetic and pharmaceutic industries. Since these compounds (pectins, dietary fibres, flavonoids, flavouring agents, citric acid, etc.) have high added market values, this use may be considered as very promising, although today it is limited by the high processing costs.

On the whole, this study, together with the eminent literature analysed, has highlighted how the competitiveness and development of the whole citrus sector may be properly relaunched by a proper citrus waste management systems the waste being turned into valuable resources.

For the immediate future, it is highly probable that the use of CPW as animal feed, when profitable for the producer, will remain an important valorisation method for a large share of citrus processing residues. However, the key factor for a completely profitable management chain is the enhancement of other ways to valorise the rest of the CPW, which currently are less profitable for citrus facilities, and thus are considered a burden for the management chain. Presumably, this portion of CPW will be increasingly used for energy production, especially after optimising treatments and storage processes prior to anaerobic digestion/ethanol production. If new processes for the extraction of high-value compounds (section 4.2.2) are developed and consolidated, certainly the amount of CPW used as animal feed will progressively reduce, while most of the other residues of the extraction processes will be used as substrates for energy production.

The consolidation of these economically and environmentally sound systems on a large scale would not only enhance the development of large agriculture-devoted areas, such as the Mediterranean basin, but may also noticeably reduce the environmental risks of waterbody and soil pollution in the case of unauthorised citrus waste disposal.

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TABLES

Table 1. Main constituents of CPW from different citrus fruit varieties (source: Pascual and Carmona, 1980, adapted).

Citrus variety	*Fresh weight (%)*	*Peel (%)**	*Segment membranes and juice sacs (%)**	*Seeds (%)**	*Other constituents (%)**
Orange	55.5	65.4	31.8	2.2	0.6
Tangerin	69.2	75.5	22.6	0.0	1.9
Mandarin	64.3	58.2	32.6	9.2	0.0
Grapefruit	62.2	65.1	33.3	1.6	0.0
Lemon	62.1	69.6	25.0	5.3	0.1

* on the dry matter weight.

Table 2. Range or mean value of physico-chemical composition of CPW.

Parameter	Measuring unit	Dried citrus waste*,[a]	Wet citrus waste*,[b]	Ensiled citrus waste*,[c]
pH	-	-	3.9-4.3	3.0-3.1
Water content	%	10.0-14.2	72.5-87.0	78.0-88.7
VS	% D.M.	93.5-94.1	93.8-96.7	94.5-96.5
Protein	% D.M.	3.3-8.5	6.53-8.3	7.3-10.9
Fat	% D.M.	1.7-3.7	0.9-3.3	9.7
Fibre	% D.M.	7.3-13.9	10.6-42.1	n.a.
NDF	% D.M.	19.3-24.2	n.a.	22.8
ADF	% D.M.	16.0-22.2	n.a.	17.0-22.0
Starch	% D.M.	2.3	<1.0-2.9	n.a.
Sugar	% D.M.	24.1-40.0	15.0-46.6	n.a.

Notes: D.M. = dry matter; VS = Volatile Solids; NDF = neutral detergent fibre; ADF = acid detergent fibre; *: adapted data; a = de Blas et al., 2010; Bampidis and Robinson (2006); Ruiz and Flotats (2014); Grohmann et al. (1994); b = Calsamiglia et al. (2004); Ruiz et al. (2016); Mahmood et al. (1998); Bampidis and Robinson (2006); Kammoun Bejar et al. (2012); c = Bampidis and Robinson (2006); Calabrò & Panzera (2017); Calabrò et al. (2018b).

Table 3. Mean value of the main chemical characteristics of wet and solar dried CPW (% of dry matter) (Tamburino et al., 2007).

Parameter	*Wet CPW*	*Dried CPW*
Organic C	50	39
Total N	1.3	1.5
C/N ratio	38	26
P_2O_5	0.28	0.36
K_2O	1.1	1.5

Table 4. Main differences between mesophilic and thermofilic digestion of CPW.

