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A step closer to circular bioeconomy for citrus peel waste: a review of yields and technologies for sustainable management of essential oils

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Abstract

This study presents a critical overview of reported essential oil (EO) extractions from citrus peel wastes (CPW), including harmonized data on the various citrus species and cultivars. Harmonization is vital to enable sustainable management practices. The review only includes eco-efficient extraction techniques. In total, the review contains 66 quantified examples using i) mechanical cold press ii) thermal extraction with water or steam media iii) thermal microwave-assisted extraction iv) other innovative methods (such as ultrasound). The technologies were assessed for their potential use in cascading production to achieve economies of scope, particularly considering the use of extraction residues for subsequent fermentation to produce various products from energy carriers to enzymes. Two techniques were found insufficient for direct use in fermentation. Cold press extracts an inadequate amount of EO (average yield 2.85% DW) to ensure suitable fermentation, while solvent extraction contaminates the residues for its subsequent use. Extractions using water media, such as hydrodistillation and microwave-assisted hydrodistillation (average EO yield 2.87% DW), are feasible for the liquid-based fermentation processes, such as submerged fermentation. Steam extraction is feasible for any type of fermentation. Our review highlighted solvent-free microwave extraction (average EO yield 5.29% DW) as the most effective method, which provides a high yield in a short extraction time. We also uncovered and discussed several inconsistencies in existing yields and energy consumption published data.

Keywords: essential oil, limonene, food waste, circular economy, green chemistry

1. Introduction

Citrus fruits, with a production of over 100 million tonnes per year, represent the largest fruit crop production in the world (FAO, 2016; USDA, 2020, 2018), with the major parts produced in Asia (44%), Europe (20%), and South America (18%) (Mahato et al., 2019). A large part of the citrus fruits is used in the food processing industry, mainly juice production. Approximately 50–60% of the fruit mass remains after processing, such as peels, seeds, and membrane residue. Annually, the citrus waste created by food processing industries is estimated to be over 54 million tonnes worldwide (Mahato et al., 2019), mainly composed of inedible citrus peel waste (CPW).

Currently, citrus peels represent a challenge for the waste industry from an environmental perspective (Martín et al., 2018; Siles López et al., 2010; Zema et al., 2018a). The peels are either landfilled, incinerated, composted or in some regions partly used as animal feed and pectin production (Martín *et al.*, 2018). There are several factors that limit the use of CPW for composting: a very low nitrogen content preventing fast decomposition (Mahato et al., 2019), the detriment of soil microorganisms due to antimicrobial properties, and potential groundwater pollution due to percolation (Zema et al., 2018a). Even though the use as animal feed is coherent with top priorities in the updated food waste hierarchy (Teigiserova et al., 2020), low pH of 3.4, anti-nutritional properties (Martín et al., 2018; Ani et al., 2015), and potential costs for transportation (Zema et al., 2018a) prevents widespread use of CPW in animal feed. From a circular bioeconomy perspective, the next best option is to use CPW for material recycling to extract high-value compounds (Teigiserova et al., 2020), leading to more profitable valorization (Zema et al., 2018a).

However, the presence of limonene, a strong antimicrobial compound in the essential oil (EO), hinders not only CPW use as animal feed but is also undesirable for any eventual microbial transformation (Ruiz and Flotats, 2014), including the bioenergy production (Zema et al.,

2018a). Its removal is necessary before biological treatment, as demonstrated by (Calabrò et al., 2018). Limonene is a cyclic monoterpene ($C_{10}H_{16}$) that makes up around 90% of citrus essential oils content. It can be used for a variety of applications in the food, pharmaceutical, and medical industry (Oberoi et al., 2011), from green solvent (Mahato et al., 2019), natural insecticide (Oberoi et al., 2011), to a chemo-preventive agent with anti-cancer properties (Oberoi et al., 2011). Eco-compatible, economically viable, and optimized management options are needed for CPW (Zema et al., 2018a) and can be enhanced by the extraction of limonene to ensure cascade utilization. Such cascade utilization of inedible waste streams from the citrus industry requires sustainable biorefineries involving green chemistry principles ensuring that the technology used in the extraction is environmentally sound and economically feasible (Anastas and Eghbali, 2010). The main aim of green chemistry is to reduce waste and environmental burden (including toxic materials) across all stages of the chemical life-cycle (Anastas and Eghbali, 2010). To further decrease waste and extract more high-value products, we consider cascading production, i.e., the use of residues from EO extraction. CPW contains significant amounts of sugars and low content of lignin and is thus a suitable substrate for fermentation processes (Oberoi et al., 2010). These are widely applied for various products from bioenergy (Wikandari et al., 2015), to acid, and enzymes (Teigiserova et al., 2019). The generic conversion route and considered design of CPW treatment are represented in Figure 1.

Although EO extraction represents a feasible valorization of CPW, literature-based data analysis encounters the difficulty of (i) scale dependency of results, (ii) data accuracies, (iii) the wide range of units and amounts of yields for similar process and scale, (iv) incomplete or unclear cumulative reporting of energy consumption.

To bridge this gap, the objectives of this study are as follows:

- To harmonize the existing experimental data in order to provide a comprehensive and prospective overview of quantified examples of limonene production from CPW using environmentally-friendly technologies.
- To assess the feasibility of EO extracting technologies for cascading production using fermentation in subsequent processes.

In this way, we supply key inventory data for ex-ante LCA and techno-economic assessment supporting the development of regenerative management based on strong sustainability principles (Teigiserova et al., 2019) for the citrus industry.

Abbreviations

CPW citrus peel waste

DW dry weight

EO essential oil

FW fresh weight

OP orange peels

TRL technology readiness level

2. Methods

2.1 Literature review methodology

A comprehensive literature search restricted to quantified studies for limonene extraction was performed. The keywords "citrus", "waste", "value-added", "biorefinery", "food waste", "chemical", and limonene* were used in the Google Scholar search engine and limited to the English language. The keywords were used in combination with the Boolean operator "AND" and the multi-character wildcard "*" search for limonene as it can have multiple variations, such as *d*-limonene. There was no period limit for chosen articles, however, most relevant research included is published after 2005. The abstracts and result sections were screened, and the literature without quantitative data and those including hazardous materials like hexane were excluded. Additional literature sources, applying green chemistry principles, were added through the snowballing technique, i.e., by adding the literature from the article's reference section. Overall, 18 sources were identified for a detailed review process.

Supporting Information, Table SI.1, includes more details on the extraction methods reported in this review, including data on temperature, pressure, duration, and energy. The recalculation of yields is also included. The structure of data allows easy manipulation and selection of feedstock and green methods. Table SI.2 includes data excluded from this review that reported removal efficiency rather than actual yields but include verified EO extraction methods.

2.2 Selection and harmonization procedure for extraction technologies

In order to select technologies according to the green chemistry and harmonize their results, a step-wise approach was chosen, shown in Figure 2. First, we build on general green chemistry principles (Anastas and Eghbali, 2010; Poliakoff et al., 2002), which seek to reduce hazards and design a safer process across all chemical life cycle stages, employing rules for waste prevention, energy, and reaction efficiency. Following these principles, we excluded

technologies using toxic ingredients, such as hexane, a solvent used for EO extraction (Choi et al., 2015; Wikandari et al., 2015). Hexane is restricted under international regulations such as REACH (EC 1907/2006) or IPPC (96/61/EC) (Ozturk et al., 2019). Besides following the rule "to reduce or eliminate the use and generation of hazardous substances" (Mulvihill et al., 2011), we further assessed the elimination of waste by evaluating the use of residues from EO extraction for subsequent fermentation processes. The chosen technologies are aligned with previous findings on green extraction methods (Putnik et al., 2017; Sharma et al., 2017; González-Rivera et al., 2016).

Secondly, the composition of citrus peels was reported as a different citrus cultivar and varieties from the same citrus fruit, which can have different EO yields and different EO compositions (including limonene content). Therefore, not only the type of fruit but also the cultivar and varieties represent crucial information. Additionally, geographical aspects such as soil quality, nutrient availability, temperature, climate, rainfall also influence the EO content and the phytochemical composition. However, these aspects were excluded from data reporting in this study due to a lack of information.

Thirdly, the units of the reported yields were assessed. The authors report EO extraction in two ways, either as an extraction efficiency and as an extraction yield. Extraction efficiency refers to how much (in %) of the limonene or EO have been removed by applied technology. For example, the steam distillation method efficiency was 70% limonene removal (Martín et al., 2018). More details on removal efficiencies can be found in Supporting Information Table SI.2. Such reporting of results cannot be used to know how much of the product we can extract. Without knowing the initial and final concentration of limonene (or EO), the information is insufficient to calculate the actual yields (de la Torre et al., 2019; Martín et al., 2018; Boluda-Aguilar et al., 2010). The EO extraction yields are reported in several ways A) per fresh biomass (i) weight per fresh weight substrate in %, (ii) volume of extract per fresh weight

substrate), (iii) per whole fruit (for cold pressing), B) per dry biomass C) weight per weight of solvent used (in case of supercritical CO₂ extraction). The comparison between high yield reported per dry versus per fresh basis should not be made, or should at least be highlighted to make the reader aware of such discrepancies. This is evident in the study by Ciriminna et al. (2017), where the yields based on dry weight can be five times higher than those reported per fresh weight. We harmonized these results using the moisture content of peels reported by authors. When the dry matter content of the peels was not directly mentioned, 20% DW was used, representing the typical average value as reported in Boluda-Aguilar and López-Gómez (2013), Chen et al. (2016), and Pourbafrani et al. (2010). The yields reported per whole fruit were adjusted to represent peel fraction. Additionally, the data that included the volume of EO has been recalculated using density reported previously (Kamal et al., 2011). More details can be found in Supporting Information, Table SI.1.

Lastly, we also included data on the scale of the process (small laboratory, small pilots, and industrial-scale) and data on energy use when reported.

2.3 Extraction methods

The analysis of 18 sources included 66 examples that can be categorized according to extraction methods into four categories a) mechanical - cold press; b) thermal with water or steam media (hydrodistillation, steam distillation, steam explosion); c) microwave-assisted thermal extraction, d) and other innovative methods: such as supercritical CO₂, bio-solvent extraction, and ultrasound extraction.

