Chapter

Production of Pectin from Citrus Residues: Process Alternatives and Insights on Its Integration under the Biorefinery Concept

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Abstract

This chapter describes the pectin production process from citrus residues. It discusses the importance of essential oils removal before processing through steam distillation, hydrodistillation, or solvent extraction. Also, it presents different extraction methods (acid hydrolysis, microwave-assisted acid hydrolysis, and hydrodistillation) that have been employed and different solvents that can be used for its purification. Since all these processing parameters can affect the final pectin yield and quality, a discussion is made on which processing options and conditions could be used based on recently reported data. The best operational conditions based on the percentages of pectin recovery and their relationship with quality parameters, such as the galacturonic acid content and degree of esterification are presented. Finally, a discussion is made regarding the opportunities for its integration under the biorefinery concept that could help to enhance several economic and environmental aspects of the process.

Keywords: pectin, citrus residues, bioactive compounds, biorefinery, sustainability

1. Introduction

Nowadays, residues are wrongfully disposed of and underutilized, becoming an increasingly alarming problem for the environment and the population's well-being. One of the primary sources of waste is the food industry. It is estimated that about 1600 Mton of food residues are produced annually, and about 500 Mton are entirely derived from fruits [1]. The consumption of natural fruit juices has been increasing recently, mainly due to health concerns in the population. A shift toward a healthier and more natural lifestyle implies a reduction in the intake of soft drinks that could contain a high concentration of sugars, artificial colorants, and artificial sweeteners with possible adverse effects on the human body [2]. Orange juice holds most of the market share due to its vitamin content and general health benefits. As with other citrus fruits, the majority of the fruit is discarded during the juice-making process.

The residues include peels, seeds, and remnant pulp, which represent almost 50% of the total weight of the fruit [3].

Over the years, research has been made to develop ways to use organic waste as a source of chemical substances and energy. There are many studies regarding the obtention of multiple products from citrus peels [1, 4–6]. Some of these added-value products include pectin, essential oils, bioethanol, biogas, and polyphenolic compounds. These products can serve as feedstocks for other industrial processes or as final products by themselves, so the possibilities for selling them are very extensive.

Nonetheless, pectin has been one of the main chemical substances retrieved from citrus residues with organoleptic characteristics that depend highly on the processing steps and conditions used for its production. Moreover, due to the multiple value-added products obtained from citrus residues, it is appealing to investigate the possibility of integrating all these processes under the biorefinery concept, which encompasses a series of steps aimed to transform, refine, purify, or separate different kinds of biological assets into other products [7].

This chapter intends to compile relevant information regarding the production of pectin from citrus residues and thus, determine the most efficient methods that result in the best quality and yields of the final product. Using information collected in the last ten years and reported in relevant scientific databases (Scopus, Springer Link, Wiley, Taylor & Francis, and ACS), a description of the processing alternatives for pectin production was made. Additionally, the gathered information was used to propose the most convenient alternatives and process conditions for its obtention. Finally, the possibility of integrating pectin production into a whole citrus residues biorefinery was discussed, including novel valorization pathways that could increase the process's economic, environmental, and social sustainability.

2. Unit operations and process conditions for pectin extraction from citrus residues

In the last few years, studies on developing new routes for utilizing organic citrus residues have mainly focused on pectin production. Pectin is primarily found as a component of the cell wall of plants that gives them resistance and flexibility due to its content of galacturonic acid, partially esterified with methyl ester or acetyl groups [8]. In general, the process begins by collecting citrus residues. The raw material is then washed, dried, and grinded before bioactive compound extraction. During the extraction of bio-compounds, essential oils, polyphenols, and flavonoids are removed to improve pectin's quality. After this step, pectin is retrieved from biomass by breaking down the polymer and "dissolving it" into the liquid phase. The solid phase residue contains other structural carbohydrates that could be further valorized. The liquid, rich in galacturonic acid units, is then submitted to a separation step ("precipitation"), where it is washed with alcohols or organic solvents that cause pectin to agglomerate. These solvents also eliminate remnant bioactive compounds that can alter the final pectin's organoleptic properties. Finally, solvents are evaporated from the jellified pectin to obtain the product of interest. **Figure 1** shows a diagram representing each one of the processing steps to obtain pectin.

