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Review

Valorization of Agri-Food Waste into PHA and Bioplastics: From Waste Selection to Transformation

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Abstract: The valorization of agri-food waste is a pivotal component in developing the circular economy, wherein waste is given a second life through various conversion technologies. This review aims to provide an overview of the current state of knowledge on the valorization of agri-food waste, with a particular focus on volatile fatty acids (VFAs) and subsequent bioplastics production. To this end, a comprehensive literature search was conducted using specialist bibliographic databases. The study primarily focuses on reviewing the biological production of PHBV (poly(3-hydroxybutyrate-co-3-hydroxyvalerate)), a type of PHA, due to its relevance as a substitute for fossil-based plastics. Significant attention has been directed toward exploring the potential of agri-food wastes, such as whey, potato peelings, and brewery bagasse, as raw materials for their transformation into a tailor-made VFA solution, rich in valeric and propionic acids. Additionally, existing operational strategies and waste co-treatments have been reviewed. The produced VFAs present multiple applications, including single-cell oils, Omega-3-rich oils, and different types of PHA. Factors influencing the bio-polymerization of VFAs to PHBV, such as the type of substrate, operating conditions (pH and retention time), and the presence of specific microorganisms, have also been reviewed. Due to its physicochemical properties, PHBV has applications in sectors such as agriculture and packaging. This review concludes that transforming agri-food waste into PHBV has the potential to integrate environmental and economic benefits within a circular bioeconomy model, fostering technological innovation and the sustainable use of waste resources.

Keywords: agri-food waste valorization; dark fermentation; volatile fatty acid; polyhydroxyalkanoate; PHBV

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1. Introduction

The generation of waste from the agri-food industry poses significant environmental, economic, and social challenges for Europe. According to the European Commission, around 20% of all food produced in the European Union is wasted annually, totaling over 88 million tons [1]. Of this waste, the agri-food sector (excluding household waste) is responsible for a substantial portion, distributed as follows:

- Food processing: about 39% of the waste.
- Primary production (agriculture and livestock): about 33%.

- Distribution and retail: about 5%.
- Restaurants and catering: about 14%.

The substantial volume of waste generation exerts a considerable environmental impact. However, if the recovery and transformation of agri-food waste were effectively managed, it could represent a significant economic market. Therefore, it is vital to adequately identify and manage by-products apart from non-valuable residues. In this sense, it is possible to gradually transform the current linear economy model into a circular one, where waste is introduced into the value chain. The circular economy model is based on minimizing waste and producing goods sustainably.

Although European environmental policy is shifting toward a circular economy through various directives released by the European Parliament [2], there is still a long way to go. Large amounts of agri-food waste continue to be landfilled or incinerated without any possibility of recovery. This not only represents poor economic management of available resources but also contributes to climate change through the release of methane (CH_4), a greenhouse gas (GHG) produced in landfills. CH_4 traps around 120 times as much heat as CO_2 does. However, this does not mean that CH_4 is 120 times as potent a greenhouse gas as CO_2. Depending on how it is measured, CH_4 is usually counted as between 28 and 80 times as powerful a GHG as CO_2 [3]. This variation can be explained by the time span used to do the balance and the lifetime of CH_4 and CO_2 in the atmosphere. When CH_4 is released into the atmosphere, it immediately begins to trap heat—at least 100 times as much as CO_2. However, CH_4 starts to break down and disappear from the atmosphere relatively quickly compared to CO_2. As more time goes by, more CH_4 disappears, reducing its warming effect. Over 20 years, CH_4 would trap about 80 times as much heat as CO_2. Over 100 years, CH_4 would trap about 28 times as much heat as CO_2 [4]. In light of these challenges, the European Union (EU) has set its sights on achieving climate neutrality by 2050, a goal that encompasses all greenhouse gasses, including CH_4. Since 1990, emissions of this particular gas have declined by 36%, and experts project a further reduction of 44% by 2030. Despite the present difficulties posed by the energy crisis, there is an anticipated rise in ambition regarding both renewable and energy efficiency. Moreover, the European Commission is contemplating the incorporation of CH_4 as a regulated pollutant in the revision of the NEC Directive by 2025 [5].