	Conditions	
	Mesophilic (28-45 °C)	Thermophilic (45-57 °C)
Advantages	- Lower temperature required - Simpler setup of temperature in cold climate region - More stable process	- Faster degradation and biogasification rates - Higher pathogen destruction (Koppar and Pullammanappallil, 2013) - Increased biogas/biomethane yields (due to higher micro-organisms activity) - Shorter hydraulic retention times (leading to reduction of digester volume) (Martín et al., 2010) - Improved post-treatment sludge dewatering (Lo et al., 1985) - Unnecessary pre-treatments as steam distillation to strip volatile compounds (Koppar & Pullammanappallil, 2013)
Disadvantages	- Lower biogas/biomethane production - Lower hydrolysis rate (Converti et al., 1999) - Lower organic loading rates (Martín et al., 2010) - Partial degradation of carbon source (Converti et al., 1999)	- Higher energy inputs requirements for substrate pre-heating and temperature maintenance of the reactor (Lo et al., 1985). - Occasional process instability (Chen et al., 2008) - Poorer effluent quality (due to the abundance of dissolved solids) (Lo et al., 1985) - Lower tolerance to EOs (Zema et al., 2018; Calabrò et al., 2016)

Table 5. Mean value of the ~~C~~composition of essential oil of citrus fruits (%).

	Genus, species, variety				
EO component	*Citrus sinensis (sweet orange)*[a]	*Citrus aurantium (bitter orange)*[b]	*Citrus bergamia (bergamot)*[c]	*Citrus limon*[d]	*Citrus reticulata L. (clementine)*[e]
Limonene	89.9	90.3	72.9	59.1	88.9
α-pinene	2.3	1.5	1.4	5.2	-
Sabinene	1.0	-	-	0.9	0.2
β-pinene	0.1	0.2	0.1	5.2	-
Myrcene	1.0	-	-	0.9	2.3
ϒ-terpinene	-	-	-	9.7	4.8
Valencene	0.3	0	0	0.8	0
Geranial	0.1	-	-	2.1	0
Linalool	0.3	1.5	10.2	0.2	0.5
α-terpineol	0.45	1.1	0	0	0.4
Methanol	0.4	0.3	0.3	-	-
Isopropanol	0.9	0.8	0.3	-	-
cis-p-mentha-2,8-dien-1-ol	0.7	-	-	0.1	-
trans-carveol	0.6	-	-	0.1	-
Carvone	0.6	-	-	0.1	-
3-heptanone	0.4	1.2	0.9	-	-
Butylacetate	-	0	5	-	-

Notes: a = Espina et al. (2011); Moufida and Marzouk (2003); Badee et al. (2011); b = Moufida and Marzouk (2003); c = Moufida and Marzouk (2003); d = Espina et al. (2011); e = Droby et al. (2008).

Table 6. Dietary fibre (DF, g/100 g of dried fruit) and polyphenol~~s~~ (mg/100 g of wet fruit) content in peeled lemons and oranges and their peels (Gorinstein et al., 2001).

Waste		*DF*			*Total polyphenols*
		Total	*Soluble*	*Insoluble*	
Lemon	Peeled	7.34±0.8	2.49±0.3	4.83±0.5	164±10.3
	Peel	14±1.3	4.93±0.4	9.04±0.9	190±10.6
Orange	Peeled	7.28±0.8	2.45±0.3	4.82±0.5	154±10.2
	Peel	13.9±1.3	4.71±0.5	9.18±1	179±10.5

Table 7. Fibre composition (% dry weight) of different CPW (Fernández-López et al., 2004; adapted from Marìn et al., 2003).

Compounds	*Lemon*	*Orange*
Pectin	7.50±0.06	6.50±0.05
Hemicellulose	11.0±0.09	6.50±0.05
Cellulose	36.25±2.90	20.75±1.90
Lignin	22.5±1.90	14.75±1.01