2.1 Preparation of the material

As seen in **Figure 1**, the process begins by washing the material to eliminate excess dirt. After that, citrus residues are prepared for further processing by drying,

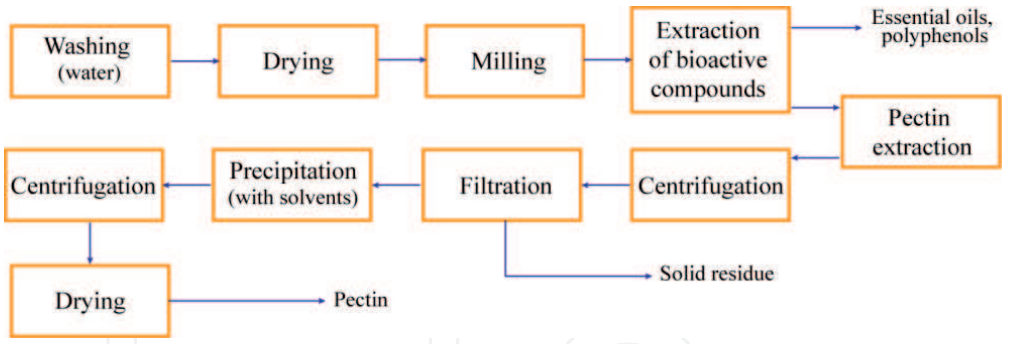

Figure 1.
Process block diagram representing the unit operations to produce pectin from orange residues.

which guarantees their storage for long periods. The material's drying process is usually carried out at temperatures around 40–60°C and drying times up to 2 days. However, the highest drying temperature reported is 95°C [9], which reduces the drying time but could cause the degradation of bioactive compounds. Also, it is desired to achieve low humidity (approximately 10%) as a way to extend the storage time of the raw material and to achieve a small particle size (< 1 mm) that generates a higher contact surface and a better performance during extraction [9].

2.2 Extraction of essential oils and bioactive compounds

It is important to remove certain bioactive compounds such as essential oils and flavonoids, besides some sugars interfering with the pectin's final quality. The purpose of removing these compounds is to improve pectin's esterification degree, galacturonic acid content and guarantee its physicochemical characteristics. At this stage, the principal compound of interest is the essential oil coming from the flavedo of the citrus peel. The essential oils from citrus fruits are conformed mostly by terpenes, which are organic substances responsible for the vegetal material's organoleptic properties. With terpenes removal, unpleasant flavors are avoided, which improves the quality of the final product [10].

Multiple methods such as vapor explosion, hydrodistillation, steam distillation, and in some cases solvent extraction can be implemented to perform essential oil extraction. The most common method used is steam distillation. In this method, the organic material is placed in a container where steam can pass and reach the sample uniformly. On the other hand, hydrodistillation works by placing the residue in direct contact with boiling water. The essential oils are retrieved once the water vapor rich in terpenes and terpenoids is condensed in both cases. Nonetheless, hydrodistillation can present agglomerations due to the direct contact of the submerged material with the liquid, which interferes with steam access to specific system zones. Another extraction method is Solid–Liquid Extraction, which can be done with various polar and non-polar solvents to retrieve the bioactive compounds selectively. However, SLE can also be assisted by heat, agitation, ultrasound, or microwaves, increasing the yields of the desired compounds.

In **Figures 2** and **3**, the yields of essential oils and the limonene content reported using different extraction methods for orange residues are shown in relationship with the pectin process. In **Figure 2**, the highest essential oil yields were obtained using Solid–Liquid Extraction with acetone (~2.2%) [1]. Nonetheless, the Solid–Liquid Extraction with acetone would require further separation of the polar and non-polar compounds due to the polarity of the solvent. For steam distillation, yields of 0.7% [11] and 0.84% [9] were obtained, which are slightly lower than those obtained by Hilali et al. with hydrodistillation and solar hydrodistillation ~1% [12]. Differences observed in yields for steam distillation could be attributed to the

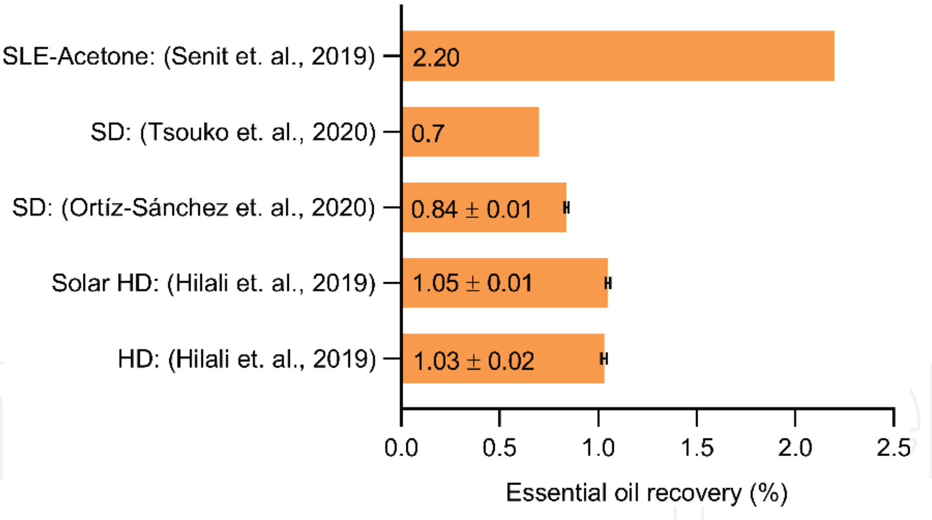

Figure 2.
Essential oil recovery.