Cold press is one of the oldest oil extraction methods (Karaman et al., 2015), where the oils are released by applying mechanical pressure via tapered screw press (Ferhat et al., 2007), using needles to lacerate the oil glands in the peels (Mahato et al., 2019). The resulting oil fraction is a watery emulsion (Mahato et al., 2019), which is then centrifuged to recover the citrus EO

(Ferhat et al., 2007). Without any heat application, EO retains most of the volatile compounds and waxes, which are important for their aromatic properties (Rassem et al., 2016; Sawamura, 2010).

Among the reviewed literature, several technologies applied steam or water media as the primary extraction method, namely hydrodistillation, steam distillation, steam explosion, and instantaneous controlled pressure drop. They share a similarity in the physicochemical principle of applying simultaneous internal and external heat and mass transfer to the peels (Berka-Zougali et al., 2012; Mahato et al., 2019). In hydrodistillation, a long contact of water and biomass can contaminate EO with waste products from hydrolysis (Berka-Zougali et al., 2012) and with biopolymers solid residues, such as polyphenols or insoluble cellulosic matter (González-Rivera et al., 2016). Applying steam to the CPW releases the essential oil droplets (captured in the steam) that are separated after vapor is condensed (Sahraoui et al., 2011). Novel methods try to shorten the treatment time while increasing the EO yield by applying pressure, such as steam explosion (Negro et al., 2016) and instantaneous controlled pressure drop (or D.I.C) (Rezzoug and Louka, 2009). D.I.C is a patented method used for drying-texturation in food items (Rezzoug and Louka, 2009). After applying a vacuum (at 50mbar), the pressure is increased, and steam is applied, and then the mixture is quickly decompressed (Rezzoug and Louka, 2009).

Microwave-assisted extractions are relatively new methods, mostly done on the laboratory scale with a few small-scale commercial applications (Milestone reactor; Bustamante et al., 2016) and pilot-scale reactors (Milestone 75 L pilot plant, Filly et al., 2014). There are several types of EO extracting microwaves using (i) water, (ii) steam, and (iii) *in-situ* water, all performing with reduced extraction time compared to conventional methods. Applying water and steam is similar to previously described methods, but the improved process performance is a key advantage (Bustamante et al., 2016; Ciriminna et al., 2014). It can also be combined

with ultrasound technology, where the ultrasonic probe is applied simultaneously with a coaxial microwave antenna (González-Rivera et al., 2016).

Finally, microwave energy can be applied to CPW without using any solvent or media. Besides using the term Solvent-free microwave extraction (SFME), the authors in the reviewed literature use several other terms for this technique:

- "Microwave Hydrodiffusion and Gravity (MHG)" (Bousbia et al., 2009; Boukroufa et al., 2015), when gravity is used for condensation of the essential oil
- "Microwave dry distillation" (Ferhat et al., 2016)
- "solventless MW-assisted extraction approach (SMWAE)" (González-Rivera et al., 2016)
- "Microwave-accelerated distillation (MAD)" (Ferhat et al., 2007).

The agreement on the terminology could further advance the research efforts and push the scale-up of this technology further. Therefore, we refer to all of them as SFME, henceforward. All of these techniques use *in-situ* water of the plant material, which is heated and evaporates (Chemat et al., 2015), releasing EO during the break-down of the cell wall due to internal pressure (Negro et al., 2016). Solvent-free technologies are further aligned with the green chemistry principle as they avoid the use of auxiliary substances (e.g., solvents, separation agents, and so forth) (Poliakoff et al., 2002) and thus have improved reaction mass efficiency (mass of final product divided to the mass of reactants ratio) (Mulvihill et al., 2011).

Further methods include solid-liquid solvent extraction using bio-solvents or supercritical fluid and ultrasound method. Solvent extraction is a simple method but can lead to the loss of most volatile compounds and therefore change the quality of EO (Berka-Zougali et al., 2012). The green solvent included in this study follows Environmental, Health, and Safety (EHS) parameters (Ozturk et al., 2019), while CO₂ takes advantage of supercritical fluid being the

intermediate between liquid and gas for their density and viscosity (Mira et al., 1999). Lastly, ultrasound Clevenger Extraction employs an ultrasonic probe without using any solvent or water, where frequency allows EO liberation (Pingret et al., 2014).

3 Results

3.1 Citrus peel composition

Citrus peels are composed of an inner white layer called albedo and a colorful outside skin called flavedo. The essential oils are mainly contained in the flavedo part and are either absent or present in minimal amounts in the albedo (Ferhat et al., 2007). The thickness of the peels influences the moisture content of the peel and the EO yields, as albedo's sponge-like quality can soak up the oils. A high CPW moisture content implies that more energy is needed for the extraction of EO. Certain cultivars and varieties of orange have one of the lowest moisture content in peels (Pera orange 66% - Lima orange 70%), while Sweet Lime peels can have up to 79% (Barros et al., 2012). Therefore, knowing the variety and cultivar is crucial information when comparing the yields. Three authors reported yields for several varieties of citrus; however, we chose to report one variety per main citrus group, i.e., one per lemon, lime, orange, and grapefruit. The common cultivars reported are Eureka (*Citrus limon* L.), Villa Franca (*Citrus limon* L.), Marsh Seedless (*Citrus paradisi* L.), Tarocco (*Citrus sinensis* L.), Valencia late (*Citrus sinensis* L.), Washington Navel (*Citrus sinensis* L.), Tangelo Seminole (*Citrus paradisi* Macf.) (Ferhat et al., 2016; Bousbia et al., 2009), while Bousbia et al. (2009) additionally reported on lime (*Citrus aurantifolia* (Chrism.) Swing) and Ferhat et al. (2016) report on Rhobs-el-arsa (*Citrus medica* L.), sweet orange Sorbonne (*Citrus aurantium*), and sour orange Bouquetier de Nice (*Citrus paradisi*). Bustamante et al. (2016) present data on orange Navel Navelate, Midnight, and Valencia Late cultivars; Verna variety of lemons; Persian variety of limes; Star Ruby grapefruits; and Satsumas Nihowase.

Out of the fruit's total solids, peel represents ca. 21 % for lime, 25-30% for tangerine, 29-32% for lemon, 34-48 % for grapefruit, 40-46% for pomelo, and up to 42-52% for oranges (Mahato et al., 2019). The ratio of albedo to flavedo depends on the variety of the specific citrus. Valencia and Tarocco oranges are known to have a very thin peel, which can provide higher EO yields, while Bouquetier de Nice and Marsh Seedless oranges have a wider peel with a large flavedo part (Ferhat et al., 2016). The thin peel can provide four times higher yields of EO using the same technologies for extraction, such as the case of Valencia orange versus Marsh Seedless using microwave extraction, hydrodistillation, and cold-press (Ferhat et al., 2016).

The main component of the essential oil extracted from the citrus peel is monoterpene limonene. Its content can also vary based on the species of citrus and the technology used. For orange peels, the final limonene content in extracted EO is usually around 94% to 96% (González-Rivera et al., 2016; Bustamante et al., 2016; Ferhat et al., 2016). This range results from a variety of extraction methods, including microwave extraction (Ruiz and Flotats, 2014), hydrodistillation, cold press (Ferhat et al., 2016), microwave steam diffusion (Farhat et al., 2011), microwave steam distillation and steam distillation (Sahraoui et al., 2011). Other reported limonene content in EO extracted from citrus fruits is 59-78% for lemons, 88% for clementine, and 92% for grapefruit (Ruiz and Flotats, 2014). Therefore, we include reporting of EO even if the data specifying limonene content were lacking. Additionally, EO also contains other monoterpenes, such as α -Pinene, oxygenated monoterpenes, sesquiterpene, and other oxygenated compounds (Sahraoui et al., 2011).

3.2 Harmonized data on essential oil extraction and limonene from citrus peels

3.2.1 Cold pressing

Even though the cold press is applied on the industrial scale (Mahato et al., 2019; Ferhat et al., 2007), data on cold-press extraction specifying the yields are available mostly for the lab-scale

as presented in Table 1. Further, as citrus EO (not limonene) is often the final product of industrial production, limonene content is not reported. Previously, Baaliouamer et al. (1992) reported yields as high as 0.31% of EO (assumed fresh weight basis) from Tangor hybrid variety, but most yields were found to be between 0.03 % and 0.17% for oranges and clementines. The lab-scale cold press uses whole fruits (Bousbia et al., 2009; Ferhat et al., 2007) or the flavedo part of the peels in hand-press (Ferhat et al., 2016; Mitiku et al., 2000). Generally, the cold press has the lowest yield for EO extraction among the known technologies but provides a cheaper option compared to conventional methods like hydrodistillation and steam distillation (Karaman et al., 2015), as the technology is simple and the direct cold press equipment requires almost no heat in case of pelletized peels. The yields are highly dependent upon the press technology used. For example, a simple tapering screw press of Valencia oranges can provide yields around 0.14% of orange EO per tonne of fresh oranges, while most of the EO (around 67% of the initial content) remains in the residues, mainly in the spongy albedo part of the peel (NIIR Board, 2008). On the other hand, more modern screw presses (such as FMC extractor, Pipkin Peel Oil Press-peel of fruit) can yield up to 0.25% per tonne of fresh fruit (NIIR Board, 2008). These cold presses can be integrated directly into the orange juice production factories. For example, the FMC Whole Fruit Extractor (Food Machinery Corporation) separates juice and the oil fraction simultaneously (NIIR Board, 2008). The FMC extractor's efficiency is higher for both juice (about 10% higher than other extractors) and EO for most citrus fruits, especially for oranges (NIIR Board, 2008).

These differences in yield are evident from Table 1, ranging from 0.25 to 7.5 % on a DW basis. The industrial-scale reaches 2-6 times higher yields for all experiments, except the one reported by Ferhat et al. (2016). Cold-press generally uses whole fruit for extraction, but the lab-scale experiment showed that using the flavedo part of the peel resulted in higher EO yield. Fruit

type also influences limonene content, as it has a higher content in oranges (around 95%), while lime and lemon fruit contain considerably lower amounts (around 70%).