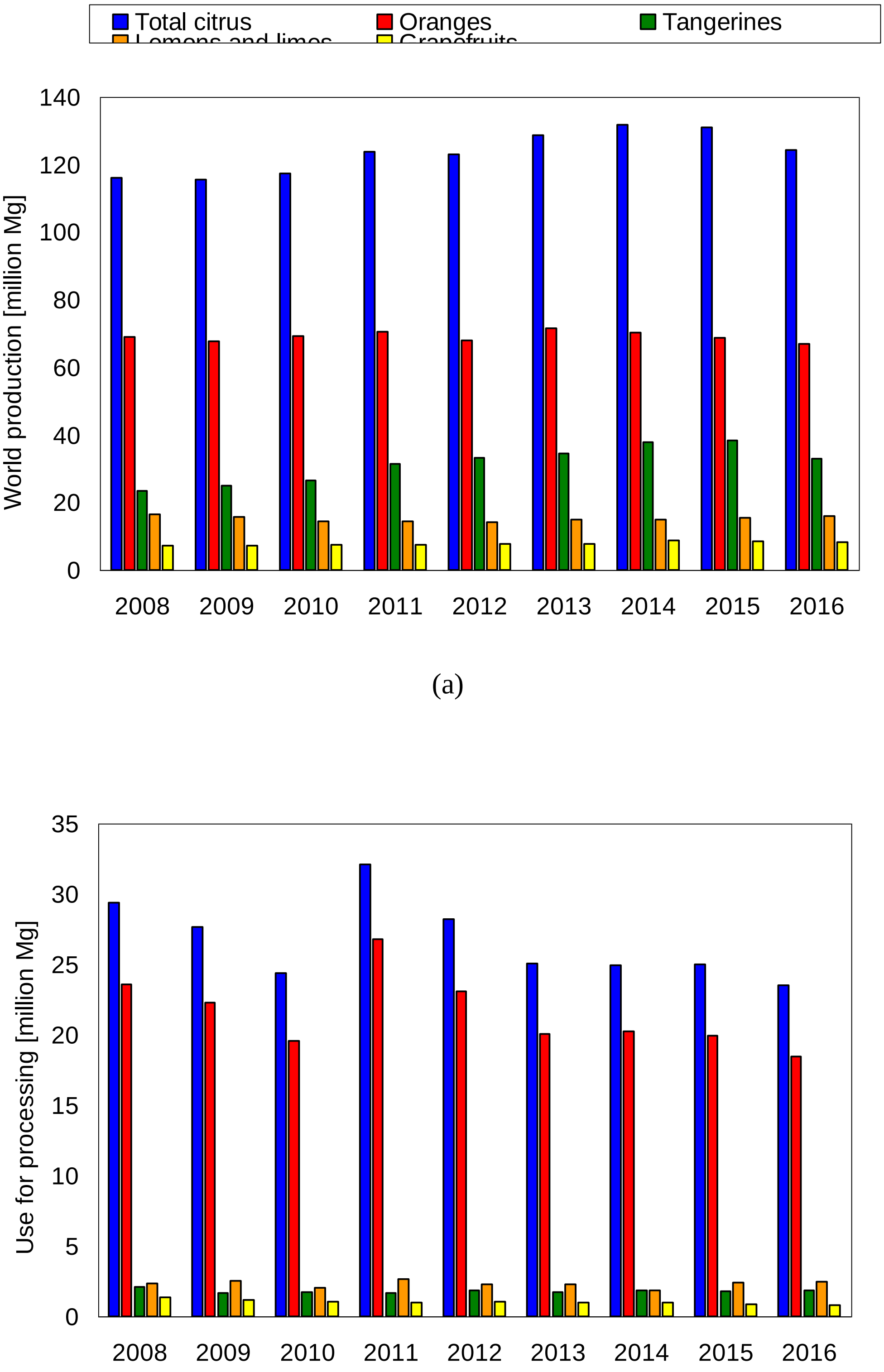
Table 8. Radical scavenging activity and total phenol and flavonoid~~s~~ contents in peels and tissues of 13 most commonly used citrus spp. (Ghasemi et al., 2009).

Citrus species	Phenols content*	Flavonoids content **	DPPH* *** IC_{50}***
C. sinensis var. Washington Navel			
- peel	160.3	23.2	1.1
- tissues	232.5	1.2	2.8
C. reticulate var. Ponkan			
- peel	172.1	5.2	0.6
- tissues	197.2	0.6	2.2
C. unshiu var. Mahalli			
- peel	170.5	31.1	1.9
- tissues	66.5	6.4	3.9
C. unshiu var. Sugiyama			
- peel	195.5	19.8	1.3
- tissues	140.9	2.2	3.6
C. sinensis var. Sungin			
- peel	153.8	2.1	1.7
- tissues	136.9	4.3	3.7
C. unshiu var Ishikawa			
- peel	148.8	4.8	1.8
- tissues	144.9	5.3	3.8
C. limon			
- peel	131.0	16.2	1.4

- tissues	102.2	2.0	3.4
C. reticulate var. Clementine			
- peel	161.7	5.7	1.7
- tissues	396.8	17.1	3.2
C. paradisi			
- peel	222.2	23.2	2.1
- tissues	112.1	0.3	3.7
C. aurantium			
- peel	223.2	7.7	1.9
- tissues	122.0	3.3	3.9
C. sinensis var. Valencia			
- peel	132.9	7.2	2.1
- tissues	124.0	3.1	3.8
C. aurantinum var. Khosheii			
- peel	164.7	7.9	1.8
- tissues	90.3	3.5	3.5
C. reticulate var. Page			
- peel	104.2	0.3	2.9
- tissues	226.2	6.8	3.7