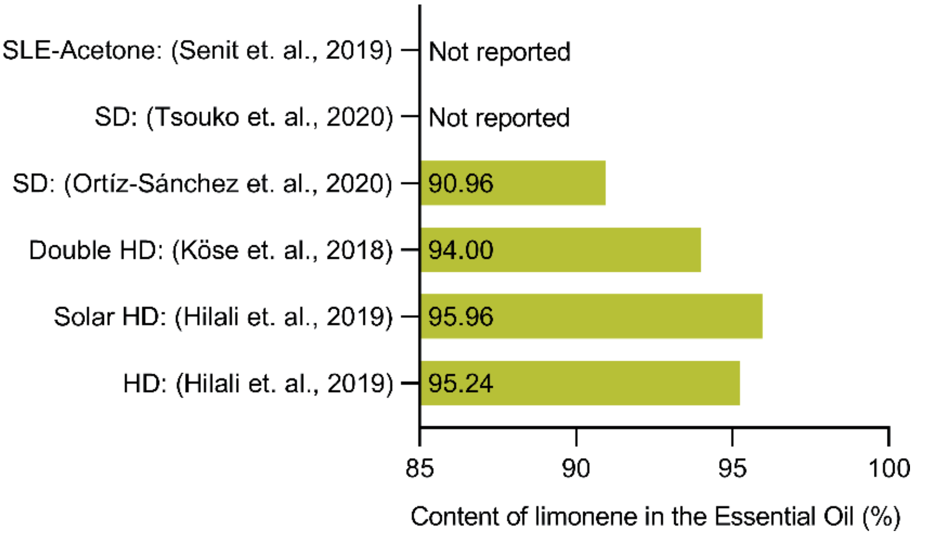

Figure 3.
Content of limonene in the essential oils extracted.

distribution of the sample in the system and how steam interacts with the residue. It is possible to increase steam distillation yields by increasing the pressure in the system (steam explosion) or performing double hydrodistillation [10, 13]. In the case of hydrodistillation, similar yields were obtained independently if the process is carried out with solar energy or not. As seen in **Figure 3**, the limonene content in the essential oils of orange residues is between 90% and 95% [9, 10, 12].

2.3 Extraction of pectin

Once essential oils and other bioactive compounds are removed, the extraction of pectin can be carried out. The first option is to use the liquid phase from hydrodistillation, rich in pectic substances released during heating in direct contact with water. Since pectin is heat-sensible and water-soluble, this option is attractive to perform both essential oils removal and pectin extraction. Hilali et al. reported a yield of ~12% for conventional hydrodistillation and ~ 8.3% for solar hydrodistillation [12]. Even though similar yields were obtained for essential oils using hydrodistillation, the way the heat is applied to the system may affect how much of the pectin is dissolved, resulting in lower yields. Similar behavior can be observed when pectin is retrieved from microwave-assisted hydrodistillation, with yields of around 15% [14].

The most common way to extract pectin from citrus residues is to employ acid hydrolysis, which consists of breaking down the bonds of pectin to obtain galacturonic acid units at high temperatures (from 80–116°C) and low pH values (1–3) with the help of dilute inorganic or organic acids. These hydrolysis reactions can also be assisted by agitation, which enhances the rate of depolymerization of pectin. **Figure 4** shows the best yields reported in recent literature for the pectin extraction process using different acids and processing conditions. From the inorganic acids in **Figure 4**, the highest yields were obtained using sulfuric acid (30.5%) [15], phosphoric acid (29.4%) [16], and hydrochloric acid with (~25%) [11]. It is important to note that the hydrolysis performed with sulfuric acid was completed at shorter times and higher temperatures (10 min and 116°C) [15] than the ones done with phosphoric acid (120 min, and 95°C) [16].

Moreover, the similar yields of pectin obtained from citrus residues using hydrochloric acid with different processing times [11, 17, 18] allow us to hypothesize that longer times could only cause a slight increase in the yield of pectin when temperatures are higher than 95°C at low pH values (1.6–1.8). On the contrary, lower temperatures (around 80°C) with hydrochloric acid reduce pectin yields. As seen in **Figure 4**, pectin yields decreased down to 16–20% [1, 19]. On the other hand, the hydrolysis of citrus residues using organic acids is mainly done with citric acid. The highest pectin yield reported using citric acid is 32.6% (160 min, at 90°C, and pH 2) [11], attributed to the long hydrolysis time. In **Figure 4**, it is possible to see that a short time of hydrolysis with citric acid results in lower yields. Once again, the use of temperatures around 80°C decreases pectin yields considerably, a behavior that was also observed when using inorganic acids. In the work of Rodsamran et al., microwave-assisted acid hydrolysis of lime residues was performed, with yields of ~16% and ~ 10% of pectin, for hydrochloric acid and citric acid, respectively [18];