Cold press extraction uses fresh oranges, minimizing pretreatment technology (such as drying or solvent use). Because the residues are not contaminated with chemicals from the pretreatment, they are usable for subsequent recovery or processing for other fractions and compounds (Karaman et al., 2015). Techniques such as steam distillation and hydrodistillation can be further applied to extract leftover EO from the residues (NIIR Board, 2008).

3.2.2 Thermal extraction with water or steam media

A typical pretreatment for these methods is crushing or milling of the peels into particles size of 7 mm or smaller (de la Torre et al., 2019; Martín et al., 2018; González-Rivera et al. 2016; Boluda-Aguilar and López-Gómez, 2012), cutting to size around 3 centimeters (Ruiz et al., 2016) or separating the flavedo part (Ferhat et al., 2016; Ferhat et al., 2007). Dilute sulfuric acid can be used as a catalyst during the steam explosion of citrus peels at a laboratory-scale (John et al., 2017) and at a pilot-scale (Pourbafrani et al., 2010). Even though the pretreatment technique is an important step for industrial applications, it is often excluded from reporting in the lab-scale experiments (Boukroufa et al., 2015; Farhat et al., 2011; Sahraoui et al., 2011; Wilkins et al., 2007).

Table 2 represents the overview of EO and limonene extracted by these technologies. As with the cold press, lemon and lime provide a lower amount of limonene in the EO, but the EO yields are relatively high for *Villa Franca* lemons. The EO yield fluctuates between 1.7 to 9.5 % on a DW basis. HD resulted in the highest EO amount, with the highest EO and limonene content in the peel of *Valencia late* oranges. The yield from SD exhibited the least fluctuations. While DIC and SE are promising technologies, the limited data showed lower limonene yield.

Among the four methods, hydrodistillation has a high energy consumption due to the amount of water that needs to be heated and volatile compounds that need to be evaporated (Berka-Zougali et al., 2012). Despite this, hydro- (Filly et al., 2014) and steam distillation (Bustamante et al., 2016; NIIR Board, 2008) are the two most evolved and applied methods for the extraction of EO from CPW at the laboratory and industrial scale. The steam explosion has not yet been automatized (Negro et al., 2016) and would be economically feasible only on a large-scale (Ruiz et al., 2016). This is due to pressurized equipment representing higher initial investment and energy use, which at the industrial-scale can be partially balanced by energy recovery and utilization.

3.2.3 Microwave-assisted extraction

SFME has similar yields as the conventional steam distillation with a considerably shorter extraction duration (Boukroufa et al., 2015, Farhat et al., 2011, Sahraoui et al., 2011). The time of extraction ranges from 5 minutes (González-Rivera et al., 2016) to 30 minutes (Ferhat et al., 2016) except for one example involving 90 minutes at a very low energy setup (employing only 150W) (Chen et al., 2016), making SFME very energy-efficient technology. Another advantage is the direct extraction of EO without the post-treatment steps, which are necessary for conventional extraction (Ferhat et al., 2007). All experiments found are summarized in Table 3. It is important to consider that while high power applied can result in a very short time of extraction, it can degrade volatile compounds and the plant material (Filly et al., 2014). Similarly, Boukroufa et al. (2015) found that low powers result in low EO recovery, while high powers can destroy the citrus peel matter.

Li et al. (2012) highlight that microwave-assisted extraction can also have the same advantages (less energy and shorter time) when scaled-up. Sahraoui et al. (2011) include a potential scaling setup, where microwave coaxial antenna could be added to large-scale reactors feasible for the batch of 10kg, 20kg, or 100 kg of the fresh OP. SFME exists on a commercial pilot-scale, such

as ETHOS X and MAC-75 reactors (Milestone, 2020), and can provide high returns on capital investment and low maintenance costs (Filly et al., 2014).

Pretreatment for microwave-assisted extraction includes grinding and milling to small particle sizes (de la Torre et al., 2019; Bustamante et al., 2016; González-Rivera et al., 2016); cutting of peels for immediate use (Chen et al., 2016); and separation of flavedo part (Ferhat et al., 2016; Ferhat et al., 2007). It should be noted that several authors do not mention any prior treatment of the peels (Boukroufa et al., 2015; Sahraoui et al., 2011; Farhat et al., 2011; Bousbia et al., 2009).

Microwave methods displayed a high range for EO yields from 0.4 to 10.5 % on a DW basis. Generally, SFME provides the highest yields and follows a similar trend with high limonene content for oranges and lower for lemon and lime. The use of MAHD led to unusually low limonene content in EO for both citrus fruits tested (oranges and lemons). Employing steam and ultrasound showed potential as both EO and limonene are in high ranges of content.

3.2.4 Solvent and ultrasound extraction

Three other green methods for EO extraction were reviewed, namely bio-solvent extraction, supercritical CO₂ extraction, and ultrasound extraction. Ozturk et al. (2019) vacuum dried and powdered peels to 1-millimeter particle size and investigated nine bio-solvents, which significantly outperformed conventional hexane: ethyl lactate, isopropyl alcohol, polyethylene glycol 300, isopropyl acetate, dimethyl carbonate, methyl ethyl ketone, 2-methyl-tetrahydrofuran and ethyl acetate, with the most efficient for limonene extraction found to be Cyclopentyl methyl ether. All solvents produced from biomass reflect Environmental, Health, and Safety parameters and properties for green solvents. There is also a possibility to use the supercritical fluid as the solvent, such as in supercritical carbon dioxide extraction (SC-CO₂) (Mira et al., 1999). This technique has the potential to reach yields up to 13 times greater than

conventional cold press (Mahato et al., 2019), removing 100% of limonene (Mira et al., 1999) (Table 4). However, it is impossible to compare the efficiency of this technology to others as yield is given per amount of CO₂ used.

As the variety of the orange used for Ultrasound Clevenger Extraction is unknown (Pingret et al., 2014), it is impossible to know if the lower limonene content in EO was due to technology itself or related to the cultivar (Table 4), but it is unusually low for orange peel, while EO amount is quite high. Even though this method provides a faster extraction process, more examples are needed to validate this technology and its relevance to be considered for scale-up and its potential for industrial limonene extraction.

4. Discussion

4.1 Economies of scope: technologies enabling subsequent fermentation for cascading production according to the green chemistry principles

Once limonene has been removed and recovered for the market, the leftover residues can be treated further. Even though the end-of-life treatment of residues from EO extraction can be plentiful, we aim to provide clarification for its applicability for fermentation processes. To further enhance waste management opportunities, the residues can be implemented in cascading production, creating economies of scope. The limonene-free (or limonene-low) peels represents a suitable feedstock for further cascade utilization applying fermentation processes, which are also aligned with green chemistry principles (Dahiya et al., 2018; Mitchell et al., 2006) and provide a large variety of bio-based chemicals and materials (Teigiserova et al., 2019; Lizardi-Jiménez and Hernández-Martínez, 2017). Fermentation processes are industrially applied (Mitchell et al., 2006) and capable of using both liquid and solid inputs (López et al., 2010; Mitchell et al., 2006) with on-going research unfolding novel designs such as innovative improvement of solid-state fermentation (Pourbafrani et al., 2010; Mitchell et al.,

2006). Nonetheless, it is crucial to extract the maximum yield of limonene in order to use residues for any treatment with microorganisms. The inhibitory effect depends on fermentation type, microorganism, and other reaction specific criteria. Inhibitory limonene content can be as low as 0.01% w/v is for fermentation with *S. cerevisiae* (Pourbafrani et al., 2010), 0.05% to 0.15% v/v for *Saccharomyces cerevisiae* and *Klyuveromyces marxianus* (Wilkins et al., 2007a), and 0.05% v/v for *Zymomonas mobilis* (Wilkins, 2009). Additionally, limonene inhibition can also arise due short adaptation period of the microbial population, and CPW must be loaded in a way to keep the daily rates below the inhibition limits, with further influences explained in Zema et al. (2018b). Limonene removal can also enhance previously explored valorization, such as biogas production via anaerobic digestion (Calabrò et al., 2019; Lotito et al., 2018; Pourbafrani et al., 2010). In fact, even if the extraction of limonene is a high-cost procedure, it is a key step for cascade utilization with fermentation (Calabrò et al., 2018).

Among the technologies investigated in section 3.2 and compared in Figure 3, the efficiency of limonene removal for cold-press is insufficient (see Table 1), and leftover limonene could hamper microbial growth. However, there are differences in yield when using lab-scale equipment (1.45 % on DW basis) versus industrial and optimized machines (4.25% on DW basis). In the case of solvent extraction, there is a necessity to eliminate or separate the employed solvent from CPW residues after EO extraction, as the solvent can be detrimental for bacterial growth, for example, in anaerobic digestion (Calabrò et al., 2020; Ruiz and Flotats, 2014) and citric acid fermentation (Torrado et al., 2011). Further, there is a necessity to dry the CPW to fine particles before solvent extraction, which increases the energy intensity and costs (Ozturk et al., 2019).

On the other hand, as given in Figure 3, steam and water are feasible media for limonene extractions prior to fermentation processes, which enables the use of liquid residues for microbial growth. Their efficiency and specificity have been previously discussed in 3.4 and

3.5. Steam distillation of OP was found to be a suitable first step treatment to produce biogas, reaching considerably higher biodegradability than other agro-industrial waste (Martín et al., 2018). But it also decreases the alkalinity (1950 to 445 mg CaCO₃/L) (Martín et al., 2018), which may require some additional steps for subsequent processing. Steam explosion was found as a feasible pretreatment for the thermophilic anaerobic co-digestion of citrus waste with the organic fraction of municipal solid waste (Ruiz et al., 2016). The highlight of this technology is the possibility to recycle water (John et al., 2017). However, this method provides incomplete disruption of the cell wall matrix and loss of the xylan fraction (John et al., 2017). Hydrodistillation poses a risk of thermal degradation of thermolabile molecules and loss of sugars during the boiling (Bustamante et al., 2016; Negro et al., 2017). These technologies face the same issues when combined with microwave energy.