Notes: * mg gallic acid equivalent/g of extract powder; ** mg quercetin equivalent/g of extract powder; ***mg/ ml (IC_{50} values denote the concentration of sample, which is required to scavenge 50% of DPPH free radicals).****DPPH 2,2-diphenyl-1-picrylhydrazyl (used in tests to estimate antioxidant capacities of fresh fruits and vegetables for clinical studies (Brand-Williams et al., 1995; Gil et al., 2002; Thaipong et al., 2006).

FIGURES



(a)

(b)

Figure 1a and 1b. Produced and processed citrus fruits in the World

(source: FAOSTAT 2017).

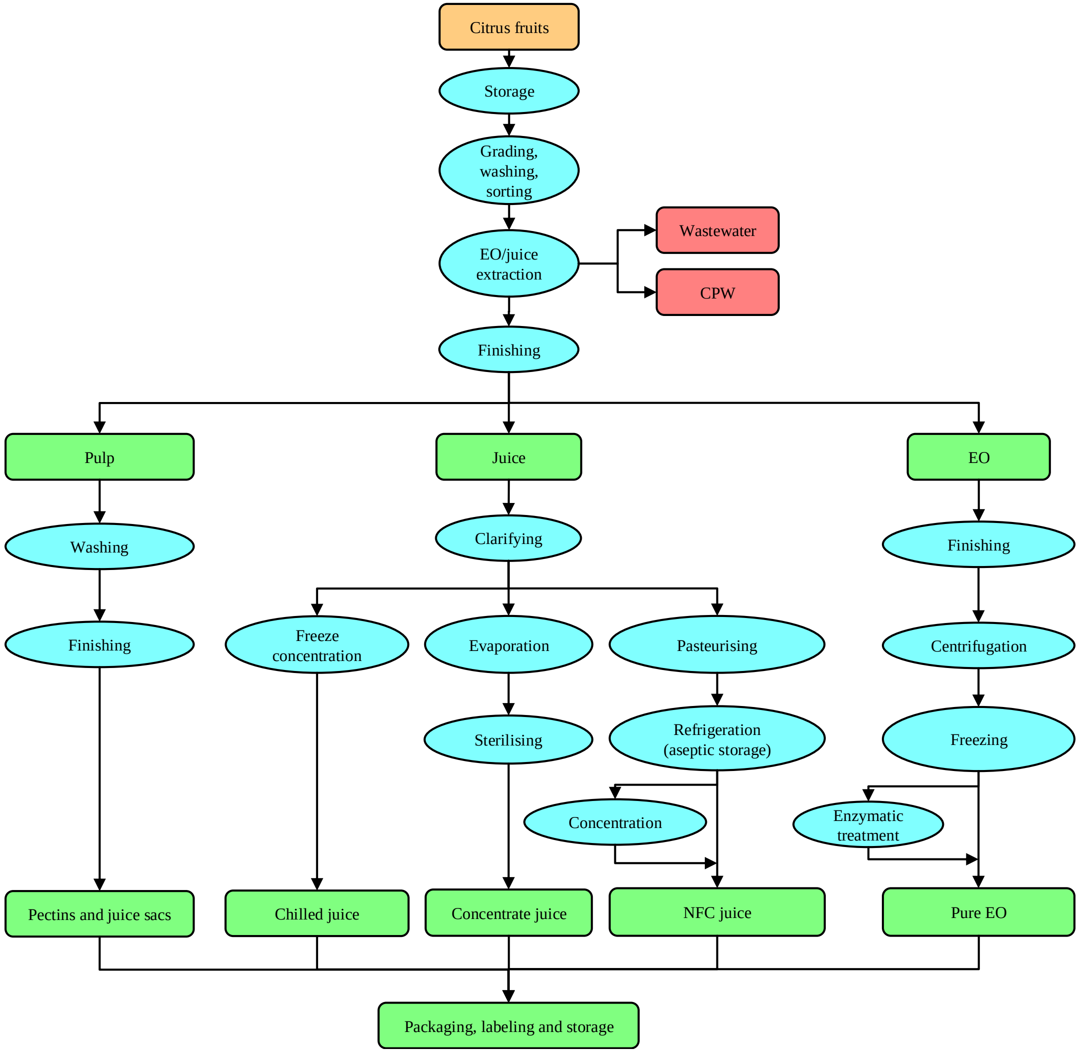
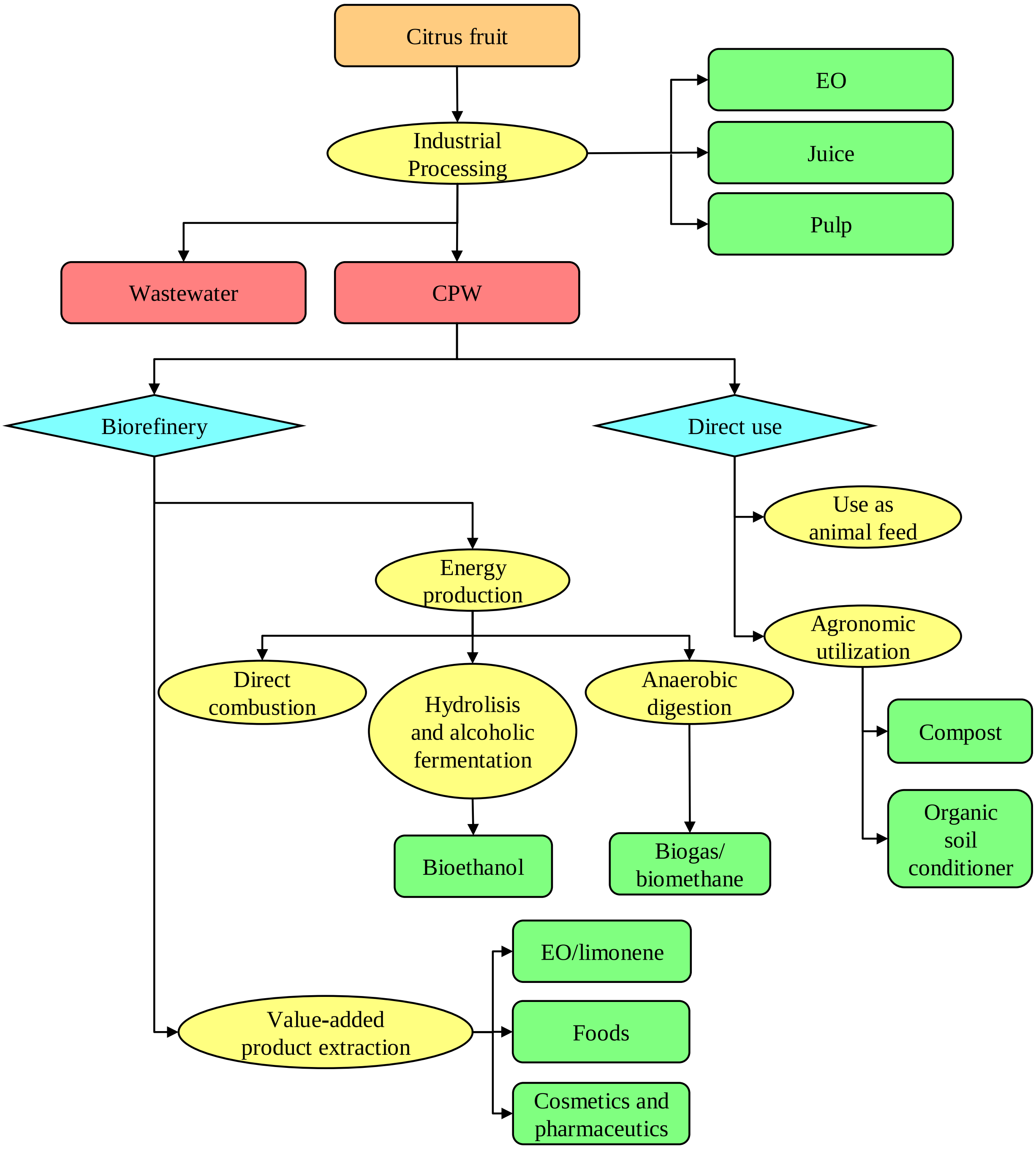


Figure 2. Scheme of the citrus processing chain.