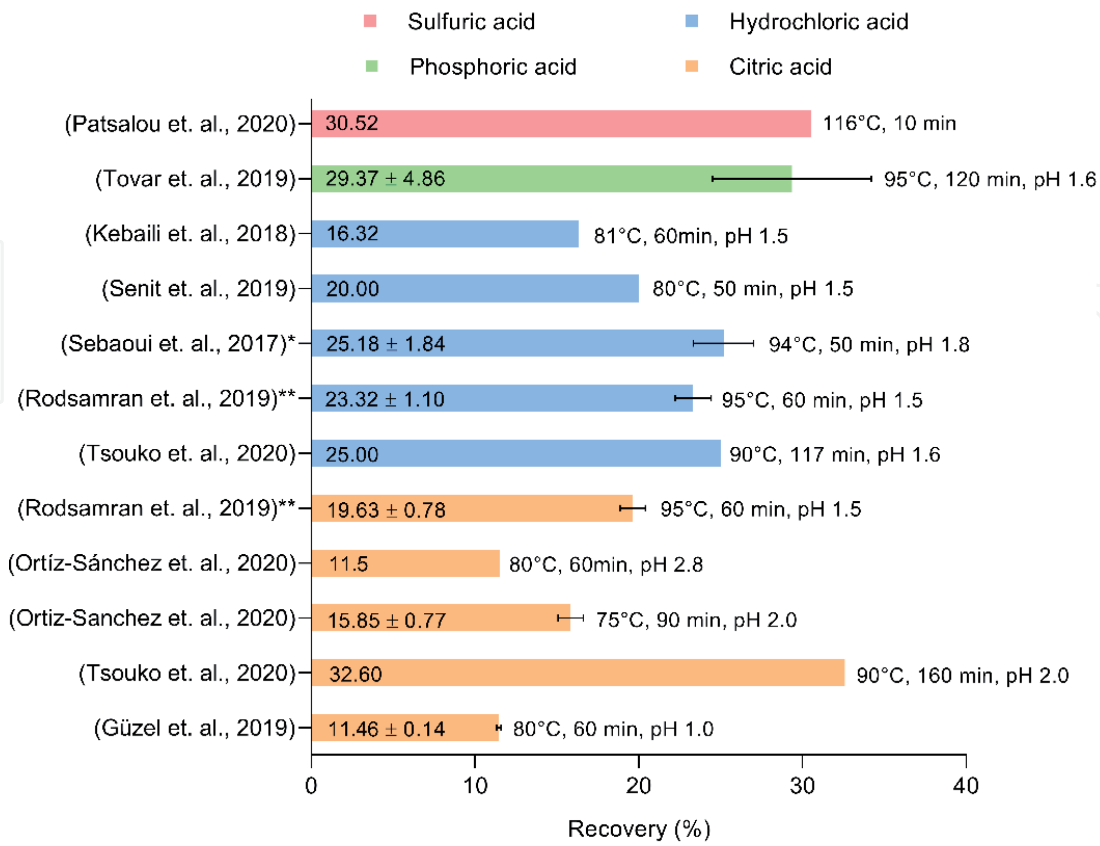

Figure 4.
*Yield of pectin obtained from acid hydrolysis of citrus residues (Orange peel, *lemon peel, **lime peel) using sulfuric acid, phosphoric acid, hydrochloric acid, and citric acid.*

once again, the yields obtained with the inorganic acid resulted higher. The implementation of microwave-assisted hydrolysis has the benefit of implementing shorter process times (~5 min) but has the disadvantage of altering the final color of pectin, making it more brownish than the desired one for commercial pectin [18].

The reported data in **Figure 4** shows that the use of strong acids results in a better hydrolysis performance than organic acids due to their affinity for Ca^{2+} ions, which are responsible for stabilizing pectin chains [18]. However, it has been evidenced that the use of strong acids could be problematic since it causes the loss of some volatile compounds, environmental impacts such as the acidification of rain and water sources [20], and the degradation of valuable remnant substances that could have been further valorized due to their over hydrolysis. Conversely, the use of citric acid may cause lower environmental impacts than those resulting from the use of inorganic acids in the process. In addition, citric acid has been reported to cause less harsh depolymerization of pectin [18]. Also, it is easier to handle its traces during food formulations in comparison to inorganic acids.

2.4 Purification of pectin

The liquid phase that results from the hydrolysis, rich in galacturonic acid, is then retrieved and mixed with alcohols such as ethanol, methanol, 1-propanol, or its isomer isopropanol to separate pectin due to its insolubility in this type of solvents [21]. Most of the authors highlight the use of ethanol, acidified ethanol, or acetone to precipitate citrus pectin. Precipitation of pectin with ethanol is mainly done at 20–25°C, leaving the samples overnight (18 - 24 h) [17, 18, 22]. Depending on the degree of purification desired, different concentrations of ethanol can be used. At least one wash with ethanol at 96% (v/v) is made after pectin extraction. What is more, there are some cases in which the sample is washed three times or more with ethanol at different concentrations (50%, 70%, and 96%), not only to separate pectin but also to remove sugars, polyphenols, and essential oils that remain [1, 8–10, 16, 17, 22, 23]. The removal of these undesired substances helps to obtain pectin in its whitened form. In addition, ethanol could be ideal since it avoids the precipitation of other non-desired compounds [24] and can absorb water from the pectin. Ethanol could also be beneficial for the process since it can be further recovered and reused.