Further, using *in-situ* water for the EO extraction provides "dry" residues feasible for the number of subsequent processes, such as Solid State Fermentation. These technologies are ultrasound extraction (Pingret et al., 2014) and solvent-free microwave extractions (Bustamante et al., 2016; Chen et al., 2016). Another advantage of these methods is the simple pretreatment of CPW consisting mainly of washing and cutting.

However, there is a natural uncertainty associated with literature-based investigation and review as the evaluated technologies are at different TRL and (environmental) technology performance (Figure 3). Promising technologies for both TRL 3-4 and TRL 5-6 need scale-up procedures, cradle-to-grave approach, sensitivity analysis, what-if analysis, and one factor analysis, while 3-4 also requires further harmonization of the costs (Thomassen et al., 2019). TRL identification is crucial to identify research needs. For example, while all technologies within TRL 3-6 need data on scale-up, SFME has already been employed for small-scale commercial applications (Milestone, 2020). The next step is to provide experimental data for limonene extraction from CPW using the pilot scale, such as those in Filly et al. (2014). The

microwave and radiofrequency heat inductions are technically sophisticated and technologically advanced methods, and they are still subject to economic and efficiency evaluation at large industrial scales. Their success and future application at a large-scale also depend on their future technological development and intensification (Meredith, 1998). On the other hand, caution should be taken when comparing to TRL 9, which are often downscaled to lab size but do not provide the same efficiency as their industrial version (hydrodistillation and cold press) (Ferhat et al., 2016).

For example, the data included in this review are lab-scale for all technologies apart from cold-press, which has the average yield at lab-scale 1.45 % on a DW basis, while at industrial-scale, the average yield is 4.25 % on a DM basis. Similar differences can be found when comparing the energy intensity of the process where industrial cold-press is much more optimized and less energy-intensive than lab-scale ones (Quinsac et al., 2016), included as such in Figure 3. General trends reported by authors are high energy intensity for hydrodistillation due to length of the process and energy required to heat the water (Ferhat et al., 2016; Sharma et al., 2017), steam extraction also requires higher energy inputs (Farhat et al., 2011; Sahraoui et al., 2011), and microwave is reported to be the least energy-intensive process (Bousbia et al., 2009; Bustamante et al., 2016) together with solvent extraction (Sharma et al., 2017). This energy trend is confirmed by comparative measured performance in several experiments (Bousbia et al., 2009; Bustamante et al., 2016; Ferhat et al., 2007). All quantitative data is included in SI Table SI.2.

4.2 A crucial step: transparent and harmonized methodology

Even though data reporting includes uncertainties tied to technology (such as random errors, TRL variation, different equipment used) and natural variability (such as phytochemical variations due to geographical aspects), some data reporting improvements can be achieved. Firstly, reporting the yield per unit of mass enables comparison across different extraction and

citrus types. As stressed out in section 2.2, removal efficiency simply stating the percentage of limonene removed, without providing information on the initial concentration, is not sufficient, as it cannot be compared to other extraction methods. Similarly, reporting of limonene extracted per amount of solvent or per volume limits the option of comparison to other extractions.

Secondly, the data on cultivar and variety of citrus should always be included as such information are important for the feedstock value tied to limonene/EO yield. For example, some natural variation can be observed in *Valencia Late* oranges, which showed the highest yield for EO and limonene throughout all experiments, while lemon and lime fruit generally contain less limonene in the EO.

Thirdly, including energy consumption details, is crucial to compare the environmental and economic performance of individual extraction methods. It is also essential for scale-up from low to high TRL and performing life cycle assessment (Beccali et al., 2010; Righi et al., 2018), crucial to picking the most sustainable CPW management pathways. Only one experiment included energy consumption data expressed per mass (kWh/kg) (Farhat et al., 2011).

5 Conclusion

This study presents an overview of 66 quantified EO extraction examples from CPW, reported mostly for the lab-scale experiments. The review includes comparable harmonized data, as these are often missing (e.g., energy and cultivar/variety), are unclear and inconsistent. It is crucial to include technology performance data in the original research papers of emerging technologies, such as yields expressed per mass, to enable a comparison of different technologies at different scales and TRL. Among the reviewed technologies, the most industrially established is cold-press and hydrodistillation. CP provides lower EO yields at the lab-scale (0.25-4% on DW basis) but high yield at the industrial-scale (1.5%-7.5% on DW

basis), while HD provides higher yields (4%-9.5% on DW basis) but is a relatively long and energy-intensive process. Microwave energy is a novel design to shorten the extraction time (20-60 minutes), hence energy consumption, and to provide higher yields at the same time (1-10.5% EO yields on DW basis). Microwave-assisted extraction is one of the least energy-intensive EO extraction technologies, with economic performance opportunities at the industrial-scale being crucial for its future development and market entry.

With the exception of cold-press and solvent extraction, reviewed techniques are suitable for cascading production employing subsequent fermentation processes using residues from EO extraction. Residual fractions with high water content such as those coming from hydrodistillation are feasible for fermentation using liquid fraction (ex. submerged fermentation), while fermentation requiring solid substrates (solid state fermentation) is feasible after employing solvent-free microwave extraction.

Harmonized methodology, quantifications, and the identification of optimal cascading biorefinery designs are the key research elements needed for the full valorization of CPW and towards the low fossil economy pathways.

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Declaration of interest

None

References

- Anastas, P., Eghbali, N., 2010. Green chemistry: Principles and practice. *Chem. Soc. Rev.* 39, 301–312. <https://doi.org/10.1039/b918763b>
- Ani, A., Iloh, E., Akinsola, O., 2015. Dietary Effect of Processed Orange Peels on Growth Performance of Broiler Finisher Birds. *Br. J. Appl. Sci. Technol.* 9, 576–583. <https://doi.org/10.9734/bjast/2015/6052>
- Baaliouamer, A., Meklati, B.Y., Fraisse, D., Scharff, C., 1992. The Chemical Composition of Some Cold-pressed Citrus Oils Produced in Algeria. *J. Essent. Oil Res.* 4, 251–258. <https://doi.org/10.1080/10412905.1992.9698058>
- Barros, H.R. de M., Ferreira, T.A.P. de C., Genovese, M.I., 2012. Antioxidant capacity and mineral content of pulp and peel from commercial cultivars of citrus from Brazil. *Food Chem.* 134, 1892–1898. <https://doi.org/10.1016/J.FOODCHEM.2012.03.090>
- Beccali, M., Cellura, M., Iudicello, M., Mistretta, M., 2010. Life cycle assessment of Italian citrus-based products. Sensitivity analysis and improvement scenarios. *J. Environ. Manage.* 91, 1415–1428. <https://doi.org/10.1016/j.jenvman.2010.02.028>
- Berka-Zougali, B., Ferhat, M.-A., Hassani, A., Chemat, F., Allaf, K.S., 2012. Comparative Study of Essential Oils Extracted from Algerian *Myrtus communis* L. Leaves Using Microwaves and Hydrodistillation. *Int. J. Mol. Sci.* 13, 4673–4695. <https://doi.org/10.3390/ijms13044673>
- Boluda-Aguilar, M., García-Vidal, L., González-Castañeda, F. del P., López-Gómez, A., 2010. Mandarin peel wastes pretreatment with steam explosion for bioethanol production. *Bioresour. Technol.* 101, 3506–3513.

<https://doi.org/10.1016/J.BIORTECH.2009.12.063>

Boluda-Aguilar, M., López-Gómez, A., 2013. Production of bioethanol by fermentation of lemon (*Citrus limon* L.) peel wastes pretreated with steam explosion. *Ind. Crops Prod.* 41, 188–197. <https://doi.org/10.1016/J.INDCROP.2012.04.031>

Boukroufa, M., Boutekedjiret, C., Petigny, L., Rakotomanomana, N., Chemat, F., 2015. Bio-refinery of orange peels waste: A new concept based on integrated green and solvent free extraction processes using ultrasound and microwave techniques to obtain essential oil, polyphenols and pectin. *Ultrason. Sonochem.* <https://doi.org/10.1016/j.ultsonch.2014.11.015>

Bousbia, N., Vian, M.A., Ferhat, M.A., Meklati, B.Y., Chemat, F., 2009. A new process for extraction of essential oil from Citrus peels: Microwave hydrodiffusion and gravity. *J. Food Eng.* 90, 409–413. <https://doi.org/10.1016/J.JFOODENG.2008.06.034>

Bustamante, J., van Stempvoort, S., García-Gallarreta, M., Houghton, J.A., Briers, H.K., Budarin, V.L., Matharu, A.S., Clark, J.H., 2016. Microwave assisted hydro-distillation of essential oils from wet citrus peel waste. *J. Clean. Prod.* 137, 598–605. <https://doi.org/10.1016/J.JCLEPRO.2016.07.108>

Calabrò, P., Fazzino, F., Folino, A., Paone, E., Komilis, D., 2019. Semi-Continuous Anaerobic Digestion of Orange Peel Waste: Effect of Activated Carbon Addition and Alkaline Pretreatment on the Process. *Sustainability* 11, 3386. <https://doi.org/10.3390/su11123386>

Calabrò, P.S., Fazzino, F., Sidari, R., Zema, D.A., 2020. Optimization of orange peel waste ensiling for sustainable anaerobic digestion. *Renew. Energy* 154, 849–862. <https://doi.org/10.1016/j.renene.2020.03.047>