The European Union initiated 135 new research projects in 2024 related to the circular economy model. These projects span a wide range of fields, including food and agriculture. Notably, 23 of these European projects apply different approaches to the reduction and valorization of agri-food waste. These 23 projects exemplify the ongoing commitment to the transition towards a circular bioeconomy [6]. Some of these projects are outlined below:

- **LIFE Biogas.** Focuses on the development of technologies for the production of biogas from organic waste. It also aims to improve the efficiency of converting waste into renewable energy and fertilizer [7].
- **RES URBIS (Resources from Urban Bio-Waste)**. Focuses on the conversion of urban organic waste into bioplastics, in particular, polyhydroxyalkanoates or PHA's. It explores different ways of integrating urban waste into biorefineries [8].
- **AgriMax.** Aims to valorize agricultural by-products and crop residues through biorefineries. In addition to converting them into bioproducts, the project focuses on reducing waste in the food supply chain and maximizing the use of agricultural by-products. The project yielded a number of products, including bioplastics, food additives (such as lycopene), and biocomposite fibers. The bioplastic obtained was polyhydroxyalkanoate (PHA), produced from agricultural and food waste. One of the fibers obtained was for biocomposites, using agricultural waste such as tomato bagasse and cereal

husks. These fibers were integrated into bioplastics, creating biocomposite materials for applications such as sustainable packaging and other industrial products [9].

- **WASTE2FUNC.** The project yielded the production of biosurfactants, including sophorolipids, and lactic acid. The project aims to create a supply chain that collects organic waste and turns it into high-value-added products, helping to reduce the environmental impact of the agri-food sector [10].

It is evident that environmental concern is not exclusive to Europe. Indeed, other countries have also updated their environmental policies with a particular focus on agri-food waste recovery and environmental sustainability, through the implementation of a multitude of projects and initiatives. The following examples, drawn from a variety of countries, illustrate this point.

- **United States**. In 2024, the United States Department of Agriculture (USDA) entered into 38 cooperative agreements with the objective of supporting innovative and scalable waste management schemes, with the ultimate goal of reducing and diverting food waste from landfills [11].
- **China.** One illustrative example is the AgriLoop project, an international collaboration since 2024 that involves 13 Chinese academic and industrial organizations and 22 European partners. The objective of this project is to develop sustainable processes for the conversion of agri-food waste into high-value-added products. A cascade biorefinery approach will be employed to develop sustainable integrated processes for the conversion of agri-food waste (including tomato, soybean, straw, potato, brewery, winery, livestock, and other materials) into high-value, environmentally friendly products. These products will include plant and microbial proteins, polyesters, and other bio-based chemicals for use in food, feed, health, and material applications, particularly within the agricultural sectors [12].
- **Russia.** The EU-funded SUST-RUS project developed until the end of 2011 a spatial, economic, and ecological model for the assessment of sustainability policies in Russia. The project team collated and verified a comprehensive database comprising social, economic, and environmental data, with the objective of reconciling disparate policy objectives and advancing sustainable development in the country [13].
- **The United Arab Emirates (UAE).** The management of sustainable agricultural waste has become a prominent issue in recent years. A notable case in point is the project that has been implemented in Hatta since 2024, where approximately 27 tons of agricultural waste is managed on a daily basis. The waste is transported in an appropriate manner to Warsan's waste-to-energy plant, thereby contributing to a reduction in landfill waste and the generation of clean energy [14]. Therefore, the project bets for an energy valorization instead of a material valorization.

All these projects positively impact the environment by reducing greenhouse gas emissions, decreasing dependence on fossil fuels, and optimizing the use of natural resources. Consequently, there is a global commitment to transforming the current economic model into a circular one. By focusing on the production of volatile fatty acids (VFAs) from organic waste, these VFAs could reduce the chemical industry's dependency on fossil fuels. Economically, waste valorization not only helps to reduce the costs associated with waste management but also creates new sources of income for agri-food producers and related industries. This fosters a sustainable business model where waste becomes part of a new value chain, leading to the creation of green jobs and promoting technological innovation within the context of the circular economy. Therefore, the valorization of agri-food waste is a sustainable solution to the problem of waste generation. Various technologies and methods for waste conversion have been studied for decades to mitigate the impact of the

agri-food industry on the environment and ecosystems. Among them, the following can be highlighted:

- **Aerobic fermentation for bioplastics production:**
  - **Polyhydroxyalkanoates (PHAs).** PHAs are biopolymers produced by microorganisms, such as bacteria, under specific microbial stress conditions: excess carbon and lack of nutrients (e.g., nitrogen or phosphorus). Their properties, similar to those of conventional plastics, together with their biodegradability, make them of particular interest in the search for sustainable alternatives to petroleum-based products [15]. These biopolymers can be produced from any agri-food waste that can be previously transformed into a VFA solution.
  - **Polylactic acid (PLA).** From whey, lactic acid can be produced by fermentation, which will be used as a raw material for the synthesis of PLA, a biodegradable bioplastic [16].
  - **Polybutylene succinate (PBS).** A biodegradable biopolymer derived from renewable raw materials or agricultural waste, such as agri-food by-products. It stands out for its biodegradability and is a flexible, resistant material used in applications such as packaging and single-use products, especially in the food and agricultural sector [17].
- **Composting**. Compost improves soil structure by increasing water-holding capacity and promoting biological activity. It is produced by the aerobic decomposition of organic matter in by-products such as fruit peels, vegetable waste, manure, etc. It is one of the most common forms of waste valorization [18].
- **Vermicomposting**. This is a variation in the previous process in which worms (e.g., *Eisenia fetida*) are used to speed up the process. The result is a biofertilizer with properties similar to or better than conventional compost because it contains a higher number of beneficial microorganisms and readily available nutrients [19].
- **Biochar.** Biochar is a solid by-product from the pyrolysis of agricultural and food waste that can be used as a soil amendment. It improves the soil's ability to retain nutrients and water, while increasing the stability of organic matter in the soil [20].
- **Anaerobic digestion**. Agri-food waste is transformed in the absence of oxygen by microorganisms. The product is a gaseous mixture (biogas), and a stabilized residue or sludge (digestate) containing microorganisms responsible for the degradation of organic matter. The process is characterized by four distinct metabolic stages: hydrolysis, acidogenesis, acetogenesis, and methanogenesis. These stages are mediated by different groups of specialized microorganisms [21]. In terms of valorization, digestate is used as a biofertilizer. It may or may not undergo additional stabilization processes [22]. Furthermore, the gas phase is predominantly composed of CO_2 and CH_4, with the latter being a viable energy source [23].
- **Dark fermentation.** It is an anaerobic fermentation stopped at the acidogenesis step where agri-food waste produces a VFA solution. The VFA can be used to produce biofuels or high-value-added compounds such as bioplastics. The gas phase is rich in biohydrogen, which can be valorized [24].

As shown, each one of these valorization strategies contributes with different bioproducts to the circular economy model. The combination of dark fermentation followed by aerobic fermentation results in the biotransformation of agri-food waste into bioplastics. Because of that, this review will focus on the production of VFA from agri-food wastes for the subsequent production of poly(3-hydroxybutyrate-co-3-hydroxyvalerate) or PHBV.

The liquid fraction resulting from the dark fermentation is rich in VFAs. These VFAs are short-chain organic compounds formed from carboxyl groups, including low molecular weight acids such as acetic, propionic, butyric, valeric, and isovaleric acids. They are mainly formed during the anaerobic fermentation of organic matter, as an intermediate product of the acidogenesis step. Their production is influenced by several factors, such as:

- Type of substrate. This influences the type and quantity of VFAs. Waste rich in carbohydrates generally favors the production of acetic acid, whereas waste rich in fat can increase the production of butyric acid.
- Operating conditions. Factors such as pH, solids concentration, and temperature also influence the type and amount of VFA produced.
- Microorganisms. The microorganisms present in the fermentation medium are also important factors in an anaerobic fermentation process. Genera such as *Clostridium*, *Lactobacillus*, and *Bacteroides* play an important role in VFA production [25].

In the context of VFA production from agri-food waste, several projects in Europe have demonstrated the success of this type of waste valorization. One example is the NoAW (No Agro-Waste) project. Its aim is to use agricultural waste to produce high-value bioproducts, including VFAs. Wine industry residues, cereals, and dairy products have been used to produce biofuels, making a significant contribution to waste reduction and promoting the circular bioeconomy and sustainable development [26].