Moreover, since pectin requires acidic conditions for its precipitation, it is necessary to use acidified ethanol (0.5% HCl) when pectin is obtained from hot water extraction [10], as happens when doing hydrodistillation. It is also possible to remove other remnant substances from pectin and increase the organoleptic characteristic of the final product by using a final wash with acetone. For example, Rodsamran et al. used three ethanol washes and a final acetone wash to guarantee almost a complete removal of bioactive compounds and increase the purity of pectin [18].

At this point, some authors report the use of centrifugation to facilitate the separation of pectin from the solvents once they had made effect. Centrifugation has been carried out at low temperatures (4–10°C) using speeds from 4000 rpm to 9000 rpm in a time range of 10 to 20 min [9, 11–13, 22, 23]. After pectin is fully separated, it can be dried at low temperatures that guarantee the thermal stability of the polymer. It is possible to used use vacuum drying at 40°C for short periods of time (1-2 h) [1, 11, 16, 19] or convection drying at 50–55°C for 16 to 24 h [8, 9, 12, 15, 17, 18, 22, 23, 25]. It is important to highlight that pectin yields are primarily affected by other process stages, not by the drying step. However, to guarantee pectin's quality, it is recommended to avoid the exposure of the material to high temperatures for long periods.

2.5 Quality parameters of the final product

To evaluate the final quality of the obtained pectin after purification, the galacturonic acid content and the degree of esterification are the two main characteristics that should always be considered. The galacturonic acid content reveals how much of the retrieved sample contains the primary units to form the polymer. The degree of esterification describes how many carboxyl groups of the galacturonic acid in pectin are esterified with methanol which influences the gelling capacity of pectin. Consequently, both properties help to define the most suitable applications for the extracted pectin.

As can be seen in **Figures 5** and **6**, the highest content of galacturonic acid (~90%) and esterification degree (71–85.6%) was reported by Rodsamran et al. using hydrochloric acid and citric acid in the hydrolysis of lime peels [18]. The standalone result for the esterification degree of orange pectin obtained with phosphoric acid is also high (83.6%) [16] and suggests the necessity of further investigation of the use of this acid in the process. In orange peels, even though broad ranges of galacturonic acid content (50–75%) were reported for hydrochloric acid and citric acid, the esterification degree reported maintained a value around 65–70%. The low galacturonic acid content reported in some cases could be attributed to how the sample was washed to remove remnant phytochemicals and sugars and to the prolonged effect of temperature at low pH values. The decrease in the pH at high temperatures over long periods causes an increment in the degree of dissociation of the carboxylic acid groups [24], leading to the degradation of pectin into substances of lower molecular weight, which ethanol cannot precipitate [26].

It is possible to infer that orange pectin would have similar gelling properties no matter if it were obtained using either citric acid or hydrochloric acid at different process conditions. Since the galacturonic acid content reported in **Figure 5** is always higher than 50% and the esterification degree higher than 65%, it is possible to say that the obtained citrus pectin can be considered as high-methoxyl pectin [27, 28]. This kind of pectin forms its structure based on hydrogen bonds between hydroxyl groups, where sugars, thanks to their highly hydrophilic effect, allow the bonding between polymer chains. High-methoxyl pectin can achieve jellification in few minutes at temperatures around 95°C, suggesting the possibility of using citrus pectin in various food products. On the contrary, low-methoxyl pectin requires