- Calabrò, P.S., Paone, E., Komilis, D., 2018. Strategies for the sustainable management of orange peel waste through anaerobic digestion. *J. Environ. Manage.* 212, 462–468. <https://doi.org/10.1016/j.jenvman.2018.02.039>
- Chemat, F., Fabiano-Tixier, A.S., Vian, M.A., Allaf, T., Vorobiev, E., 2015. Solvent-free extraction of food and natural products. *TrAC Trends Anal. Chem.* 71, 157–168. <https://doi.org/10.1016/J.TRAC.2015.02.021>
- Chen, Q., Hu, Z., Yao, F.Y.-D., Liang, H., 2016. Study of two-stage microwave extraction of essential oil and pectin from pomelo peels. *LWT - Food Sci. Technol.* 66, 538–545. <https://doi.org/10.1016/J.LWT.2015.11.019>
- Choi, I.S., Lee, Y.G., Khanal, S.K., Park, B.J., Bae, H.-J., 2015. A low-energy, cost-effective approach to fruit and citrus peel waste processing for bioethanol production. *Appl. Energy* 140, 65–74. <https://doi.org/10.1016/J.APENERGY.2014.11.070>
- Ciriminna, R., Fidalgo, A., Delisi, R., Carnaroglio, D., Grillo, G., Cravotto, G., Tamburino, A., Ilharco, L.M., Pagliaro, M., 2017. High-Quality Essential Oils Extracted by an Eco-Friendly Process from Different Citrus Fruits and Fruit Regions. *ACS Sustain. Chem. Eng.* 5, 5578–5587. <https://doi.org/10.1021/acssuschemeng.7b01046>
- Ciriminna, R., Lomeli-Rodriguez, M., Demma Carà, P., Lopez-Sanchez, J.A., Pagliaro, M., 2014. Limonene: A versatile chemical of the bioeconomy. *Chem. Commun.* 50, 15288–15296. <https://doi.org/10.1039/c4cc06147k>
- Dahiya, S., Kumar, A.N., Shanthi Sravan, J., Chatterjee, S., Sarkar, O., Mohan, S.V., 2018. Food waste biorefinery: Sustainable strategy for circular bioeconomy. *Bioresour. Technol.* 248, 2–12. <https://doi.org/10.1016/J.BIORTECH.2017.07.176>
- de la Torre, I., Martin-Dominguez, V., Acedos, M.G., Esteban, J., Santos, V.E., Ladero, M.,

2019. Utilisation/upgrading of orange peel waste from a biological biorefinery perspective. *Appl. Microbiol. Biotechnol.* 103, 5975–5991.
<https://doi.org/10.1007/s00253-019-09929-2>
- FAO, 2016. Citrus Fruit Fresh and Processed. Statistical Bulletin., Trade and Markets Division, Trade and Markets Division. Rome.
- Farhat, A., Fabiano-Tixier, A.-S., Maataoui, M. El, Maingonnat, J.-F., Romdhane, M., Chemat, F., 2011. Microwave steam diffusion for extraction of essential oil from orange peel: Kinetic data, extract's global yield and mechanism. *Food Chem.* 125, 255–261.
<https://doi.org/10.1016/J.FOODCHEM.2010.07.110>
- Ferhat, M.A., Boukhatem, M.N., Hazzit, M., Meklati, B.Y., Chemat, F., 2016. Cold Pressing Hydrodistillation and Microwave Dry Distillation of Citrus Essential Oil from Algeria: A Comparative Study. *Electron. J. Biol.* S1, 30–41.
- Ferhat, M.A., Meklati, B.Y., Chemat, F., 2007. Comparison of different isolation methods of essential oil from Citrus fruits: cold pressing, hydrodistillation and microwave 'dry' distillation. *Flavour Fragr. J.* 22, 494–504. <https://doi.org/10.1002/ffj.1829>
- Filly, A., Fernandez, X., Minuti, M., Visinoni, F., Cravotto, G., Chemat, F., 2014. Solvent-free microwave extraction of essential oil from aromatic herbs: From laboratory to pilot and industrial scale. *Food Chem.* 150, 193–198.
<https://doi.org/10.1016/J.FOODCHEM.2013.10.139>
- González-Rivera, J., Spepi, A., Ferrari, C., Duce, C., Longo, I., Falconieri, D., Piras, A., Tinè, M.R., 2016. Novel configurations for a citrus waste based biorefinery: from solventless to simultaneous ultrasound and microwave assisted extraction. *Green Chem.* 18, 6399–6696. <https://doi.org/10.1039/c6gc02200f>

- John, I., Muthukumar, K., Arunagiri, A., 2017. A review on the potential of citrus waste for D-Limonene, pectin, and bioethanol production. *Int. J. Green Energy* 14, 599–612.
<https://doi.org/10.1080/15435075.2017.1307753>
- Kamal, G.M., Anwar, F., Hussain, A.I., Sarri, N., Ashraf, M.Y., 2011. Yield and chemical composition of Citrus essential oils as affected by drying pretreatment of peels. *Int. Food Res. J.* 18, 1275–1282.
- Karaman, S., Karasu, S., Tornuk, F., Toker, O.S., Geçgel, Ü., Sagdic, O., Ozcan, N., Gül, O., 2015. Recovery potential of cold press byproducts obtained from the edible oil industry: Physicochemical, bioactive, and antimicrobial properties. *J. Agric. Food Chem.* 63, 2305–2313. <https://doi.org/10.1021/jf504390t>
- Li, Y., Radoiu, M., Fabiano-Tixier, A.-S., Chemat, F., 2012. *From Laboratory to Industry: Scale-Up, Quality, and Safety Consideration for Microwave-Assisted Extraction.* Springer, Boston, MA, pp. 207–229. https://doi.org/10.1007/978-1-4614-4830-3_8
- Lizardi-Jiménez, M.A., Hernández-Martínez, R., 2017. Solid state fermentation (SSF): diversity of applications to valorize waste and biomass. *3 Biotech* 7, 44.
<https://doi.org/10.1007/s13205-017-0692-y>
- Lotito, A.M., De Sanctis, M., Pastore, C., Di Iaconi, C., 2018. Biomethanization of citrus waste: Effect of waste characteristics and of storage on treatability and evaluation of limonene degradation. *J. Environ. Manage.* 215, 366–376.
<https://doi.org/10.1016/j.jenvman.2018.03.057>
- Mahato, N., Sinha, M., Sharma, K., Koteswararao, R., Cho, M.H., 2019. Modern Extraction and Purification Techniques for Obtaining High Purity Food-Grade Bioactive Compounds and Value-Added Co-Products from Citrus Wastes. *Foods* 8, 1–81.
<https://doi.org/10.3390/foods8110523>

- Martín, M.A., Fernández, R., Gutiérrez, M.C., Siles, J.A., 2018. Thermophilic anaerobic digestion of pre-treated orange peel: Modelling of methane production. *Process Saf. Environ. Prot.* 117, 245–253. <https://doi.org/10.1016/J.PSEP.2018.05.008>
- Meredith, R.J., 1998. *Engineers' handbook of industrial microwave heating*. Institution of Electrical Engineers.
- Milestone, 2020. *Innovative Laboratory Microwave Systems for sample preparation - Milestone [WWW Document]*. URL <https://www.milestonesrl.com/> (accessed 2.18.20).
- Mira, B., Blasco, M., Berna, A., Subirats, S., 1999. Supercritical CO₂ extraction of essential oil from orange peel. Effect of operation conditions on the extract composition. *J. Supercrit. Fluids* 14, 95–104. [https://doi.org/10.1016/S0896-8446\(98\)00111-9](https://doi.org/10.1016/S0896-8446(98)00111-9)
- Mitchell, D.A., Berovič, M., Krieger, N., 2006. Introduction to solid-state fermentation bioreactors, *Solid-State Fermentation Bioreactors: Fundamentals of Design and Operation*. https://doi.org/10.1007/3-540-31286-2_3
- Mitiku, S.B., Sawamura, M., Itoh, T., Ukeda, H., 2000. Volatile components of peel cold-pressed oils of two cultivars of sweet orange (*Citrus sinensis* (L.) Osbeck) from Ethiopia. *Flavour Fragr. J.* 15, 240–244. [https://doi.org/10.1002/1099-1026\(200007/08\)15:4<240::AID-FFJ902>3.0.CO;2-F](https://doi.org/10.1002/1099-1026(200007/08)15:4<240::AID-FFJ902>3.0.CO;2-F)
- Mulvihill, M.J., Beach, E.S., Zimmerman, J.B., Anastas, P.T., 2011. Green Chemistry and Green Engineering: A Framework for Sustainable Technology Development. *Annu. Rev. Environ. Resour.* 36, 271–293. <https://doi.org/10.1146/annurev-environ-032009-095500>
- Negro, V., Mancini, G., Ruggeri, B., Fino, D., 2016. Citrus waste as feedstock for bio-based products recovery: Review on limonene case study and energy valorization. *Bioresour.*

- Technol. 214, 806–815. <https://doi.org/10.1016/J.BIORTECH.2016.05.006>
- Negro, V., Ruggeri, B., Mancini, G., Fino, D., 2017. Recovery of D-limonene through moderate temperature extraction and pyrolytic products from orange peels. *J. Chem. Technol. Biotechnol.* 92, 1186–1191. <https://doi.org/10.1002/jctb.5107>
- NIIR Board, 2008. *The Complete Technology Book of Essential Oils (Aromatic Chemicals)* Reprint-2011. Asia Pacific Business Press.
- Oberoi, H.S., Vadlani, P.V., Madl, R.L., Saida, L., Abeykoon, J.P., 2010. Ethanol Production from Orange Peels: Two-Stage Hydrolysis and Fermentation Studies Using Optimized Parameters through Experimental Design. *J. Agric. Food Chem.* 58, 3422–3429. <https://doi.org/10.1021/jf903163t>
- Oberoi, H.S., Vadlani, P. V., Nanjundaswamy, A., Bansal, S., Singh, S., Kaur, S., Babbar, N., 2011. Enhanced ethanol production from Kinnow mandarin (*Citrus reticulata*) waste via a statistically optimized simultaneous saccharification and fermentation process. *Bioresour. Technol.* 102, 1593–1601. <https://doi.org/10.1016/J.BIORTECH.2010.08.111>
- Ozturk, B., Winterburn, J., Gonzalez-Miquel, M., 2019. Orange peel waste valorisation through limonene extraction using bio-based solvents. *Biochem. Eng. J.* 151, 107298. <https://doi.org/10.1016/J.BEJ.2019.107298>
- Pingret, D., Fabiano-Tixier, A.-S., Chemat, F., 2014. An Improved Ultrasound Clevenger for Extraction of Essential Oils. *Food Anal. Methods* 7, 9–12. <https://doi.org/10.1007/s12161-013-9581-0>
- Poliakoff, M., Fitzpatrick, J.M., Farren, T.R., Anastas, P.T., 2002. Green chemistry: science and politics of change. *Science* 297, 807–10. <https://doi.org/10.1126/science.297.5582.807>