Currently, there is an increasing number of studies investigating the mechanisms and technologies to optimize the production of VFAs from agri-food waste. Anaerobic fermentation is the most commonly used process and has improved thanks to ongoing research and development of more efficient bioreactors and microorganisms for the degradation of organic waste [27]. However, the variability in the composition of agri-food wastes is the main challenge for the effective performance of the fermentation process. In this sense, advances in waste pretreatment and the use of co-substrates have helped to improve the production rate of VFAs, allowing their application in various industries, such as [27]:

- Biofuel production. VFAs are used as precursors in biogas production, where they are converted to CH_4 by methanogenesis during anaerobic digestion.
- Food industry. VFAs are used as preservatives, acidity regulators, and food additives due to their antimicrobial properties.
- Bioplastic production. They are used as feedstocks for aerobic fermentation in the production of polyhydroxyalkanoates (PHAs), biodegradable plastics used as alternatives to petroleum-based products.

In this work, to accurately review the state-of-the-art in agri-food waste valorization to volatile fatty acids (VFAs), special attention is given to maximizing the production of valeric and propionic acids. This involves explaining the dark fermentation process used for VFA production. Additionally, the biomasses with the highest potential for VFA biotransformation will be examined, with a particular focus on detailed studies of select biomasses such as whey and low-value-added starches. The Section 3 will review the transformation of these VFAs into valuable bioplastics, with an emphasis on their further transformation into poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV). This includes a review of the different routes of VFA transformations, the mechanisms of VFA transformation into polyhydroxyalkanoates (PHAs), and the most common microorganisms employed. Furthermore, fermentation conditions for the PHA transformation of VFAs, as well as the physico-chemical properties of PHAs and other bioplastics, will be reviewed.

2. Production of Valeric- and Propionic-Rich VFA Streams from Agri-Food Wastes

Production of PHBV (poly(3-hydroxybutyrate-co-3-hydroxyvalerate)), a biodegradable biopolymer with better thermal and mechanical properties than poly-hydroxybutyrate (PHB), is intended for use in bioplastics sectors, such as packaging (coated paper) and geotextile nets for agriculture [28]. The amount of 3HV (3-hydroxyvalerate) in the copolymer typically varies from 5% to 24%, depending on the production conditions and the precursors used. A higher 3HV content tends to reduce the crystallinity of the material, resulting in increased flexibility and improved formability [29].

In the production of PHBV from VFAs, valeric and propionic acids play a fundamental role in increasing the amount of 3HV, thereby improving the mechanical properties of the material, such as flexibility and thermal resistance [30]. Given the importance of these acids in the composition of VFAs used as precursors for bioplastic production, it is particularly important to produce a fermentation broth in which they are present in significant amounts. In the literature, Policastro et al. [31] discussed that the optimal concentration of valeric acid for increasing the 3HV fraction in PHBV can be modified to achieve fractions ranging from about 10% to as high as 90%, depending on the strain used and culture conditions. Their study also mentions that propionic acid as a precursor can achieve different levels of 3HV in PHBV.

In order to get deep into the methods to convert agri-food wastes into VFA-rich streams, the Section 2.1 introduces the methodology to transform agri-food waste into solution-rich VFAs by means of dark fermentation. Then, typical agri-food waste currently employed in this biotransformation is summarized. Finally, the most suitable wastes for obtaining the propionic- and valeric-acid-rich VFA solution will be presented.

2.1. Dark Fermentation: Method to Transform Agri-Food Waste into VFA

As previously stated, VFAs represent one of the final products of dark fermentation (DF). The dark fermentation follows a similar pattern to that of anaerobic digestion (AD), with the exception that it eliminates the final stage of methanogenesis [32], thereby enabling the accumulation of VFAs and the generation of CO_2 and H_2, that could be used as a biofuel [33].

In the context of the AD process, the conversion of organic substrates into CH_4, CO_2, and water is a complex process that involves four sequential biochemical steps. These steps can be broadly categorized as follows [21]:

(1) Hydrolysis. Complex organic polymers—carbohydrates, proteins, and lipids—are converted into simpler monomers: monosaccharides, amino acids, fatty acids, and glycerol. To do this, microorganisms secrete hydrolytic enzymes that break down the polymers.
(2) Acidogenesis. The soluble monomers produced in the previous stage are fermented by acidogenic bacteria to produce VFAs, alcohols, CO_2, and H_2, among other compounds.
(3) Acetogenesis. The VFAs and alcohols produced in the previous phase are converted to acetic acid, hydrogen, and CO_2.
(4) Methanogenesis. The compounds formed in acetogenesis are converted to biogas (mainly CH_4 and CO_2) by methanogenic archaea.