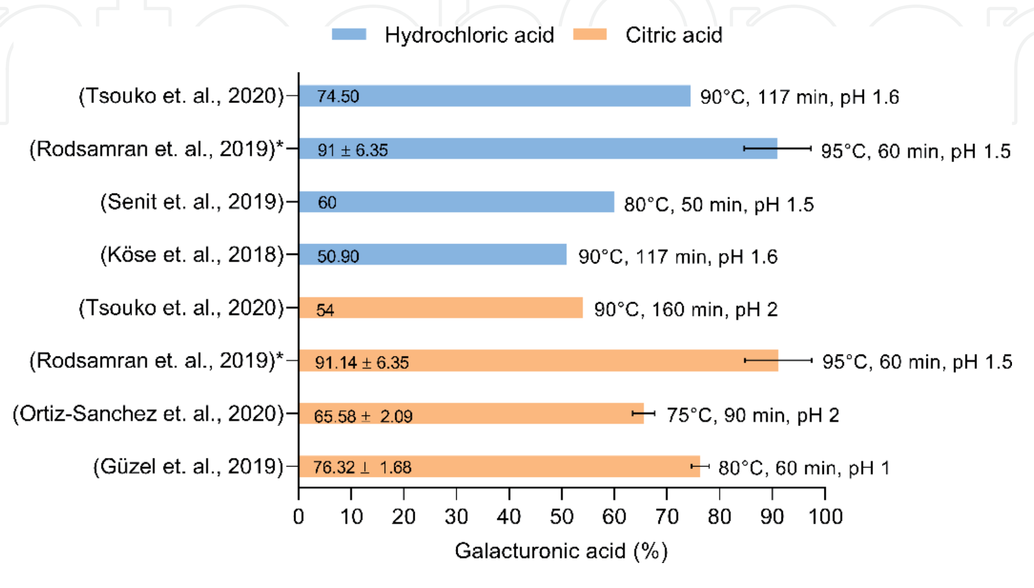

Figure 5.
*Galacturonic acid content of pectin obtained from acid hydrolysis of citrus residues (Orange peel and *lime peel) using hydrochloric acid and citric acid.*

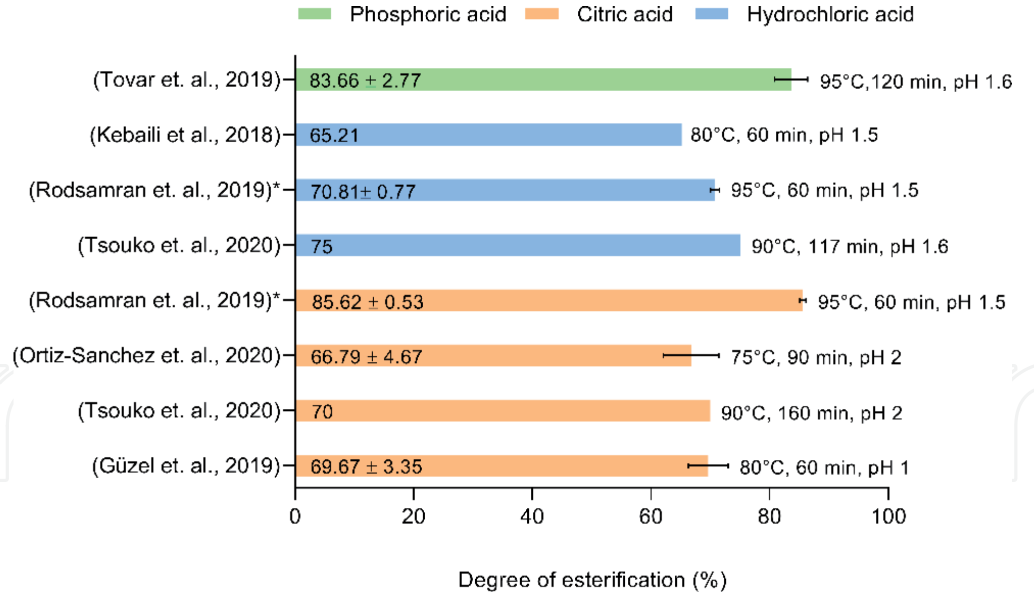

Figure 6.
*Degree of esterification of pectin obtained from acid hydrolysis of citrus residues (Orange peel and *lime peel) using phosphoric acid, hydrochloric acid, and citric acid.*

metallic cations (Ca_2^+ or Mg^{2+}) that bond between themselves and the anionic structure of pectin to form gels due to its low degree of esterification [14].

2.6 Process conditions that enhance pectin quality and recovery

Figure 7 shows a process diagram that suggests the most appropriate process conditions to obtain citrus pectin. In the first place, the raw material must be adequately dried to assure its preservation and milled to increase the contact surface which yields during essential oils extraction and hydrolysis. Secondly, steam distillation is preferable for essential oils extraction since it would selectively retrieve these valuable substances without affecting the material. Contrary to this, during hydrodistillation, the material is in direct contact with hot water, which causes its partial hydrolysis and the degradation of pectic substances, resulting in lower pectin yields; additionally, the use of hydrodistillation would require the acidification of ethanol during precipitation. Thirdly, the acid hydrolysis of pectin can be carried out either with hydrochloric acid or citric acid since the final pectin would always have high-methoxyl properties. Nonetheless, process conditions that tend to increase yields and galacturonic acid percentage should be employed. It is necessary