- Pourbafrani, M., Forgács, G., Horváth, I.S., Niklasson, C., Taherzadeh, M.J., 2010. Production of biofuels, limonene and pectin from citrus wastes. *Bioresour. Technol.* 101, 4246–4250. <https://doi.org/10.1016/J.BIORTECH.2010.01.077>
- Putnik, P., Bursać Kovačević, D., Režek Jambrović, A., Barba, F., Cravotto, G., Binello, A., Lorenzo, J., Shpigelman, A., 2017. Innovative "Green" and Novel Strategies for the Extraction of Bioactive Added Value Compounds from Citrus Wastes—A Review. *Molecules* 22, 680. <https://doi.org/10.3390/molecules22050680>
- Quinsac, A., Carré, P., Fine, F., 2016. Combining pelletizing to cold pressing in the rapeseed crushing process improves energy balance and the meal and oil quality. *Eur. J. Lipid Sci. Technol.* 118, 1326–1335. <https://doi.org/10.1002/ejlt.201400495>
- Rassem, H.H.A., Nour, A.H., Yunus, R.M., 2016. Techniques For Extraction of Essential Oils From Plants: A Review. *Aust. J. Basic Appl. Sci.* 10, 117–127.
- Rezzoug, S.-A., Louka, N., 2009. Thermomechanical process intensification for oil extraction from orange peels. *Innov. Food Sci. Emerg. Technol.* 10, 530–536. <https://doi.org/10.1016/J.IFSET.2009.05.008>
- Righi, S., Baioli, F., Dal Pozzo, A., Tugnoli, A., 2018. Integrating Life Cycle Inventory and Process Design Material Consumption Data. *Energies* 11. <https://doi.org/10.3390/en11040970>
- Ruiz, B., de Benito, A., Rivera, J.D., Flotats, X., 2016. Assessment of different pretreatment methods for the removal of limonene in citrus waste and their effect on methane potential and methane production rate. *Waste Manag. Res.* 34, 1249–1257. <https://doi.org/10.1177/0734242X16661053>
- Ruiz, B., Flotats, X., 2014. Citrus essential oils and their influence on the anaerobic digestion

- process: An overview. *Waste Manag.* 34, 2063–2079.
<https://doi.org/10.1016/J.WASMAN.2014.06.026>
- Sahraoui, N., Vian, M.A., El Maataoui, M., Boutekedjiret, C., Chemat, F., 2011. Valorization of citrus by-products using Microwave Steam Distillation (MSD). *Innov. Food Sci. Emerg. Technol.* 12, 163–170. <https://doi.org/10.1016/J.IFSET.2011.02.002>
- Sawamura, M., 2010. Citrus Essential Oils: Flavor and Fragrance, Citrus Essential Oils: Flavor and Fragrance. <https://doi.org/10.1002/9780470613160>
- Sharma, K., Mahato, N., Cho, H., Rok Lee, Y., 2017. Converting citrus wastes into value-added products: economic and environmentally friendly approaches. *Nutrition* 34, 29–46.
<https://doi.org/10.1016/j.nut.2016.09.006>
- Siles López, Á.J., Li, Q., Thompson, I.P., 2010. Biorefinery of waste orange peel. *Crit. Rev. Biotechnol.* 30, 63–69. <https://doi.org/10.3109/07388550903425201>
- Teigiserova, D.A., Hamelin, L., Thomsen, M., 2020. Towards transparent valorization of food surplus, waste and loss: Clarifying definitions, food waste hierarchy, and role in the circular economy. *Sci. Total Environ.* 706, 136033.
<https://doi.org/10.1016/J.SCITOTENV.2019.136033>
- Teigiserova, D.A., Hamelin, L., Thomsen, M., 2019. Review of high-value food waste and food residues biorefineries with focus on unavoidable wastes from processing. *Resour. Conserv. Recycl.* 149, 413–426. <https://doi.org/10.1016/j.resconrec.2019.05.003>
- Thomassen, G., Van Dael, M., Van Passel, S., You, F., 2019. Green Chemistry TUTORIAL REVIEW How to assess the potential of emerging green technologies? Towards a prospective environmental and techno-economic assessment framework †. *Green Chem.*
<https://doi.org/10.1039/c9gc02223f>

- Torrado, A.M., Cortés, S., Manuel Salgado, J., Max, B., Rodríguez, N., Bibbins, B.P.,
Converti, A., Manuel Domínguez, J., 2011. Citric Acid production from orange peel
wastes by solid-state fermentation. *Braz. J. Microbiol.* 42, 394–409.
<https://doi.org/10.1590/S1517-83822011000100049>
- USDA, 2020. Citrus: World Markets and Trade [WWW Document]. URL
<https://www.fas.usda.gov/data/citrus-world-markets-and-trade> (accessed 11.14.20).
- USDA, 2018. Citrus Annual Expected Rebound in EU-28 Citrus Production may Reduce
Imports for MY 2018/19.
- Wikandari, R., Nguyen, H., Millati, R., Niklasson, C., Taherzadeh, M.J., 2015. Improvement
of Biogas Production from Orange Peel Waste by Leaching of Limonene. *Biomed Res.
Int.* 2015, 1–6. <https://doi.org/10.1155/2015/494182>
- Wilkins, M.R., 2009. Effect of orange peel oil on ethanol production by *Zymomonas mobilis*.
Biomass and Bioenergy 33, 538–541. <https://doi.org/10.1016/J.BIOMBIOE.2008.08.010>
- Wilkins, M.R., Suryawati, L., Maness, N.O., Chrz, D., 2007a. Ethanol production by
Saccharomyces cerevisiae and *Kluyveromyces marxianus* in the presence of orange-peel
oil. *World J. Microbiol. Biotechnol.* 23, 1161–1168. <https://doi.org/10.1007/s11274-007-9346-2>
- Wilkins, M.R., Widmer, W.W., Grohmann, K., 2007b. Simultaneous saccharification and
fermentation of citrus peel waste by *Saccharomyces cerevisiae* to produce ethanol.
Process Biochem. 42, 1614–1619. <https://doi.org/10.1016/J.PROCBIO.2007.09.006>
- Zema, D.A., Calabrò, P.S., Folino, A., Tamburino, V., Zappia, G., Zimbone, S.M., 2018a.
Valorisation of citrus processing waste: A review. *Waste Manag.*
<https://doi.org/10.1016/j.wasman.2018.09.024>

Zema, D.A., Fòlino, A., Zappia, G., Calabrò, P.S., Tamburino, V., Zimbone, S.M., 2018b.

Anaerobic digestion of orange peel in a semi-continuous pilot plant: An environmentally sound way of citrus waste management in agro-ecosystems. *Sci. Total Environ.* 630, 401–408. <https://doi.org/10.1016/j.scitotenv.2018.02.168>

Tables

Table 1 Yield data on EO and limonene from citrus peels via the cold press.

Biomass ¹	Details	Scale	Yield (% EO on FW basis) ²	Yield (% EO on DW basis) ³	Limonene (% in EO)	Reference
Orange whole fresh	Tarocco (<i>Citrus sinensis</i> L.) cultivar	Lab ≤1kg	0.30	1.50	94.94	Bousbia et al. (2009)
Lemon whole fresh	Villa Franca (<i>Citrus limon</i> L.) cultivar	Lab ≤1kg	0.20	1.00	70.92	Bousbia et al. (2009)
Lime whole fresh	<i>Citrus aurantifolia</i> (Chrism.) cultivar	Lab ≤1kg	0.20	1.00	68.81	Bousbia et al. (2009)
Grapefruit whole fresh	Marsh Seedless (<i>Citrus paradisi</i> L.) cultivar	Lab ≤1kg	0.20	1.00	94.54	Bousbia et al. (2009)
Lemon whole fresh	Eureka (<i>Citrus limon</i> (L.) Burm)	Lab ≤1kg	0.05	1.25	75.68	Ferhat et al. (2007)
Orange whole fresh	Valencia cultivar <i>Citrus sinensis</i> (L.) Osbeck.	Lab ≤1kg	0.16	4.00	95.00	Ferhat et al. (2016)
Lemon whole fresh	Villa Franca (<i>Citrus limon</i> (L.)) Burm) cultivar	Lab ≤1kg	0.03	0.75	73.75	Ferhat et al. (2016)
Orange whole fresh	Bouquetier de Nice (<i>Citrus paradisi</i>) cultivar	Lab ≤1kg	0.01	0.25	96.00	Ferhat et al. (2016)
Grapefruit whole fresh	Marsh Seedless (<i>Citrus deliciosa</i> Ten C. tangerina) cultivar	Lab ≤1kg	0.03	0.75	94.54	Ferhat et al. (2016)
Orange flavedo peel fresh	Valencia cultivar (<i>Citrus sinensis</i> (L.) Osbeck)	Lab ≤1kg ⁴	0.60	3.00	96.20	Mitiku et al. (2000)
Orange flavedo peel fresh	Hamlin (<i>Citrus sinensis</i> (L.) Osbeck) cultivar	Lab ≤1kg ⁴	0.30	1.50	96.57	Mitiku et al. (2000)
Grapefruit whole fresh	Citro-Mat extractor	Industrial	0.08	2.00	N/A	NIIR Board (2008)
Grapefruit whole fresh	FMC Whole Fruit Extractor	Industrial	0.06	1.50	N/A	NIIR Board (2008)
Lemon whole fresh	Citro-Mat extractor	Industrial	0.10 - 0.25	2.50-6.50	N/A	NIIR Board (2008)
Lemon whole fresh	Mission Dry Corporation Oil Recovery	Industrial	0.30	7.50	N/A	NIIR Board (2008)
Orange whole fresh	Citro-Mat extractor Valencia and Navel cultivar	Industrial	V: 0.30; N: 0.13	V: 7.50; N: 3.25	N/A	NIIR Board (2008)
Orange whole fresh	Mission Dry Corporation Oil Recovery. Valencia and Navel cultivar	Industrial	V: 0.23; N: 0.06	V: 5.75; N: 1.50	N/A	NIIR Board (2008)
Orange whole fresh	FMC Whole Fruit Extractor. Valencia orange cultivar	Industrial	0.25	6.25	N/A	NIIR Board (2008)
Orange whole fresh	The Citrus Oil Extractor of the Hyland-Stanford Corporation	Industrial	0.10	2.50	N/A	NIIR Board (2008)

¹Citrus fruit fraction used for EO extraction as reported by authors

² Yield per FW refers to amounts reported by the authors

³ yield per DW of peel is recalculated, details can be found in Table SI.1

⁴assumed scale

EO essential oil, FW fresh weight, DW dry weight

Table 2 The EO and limonene yield from thermal extraction with water media.