Steps (1) and (2) correspond to VFA production [34]. Thus, the DF process is commonly defined as the biotransformation of a carbohydrate-rich substrate into H_2 and other by-products, such as organic acids and CO_2, in the absence of light and oxygen.

In DF, as outlined by Pandey et al. [35], complex sugars such as cellulose, hemicellulose, starch, and sugar can be obtained from organic waste, wastewater, or other types of waste that have undergone prior pretreatment (to ensure the elimination of harmful compounds),

and subsequent transformation into simple sugars that will give rise to different VFA. A summary of this synthesis pathway is presented in Figure 1.

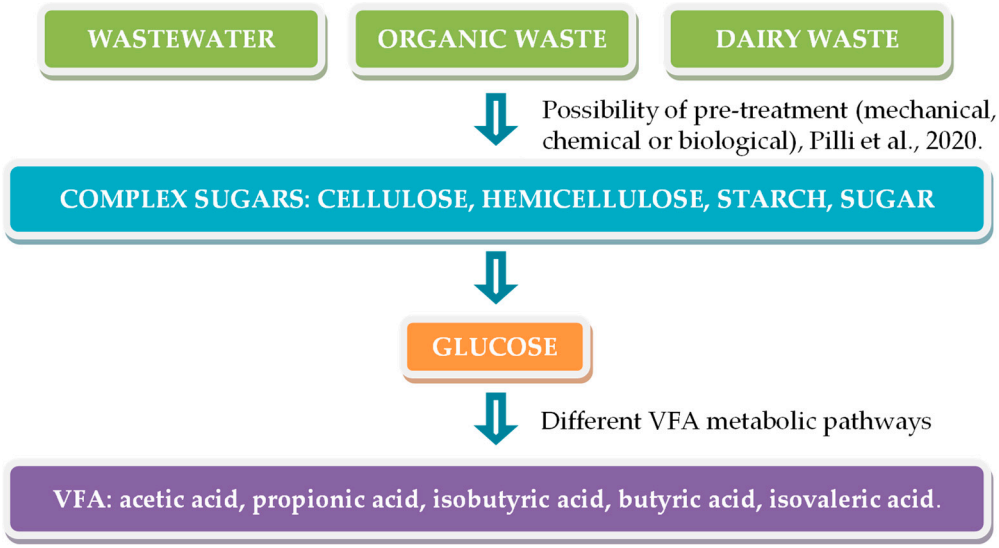

Figure 1. Schematic overview of the dark fermentation process for VFA synthesis. Adapted from Pandey et al. [35], Pilli et al. [36].

The findings of the study carried out by Pandey et al. indicate that the DF process represents an effective process for VFA production. In order to ensure optimal VFA production, instead of maximizing H_2 production, it is essential to control a range of critical parameters, including the substrate, the reactor, the microbial culture, the pH, the temperature, the solids retention time (SRT), the hydraulic retention time (HRT), and the organic loading rate (OLR). The composition of the VFA is determined by the operational parameters [36].

2.2. Agri-Food Waste Typically Used for VFA Production

A VFA solution rich in valeric and propionic acids plays a crucial role in the production of PHBV, and the substrate used, together with the anaerobic fermentation conditions, are fundamental to obtaining a high proportion of these acids. The substrate to be valorized, in this case, agri-food waste, can come from different sources, some of which are described below:

- **Vegetable waste.** Agriculture, food processing, and surplus sales generate sugar-rich wastes that can be anaerobically fermented to produce VFAs. Their high carbohydrate content favors the formation of acetic, propionic, and valeric acids, depending on the fermentation conditions. Wainaina et al. reported in 2020 that these residues can produce a high yield of VFAs, especially when an appropriate carbon-to-nitrogen (C/N) ratio is achieved [37].
- **Vegetable oil industry wastes**. Residues from oil extraction, such as palm and soybean waste, are rich in lipids and carbohydrates. Almomani et al. found in 2020 that these wastes are highly valorized for VFA production, especially when co-fermented with other wastes containing higher amounts of carbohydrates [38].
- **Whey**. A by-product of the dairy industry that is an excellent source of carbohydrates and proteins. Jiang et al. already found in 2015 that bacteria such as *Propionibacterium* can enhance propionic acid production when the pH and retention time conditions are suitable [39].