2062

2063 Figure 3. Scheme of CPW processing chain.

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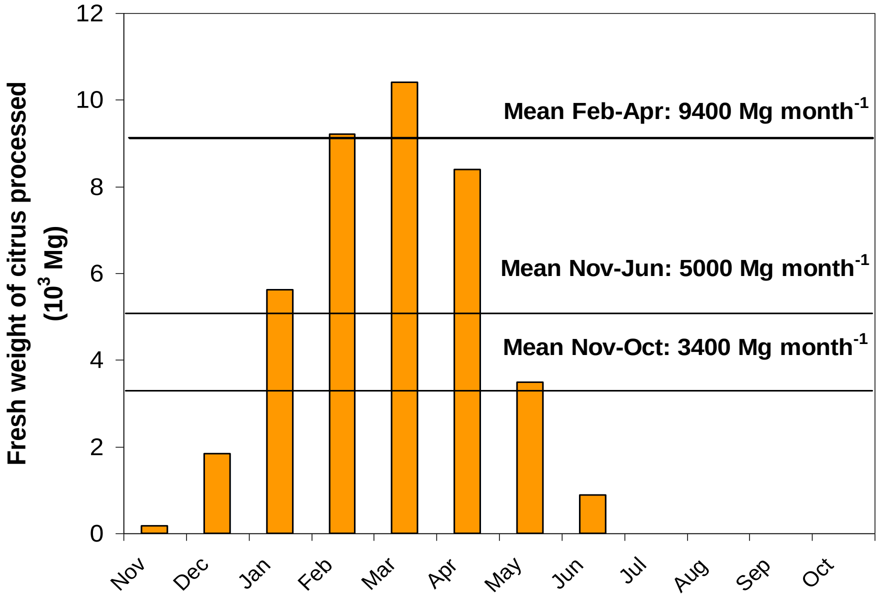

Figure 4. Typical monthly distribution of citrus production in a 40,000 Mg year^{-1} citrus processing factory (source: Tamburino et al., 2007).

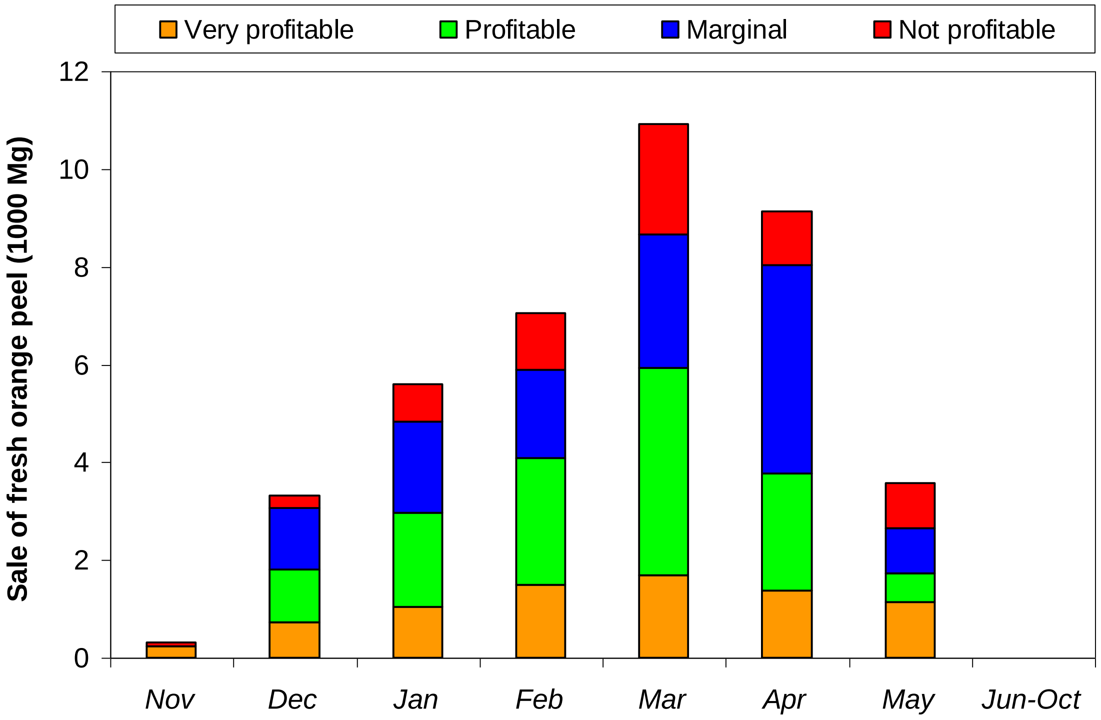

Figure 5. Wet orange peel sales (split into profit classes) to cattle breeders for a 40,000 Mg year^{-1} citrus processing factory operating in Southern Italy.