Biomass ¹	Cultivar/ Variety	Met hod	Scale	Yield (% EO on FW basis) ²	Yield (% EO on DW basis) ³	Limonene (% in EO)	Reference
Lemon peel thawed	<i>Citrus limon</i> L.	SE	Small pilot ≥1kg	6 L/tonne; 0.50% (limonene yield)	N/A	N/A	Boluda-Aguilar and López- Gómez (2013)
Orange peel fresh after juicing ⁵	<i>Citrus sinensis</i> L. Osbeck	SD	Lab ≤1kg	N/A	4.22 ⁴	N/A	Boukroufa et al. (2015)
Orange flavedo peel fresh ⁵	Tarocco (<i>Citrus sinensis</i> L.)	HD	Lab ≤1kg	1.30	6.50*	94.68	Bousbia et al. (2009)
Lemon flavedo peel fresh ⁵	Villa Franca (<i>Citrus limon</i> (L.) Burm)	HD	Lab ≤1kg	1.70	8.50*	71.22	Bousbia et al. (2009)
Lime flavedo peel fresh ⁵	<i>Citrus aurantifolia</i> (Chrism.)	HD	Lab ≤1kg	0.80	4.00*	63.44	Bousbia et al. (2009)
Grapefruit flavedo peel fresh ⁵	Marsh Seedless (<i>Citrus paradisi</i> L.)	HD	Lab ≤1kg	1.10	5.50*	94.21	Bousbia et al. (2009)
Orange peel fresh after juicing	Navel Navelate (<i>Citrus sinensis</i>)	HD	Lab ≤1kg	N/A	1.70	96.75	Bustamante et al. (2016)
Orange peel fresh after juicing	Valencia late (<i>Citrus sinensis</i> (L.) Osbeck)	SD	Lab ≤1kg	1.51	7.55*	95.00	Farhat et al. (2011)
Lemon flavedo peel fresh ⁵	Eureka (<i>Citrus limon</i> (L.) Burm)	HD	Lab ≤1kg	0.21	5.25*	72.90	Ferhat et al. (2007)
Orange flavedo peel fresh ⁵	Valencia late (<i>Citrus sinensis</i> (L.) Osbeck)	HD	Lab ≤1kg	0.38	9.50*	95.50	Ferhat et al. (2016)
Lemon flavedo peel fresh ⁵	Villa Franca (<i>Citrus limon</i> (L.) Burm)	HD	Lab ≤1kg	0.26	6.50*	75.78	Ferhat et al. (2016)
Orange flavedo peel fresh ⁵	Bouquetier de Nice (<i>Citrus paradisi</i>)	HD	Lab ≤1kg	0.11	2.75*	93.01	Ferhat et al. (2016)
Grapefruit flavedo peel fresh ⁵	Marsh Seedless (<i>Citrus deliciosa</i> Ten C. <i>tangerina</i>)	HD	Lab ≤1kg	0.11	2.75*	92.61	Ferhat et al. (2016)
Orange peel thawed	N/A	HD	Lab ≤1kg	1.55	7.75*	94.40	González- Rivera et al. (2016)
Orange peel hydrolyzed	N/A	SE	Small pilot ≥1kg	8.9L l/ton (limonene yield)	3.63 ⁴ (limonene yield)	N/A	Pourbafrani et al. (2010)
Orange peel dried	<i>Citrus sinensis</i> L.	DIC	Lab ≤1kg	N/A	2.06	94.40	Rezzoug and Louka (2009)
Orange peel fresh after juicing	Valencia late (<i>Citrus sinensis</i> (L.) Osbeck)	SD	Lab ≤1kg	N/A	5.45 ⁴	95.60	Sahraoui et al. (2011)

¹Citrus fruit fraction used for EO extraction as reported by authors

² Yield per FW refers to amounts reported by the authors

³ yield per DW as reported by authors or * recalculated with details found in Table SI.1

⁴assumed DW or FW

⁵ yield expressed by authors as g EO/g citrus fruit

EO essential oil, FW fresh weight, DW dry weight, HD hydrodistillation, SD steam-distillation, SE steam explosion, DIC Instantaneous controlled pressure drop, FW fresh weight, DW dry weight, EO essential oil

Table 3 The EO and limonene yields from microwave-assisted extractions.

Biomass ¹	Cultivar	Method	Scale	Yield (% EO on FW basis) ²	Yield (% EO on DW basis) ³	Limonene (% in EO)	Reference
Orange peel fresh after juicing	<i>Citrus sinensis</i> L. Osbeck	SFME	Lab ≤1kg	N/A	4.16 ⁴	N/A	Boukroufa et al. (2015)
Orange flavedo peel fresh ⁵	Tarocco (<i>Citrus sinensis</i> L.)	SFME	Lab ≤1kg	1.20	6.00*	95.19	Bousbia et al. (2009)
Orange flavedo peel fresh ⁵	Tarocco (<i>Citrus sinensis</i> L.)	SFME	Lab ≤1kg	1.20	6.00*	95.19	Bousbia et al. (2009)
Lemon flavedo peel fresh ⁵	Villa Franca (<i>Citrus limon</i> (L.) Burm)	SFME	Lab ≤1kg	1.60	8.00*	70.92	Bousbia et al. (2009)
Lime flavedo peel fresh ⁵	<i>Citrus aurantifolia</i> (Chrism.)	SFME	Lab ≤1kg	0.80	4.00*	60.56	Bousbia et al. (2009)
Grapefruit flavedo peel fresh ⁵	Marsh Seedless (<i>Citrus deliciosa</i> Ten <i>Citrus tangerina</i>).	SFME	Lab ≤1kg	1.00	5.00*	90.05	Bousbia et al. (2009)
Orange peel fresh after juicing	Navel Navelate (<i>Citrus sinensis</i>)	MAHD	Lab ≤1kg	N/A	1.80	97.38	Bustamante et al. (2016)
Lemon peel fresh after juicing	Verna (<i>Primofiore</i> variety)	MAHD	Lab ≤1kg	N/A	1.60	68.42	Bustamante et al. (2016)
Lime peel fresh after juicing	Persian (<i>Tahiti</i> variety)	MAHD	Lab ≤1kg	N/A	2.20	61.93	Bustamante et al. (2016)
Grapefruit peel fresh after juicing	Star Ruby	MAHD	Lab ≤1kg	N/A	2.40	89.2	Bustamante et al. (2016)
Pomelo peel fresh	N/A	SFME	Lab ≤1kg	0.25ml/100g	1.00*	86.53	Chen et al. (2016)
Orange flavedo peel fresh	N/A	MAHD	Lab ≤1kg	0.40	1.48	55.00	Ciriminna et al. (2017)
Orange peel fresh	N/A	MAHD	Lab ≤1kg	0.12	0.43	80.00	Ciriminna et al. (2017)
Orange peel fresh after juicing	N/A	MAHD	Lab ≤1kg	0.28	1.63	80.00	Ciriminna et al. (2017)
Lemon flavedo peel fresh	N/A	MAHD	Lab ≤1kg	0.26	1.34	30.00	Ciriminna et al. (2017)
Lemon peel fresh	N/A	MAHD	Lab ≤1kg	0.08	0.5	50.00	Ciriminna et al. (2017)
Lemon peel fresh after juicing	N/A	MAHD	Lab ≤1kg	0.12	0.8	65.00	Ciriminna et al. (2017)

Grapefruit peel fresh	N/A	MAHD	Lab ≤1kg	0.07	0.33	45.00	Ciriminna et al. (2017)
Orange peel fresh after juicing	Valencia late (<i>Citrus sinensis</i> (L.) Osbeck)	MSDf	Lab ≤1kg	1.54 ⁴	7.70*	94.88	Farhat et al. (2011)
Lemon flavedo peel fresh ⁵	Eureka (<i>Citrus limon</i> (L.) Burm)	SFME	Lab ≤1kg	0.24	6.00*	69.65	Ferhat et al. (2007)
Orange peel fresh ⁵	Valencia late (<i>Citrus sinensis</i> (L.) Osbeck)	SFME	Lab ≤1kg	0.42	10.50*	94.6	Ferhat et al. (2016)
Lemon peel fresh ⁵	Villa Franca (<i>Citrus limon</i> (L.) Burm)	SFME	Lab ≤1kg	0.29	7.25*	73.99	Ferhat et al. (2016)
Orange peel fresh ⁵	Bouquetier de Nice (<i>Citrus paradisi</i>)	SFME	Lab ≤1kg	0.10	2.50*	91.69	Ferhat et al. (2016)
Grapefruit peel fresh ⁵	Marsh Seedless (<i>Citrus deliciosa</i> Ten <i>C. tangerina</i>)	SFME	Lab ≤1kg	0.10	2.50*	91.63	Ferhat et al. (2016)
Orange peel thawed	N/A	MAHD	Lab ≤1kg	1.57	7.85*	94.70	González-Rivera et al. (2016)
Orange peel thawed	N/A	SFME	Lab ≤1kg	1.16	5.80*	95.00	González-Rivera et al. (2016)
Orange peel thawed	N/A	US-MWHD	Lab ≤1kg	1.53	7.65*	94.70	González-Rivera et al. (2016)
Orange peel fresh after juicing	Valencia late (<i>Citrus sinensis</i> (L.) Osbeck)	MSD	Lab ≤1kg	N/A	5.43 ⁴	96.20	Sahraoui et al. (2011)

¹Citrus fruit fraction used for EO extraction as reported by authors

² Yield per FW refers to amounts reported by the authors

³ yield per DW as reported by authors or * recalculated with details can be found in Table SI.1

⁴assumed DW or FW

⁵ yield expressed by authors as g EO/g citrus fruit

EO essential oil, FW fresh weight, DW dry weight, All methods without solvent are referred to as solvent-free microwave extraction SFMW, MAHD Microwave-assisted hydrodistillation, MSDf Microwave steam diffusion, MSD Microwave steam distillation, US-MWHD Simultaneous ultrasound coaxial MW-assisted hydrodistillation

Table 4 EO and limonene yields via solvent and ultrasound methods.