- **Fish industry waste.** The valorization of fish waste, such as tuna, for the production of biochemical compounds has been studied. In 2017, Bermúdez-Penabad et al. published a study in which they improved the efficiency of the process by adjusting the operating conditions of the bioreactor. [40].
- **Industrial wastewater from agri-food transformation sector.** This type of waste is rich in organic compounds that are suitable for anaerobic fermentation to produce VFAs [41]. According to Agler et al. (2011), by adjusting the C/N ratio and maintaining a suitable pH between 5 and 6.5, it is possible to obtain a VFA profile with high levels of valeric and propionic acids. Recent studies have shown that the co-fermentation of agro-industrial residues can maximize the production of VFAs with these compounds [41]. This type of waste includes **vinasses**, a liquid by-product of alcohol distillation in beverage production. They contain carbohydrates, organic acids, and other fermentable compounds that can be converted into VFAs, such as acetic, propionic, and valeric acids, depending on the microorganisms and conditions used in the process. Subjecting vinasse to anaerobic digestion can result in the production of VFAs where the main component is acetic acid, with lower concentrations of propionic and valeric acids, as demonstrated by Rajes and Ganesan in their study published in 2011 [42].
- **Low value-added starches**. Derived from agricultural by-products, these residues can be pre-treated, for example, by enzymatic hydrolysis, to break them down into simple sugars that can be anaerobically fermented to produce VFAs. An example of low-value starch is **brewer's spent grain**, which is rich in fiber and carbohydrates and can also be valorized by anaerobic fermentation to produce VFAs, including valeric and propionic acids, as shown by Sukphun et al. in their study (2021) [43]. Finally, Achinas et al. (2019) demonstrated that **potato processing residues**, such as peel or pulp, are also suitable for VFA production. Pretreatment and co-fermentation, as well as the adjustment of pH conditions and the inoculum/substrate ratio, can optimize valeric acid production [44].

A number of studies investigating the conditions for the production of VFAs, in particular valeric and propionic fatty acids, from some of the above-mentioned agri-food wastes are described below.

2.2.1. Production of VFA, Rich in Valeric Acid and Propionic Acid, from Cheese Whey

Cheese whey is a greenish–yellow liquid that remains in the milk after the coagulation of the milk proteins has occurred. This coagulation can be achieved using acids or rennet, as well as other plant-based coagulants [45,46]. Whey is regarded as a by-product of the cheese-making process that has a detrimental impact on the environment. It is estimated that between 2021 and 2022, 145–200 million tons of whey are produced annually [47,48], which presents a significant environmental concern when disposed of as waste with a BOD of 40,000 mg/kg [49]. Considering the environmental concerns surrounding whey, there has been a growing interest in studying its properties, composition, nutritional value, and potential technological applications. It is important to note that whey retains a high level of nutritional value, primarily due to the presence of residual proteins. This has led to a growing interest in the valorization of whey, as evidenced in 2020 by Gregg et al. [50].

The liquid remaining after the coagulation of casein in rennet- or plant-coagulated cheeses, which have a pH above 6.0, is therefore classified as "sweet whey". In contrast, the term "acid or acidic whey" is used to describe the remaining liquid after the coagulation of casein in acid-coagulated cheese, which has a pH below 5.8 [51–54]. The whey released from the production of ricotta cheese, for example, is referred to as second whey cheese [55,56].

This is an acidic whey with a lower fat and protein content than the primary whey [57–59]. Second, whey is also produced from non-acidified cheese and has a higher pH.

The chemical composition of whey varies depending on the type of cheese produced and the type of milk from which the main cheese is derived [60–63]. To illustrate, the composition of sheep's milk whey is characterized by markedly elevated levels of total solids, lipids, and proteins in comparison to cow's whey [46,64]. Furthermore, sheep's whey contains a greater quantity of β-lactoglobulin, a comparable proportion of α-lactalbumin and serum albumin, and immunoglobulins in comparison to cow's whey [65]. The composition of goat whey differs from that of cow whey. It contains approximately twice the amount of α-lactalbumin and lower levels of β-lactoglobulin, serum albumin, and immunoglobulins [66,67]. Although it depends on the type of whey, the physicochemical characteristics of whey are usually BOD 27–60 g/L and COD 50–102 g/L, so the BOD/COD ratio is usually 0.5, indicating that it is an easily degradable substrate by using aerobic or anaerobic treatments [68]. It also contains a significant amount of carbohydrates (mainly lactose, 45–50 g/L), proteins (0.6–1.1%, 6–8 g/L), lipids (0.06–0.05%), lactic acid (0.05–0.9%), total suspended solids (1.3–22 g/L), salinity (8 mS/cm), and mineral salts [69].