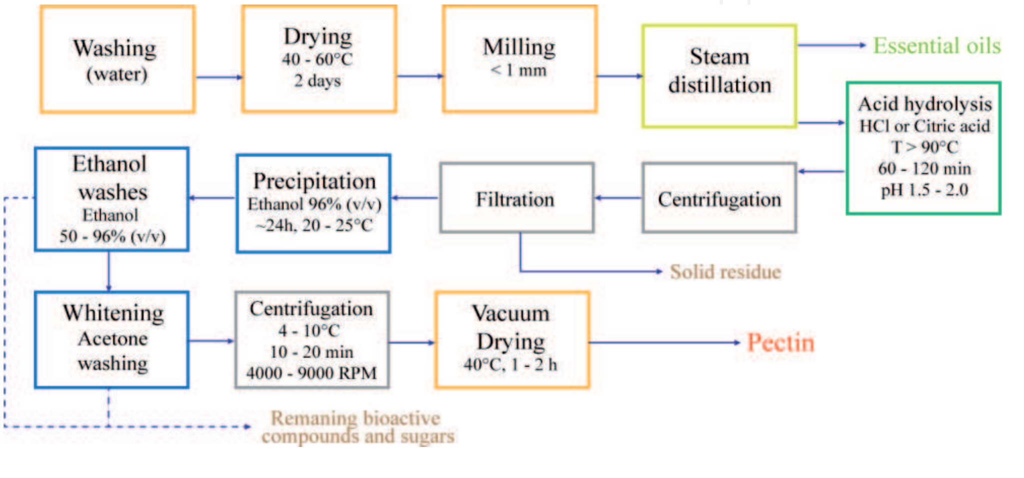

Figure 7.
The production process of citrus pectin and suggested operational conditions.

to perform a careful separation and purification during the final steps to assure high yields and purity of pectin. The last stage of pectin production will always require ethanol at 96% (v/v) for its precipitation and several washes with ethanol and acetone that remove sugars and bioactive compounds. After that, centrifugation is used to assure proper separation from the solvent (that can be later evaporated and reused) and vacuum drying to avoid the degradation of the final product. It is important to highlight that it is possible to obtain additional valuable products from the bioactive compounds extracted through steam distillation and the solids retrieved after hydrolysis rich in lignocellulose.

3. Integration of the process for pectin extraction under the biorefinery concept

It is useful to study how different processes can be integrated with the existent pectin production process under the biorefinery concept to improve the integral sustainability of the valorization of citrus residues. This means that the sustainable use of citrus residues implies the maximization of possible products and energy obtained from this feedstock. For that, it is crucial to consider a logical order in which the different compounds are extracted or produced, as the presence of some of them can impact the quality of other compounds later in the process, which relates to the concept of biomass cascading applied to the biorefinery design process [29, 30]. Additionally, other reagents used along the steps should be carefully selected and studied as they may impact the desired product itself, cause environmental issues, or affect the economic viability of the whole process. Finally, the technical aspects of each step should always be considered to guarantee the quality and yield of the different products.

In this context, citrus residues constitute the primary raw material derived from biomass, and the different processes discussed earlier help to separate it and transform said reagents into chemical substances that can be used as final bioproducts. Nonetheless, there are opportunities to produce more value-added products by integrating the pectin production process with several configurations of other technologies, which are summarized in **Figure 8**. For example, Hilali et al. proposed an orange peel biorefinery that obtains essential oils and pectin but extracts additional value from the solar hydrodistillation process by retrieving partially solubilized polyphenols (flavanones) such as Narirutin and Hesperidin [12]. In another work, Budarin et al. proposed the use of microwave-assisted steam distillation (using only the water present in the peel) and microwave-assisted hydrothermal treatment to obtain essential oils, pectin but also hydroxymethylfurfural and 5-chloromethyl furfural (CMF) which can be used as platform chemicals to produce herbicides, insecticides, pharmaceuticals, monomers, solvents and fuels [31]. Ortiz-Sanchez et al. proposed the anaerobic digestion of the solid residue obtained after acid hydrolysis to produce biogas with a high methane content [9], and also the use of hydrolyzed pectin in a fermentation process with fungi (*T. reesei*) to produce mucic acid [23]. Hydrolysates from orange peel have also been evaluated for their potential to produce other organic acids, such as succinic acid, with the help of fermenting bacteria [15, 32]. Kyriakou et al. extracted more value from orange residues by including an enzymatic hydrolysis step to the solid residue left after pectin extraction to obtain sugars that can be fermented into ethanol and produce biogas from the solid residue from the enzymatic hydrolysis [33]. The fermentation of enzymatic citrus hydrolysates using cellulose-producing bacteria has also been reported [11]. Lohrasbi et al. proposed a variation of the process by first implementing the hydrolysis and then retrieving the essential oils using a flash separator; the solid