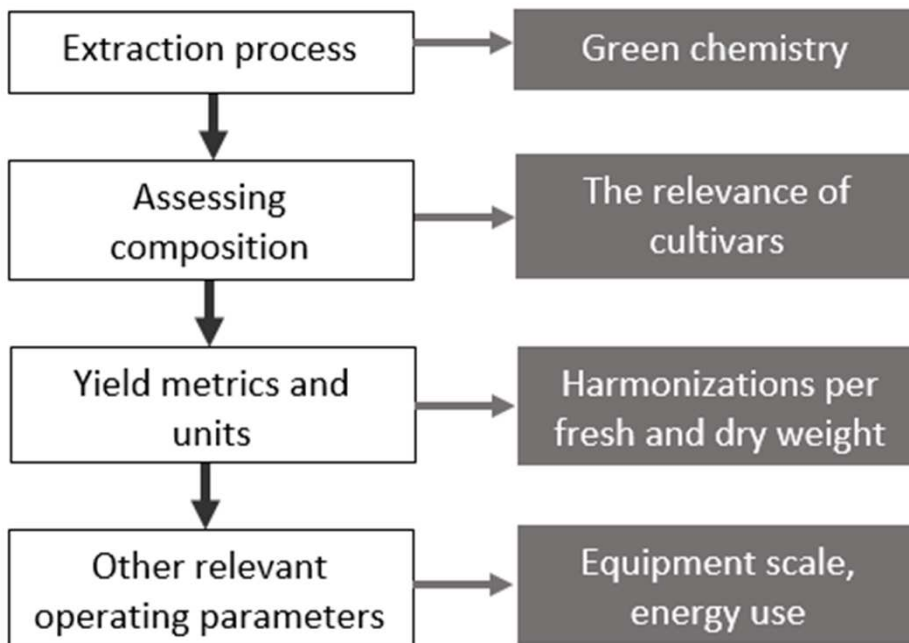
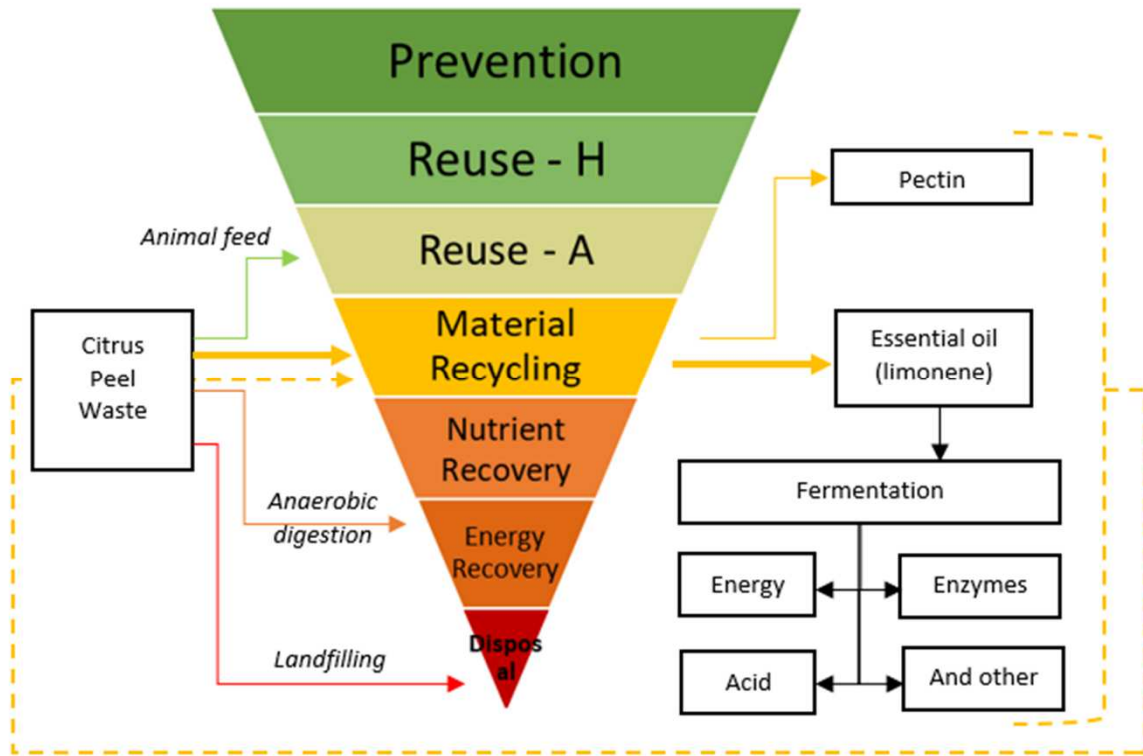
Biomass ¹	Cultivar	Method	Scale	Yield (% EO on FW basis) ²	Yield (% EO on DW basis) ²	Limonene (% in EO)	Reference
Orange peel fresh	Navelina <i>Citrus sinensis</i> (L.)	Supercritical CO ₂ extraction	Lab ≤1kg	2-10 mg/gCO ₂	N/A	99.50	Mira et al. (1999)
Orange peel dried	N/A	Bio-solvent extraction	Lab ≤1kg	N/A	1.78 (limonene yield)	N/A	Ozturk et al. (2019)
Orange peel fresh	N/A	Ultrasound Clevenger Extraction	Lab ≤1kg	N/A	7.00	71.20	Pingret et al. (2014)

¹Citrus fruit fraction used for EO extraction as reported by authors

² Yield amounts reported by the authors

EO essential oil, FW fresh weight, DW dry weight

Figures



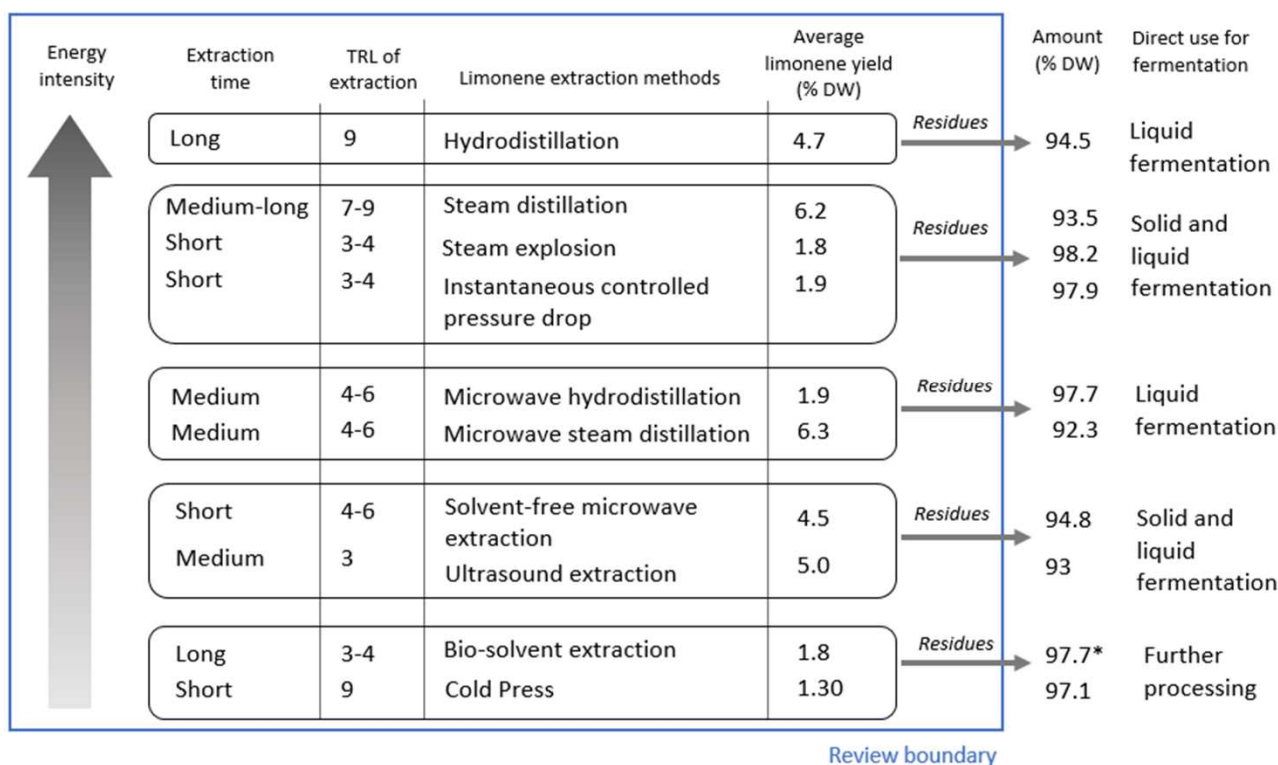


Figure 1 The global route of citrus peel waste valorization, according to the food waste hierarchy presented in Teigiserova et al. 2020. This review considers material recycling for essential oil extraction and its potential use for subsequent fermentation to further decrease waste amount, and increase the value.

Figure 2 Step-wise harmonization approach performed in this review.

Figure 3 Summary of the main technologies enabling subsequent fermentation for cascading production (right side of the figure) based on reviewed literature. The extraction time is related to the time and information reported by authors in the reviewed literature, and the TRL consider the technology for essential oil extraction, and not the technology itself. All yields are reported for lab-scale. The residual amount (in %) feasible for fermentation

illustrates potential quantities, as it doesn't consider losses, and it subtracts the amount of EO.

*assuming 80% limonene in EO