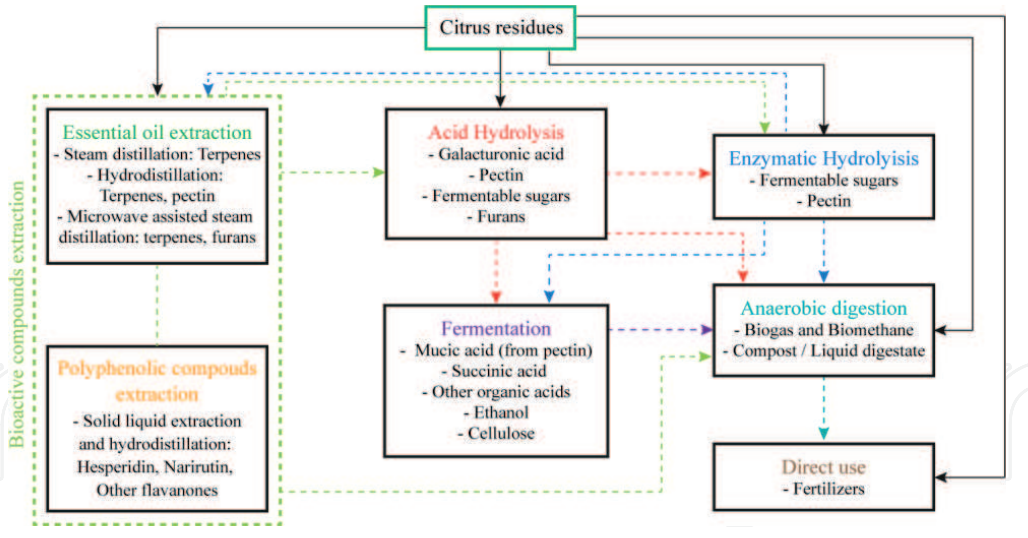

Figure 8.
Alternatives for the integration of the pectin production process under the biorefinery concept.

residue is also used here to produce purified methane, and the digestate obtained from anaerobic digestion is further valorized into compost [34]. As a final option, it has been mentioned that residues from an orange waste biorefinery can be used directly as fertilizers [15].

The biorefinery concept can be associated with several relevant terms such as bioeconomy, circular economy, and industrial symbiosis. Many countries have started promoting policies and programs regarding the bioeconomy as a sustainable development strategy [7]. Circular economy and industrial symbiosis have also gained popularity among the policymakers and stakeholders of different companies. Generally speaking, these three concepts can be summarized as approaches that include the use of biomass-derived feedstocks obtained from various processes from different industries and that contribute to closing down the cycle of industrial processes by using one industry's residues as the feedstocks for another. Not only the value-added products are being produced, but a significant quantity of residues could be used as raw material, a material that would typically end up in a landfill with no further treatment. With this in mind, it is clear why incorporating the processes described above under the biorefinery concept results in a relevant field of study for the valorization of citrus residues and the sustainability of pectin production.

More studies must be performed to determine the feasibility of integrating the possible biorefinery configurations shown in **Figure 8**, the most convenient processing scale [4], and their sustainability. It would be interesting to include not only technical but also environmental, economic, and social aspects into the evaluation of the sustainability of biorefineries from citrus residues by performing an Early-Stage assessment, a methodology that allows the evaluation of multiple biorefinery pathways without the need for vast amounts of data [35–38]. However, the integrated biorefinery's isolated technical, economic, and environmental viability analysis is not enough. It is also essential to demonstrate the sustainability of those bio-based products to promote the deployment of a circular bio-based economy [39] because using residues as feedstocks does not necessarily mean that a process is sustainable. Additionally, in terms of industrial symbiosis, several strategic alliances could be built by selling some of the obtained added-value products to companies that use them as feedstocks. For example, essential oils and polyphenols are mainly used in cosmetics, toiletries, and fragrances due to their essence and benefits for the skin. Also, the market has seen a shift toward organic and natural products, increasing the popularity of essential oils both in pure form and as additives in skin care and hair products. Other products formulated using biorefinery products are jellies, jams, and frozen foods using pectin. In addition, pectin is widely used in the pharmaceutical industry to reduce blood cholesterol levels and treat gastrointestinal disorders [40]. Other applications include paper substitutes, foams, and plasticizers. Knowing this, the potential benefits of the biorefinery increase, as it would not only align with the current strategies for developing a greener industry, but other companies would also benefit from the possible sustainable-produced chemical substances, materials, and energy derived from the pectin production process.

4. Conclusions

After studying the different options available for pectin extraction, some key findings were made. First, it is crucial to remove essential oils and bioactive compounds beforehand, as they can interfere with the yield and quality of pectin. Citrus essential oil is most commonly removed by steam distillation. However, hydrodistillation and Solid–Liquid Extraction have been shown as an alternative. One advantage of hydrodistillation is that it can also partially extract pectin while the essential oil is retrieved, thus reducing time and resources. Pectin is mainly obtained through acid hydrolysis using different solvents. Hydrochloric acid and citric acid have shown better yields than other solvents, and both result in the obtention of high-methoxyl pectin with rapid jellification. However, when considering an industrial approach, the environmental and safety hazards should be revised; because of this, citric acid represents a better option. It is essential to perform a careful separation and purification of pectin with ethanol and acetone to achieve the appropriate organoleptic properties of citrus pectin. Finally, when considering a biorefinery approach, other valorization alternatives such as the recuperation of flavonoids, the use of sugar-rich hydrolysates to produce ethanol, organic acids, and cellulose, the anaerobic digestion to produce biogas and liquid digestate, and the possibility to use citrus residues directly as fertilizers, are presented as novel possibilities to improve the pectin production process under the biorefinery concept.

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Conflict of interest

The authors declare no conflict of interest.

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