In terms of whey valorization, in the present era, the principle of the circular economy suggests the utilization of whey in the production of an array of products, including whey cheeses, whey powders, edible wraps, beverages, and food supplements. As a valuable by-product, whey is esteemed for its constituent components and functional properties, which have informed the development of food-related applications containing whey components, particularly proteins [70–73].

In addition to the aforementioned types of whey recovery, there are others which should be considered. For instance, energy recovery from cheese whey by means of a bioelectrochemical system consisting of a two-stage process [74] is a notable example. Furthermore, Čechmánková et al. [75] produced, in 2021, biofertilizers from whey in sustainable agriculture, reporting environmental and productive benefits. Additionally, Ghaly et al. [76] reported studies of biomethane production in a two-stage anaerobic digester.

Nevertheless, the type of valorization that is of most interest for the purposes of this review is the production of VFAs. Research studies dated from 2020, for example, that of Calero et al. [77], conclude that whey is a suitable substrate for VFA production due to its high content of fermentable organic matter. These studies analyze how pH, solid retention time, and organic loading rate affect VFA production. Molinuevo-Salces et al. [78] analyzed, in 2024, the conversion of organic matter from whey to VFAs and the effect of the pH control on the process using a new method based on gas permeable membranes. The outcomes of this study demonstrate that up to 54% of bioconversion was achieved under acidic conditions with sequential pH control. In contrast, under alkaline conditions, the pH control led to a decrease in bioconversion to VFAs. This finding indicates the feasibility of recovering and concentrating VFAs through the utilization of the gas-permeable membrane-based method. Another recent study is that of Méndez-Acosta et al. [79], where the production of VFAs from whey is analyzed using controlled temperature and pH conditions. In this study, a multiscale analysis is used to optimize the dark fermentation process. The study also concludes that the rescaled range fractal methodology can be used for indirect monitoring of VFA production under different operating conditions.

The studies mentioned above are only examples of the wide range of variables and study parameters that exist throughout the production of VFAs from whey. This review addresses the different points of optimization, focusing on the production of the VFAs of interest: valeric and propionic. Based on two main studies [77,80] the variables and

fermentation process conditions to be maintained in order to maximize the production of valeric and propionic acids from whey are detailed below:

- Substrate. A high Kjeldahl nitrogen content has been shown to increase the propionic acid yield to 78% of the total VFA production. Therefore, the characteristics and composition of the substrate are some of the most important factors influencing VFA production and composition [80].
- Retention times. In an anaerobic digestion process, a distinction must be made between the SRT—the average time the microorganisms are in the digester—and the HRT—the time the wastewater or sludge is in the digester. Both times coincide with suspended growth digesters where there is no recirculation. Calero et al. [77] studied three different HRTs in dark fermentation: four, six, and ten days at three different pH levels. They used a sequential bioreactor (SBR) type anaerobic reactor with a working volume of 2 L, with two daily cycles of 12 h, each with four stages: loading, reaction, sedimentation, and liquid extraction. It was operated at a temperature of 30 °C. Under these operating conditions, they concluded that the conditions that maximized the production of valeric and propionic acids were an increase in the SRT, up to 10 days, regardless of the pH used. When the SRT was increased from 4 to 10 at pH 5, propionic acid increased from 13% to 24% of the final VFA composition. Similarly, at pH 5.5 and 6, propionic acid increased from 17% to 24% and 24% to 36%, respectively. In the case of valeric acid, its concentration increased with increasing SRT independently of pH, from 12% to 25%, from 10% to 22%, and from 9% to 15% for pH 5, 5.5, and 6, respectively. Thus, increasing the SRT from 4 to 10 days tended to stimulate the formation of odd VFA (propionic and valeric) to the detriment of even VFA such as acetic and butyric.
- pH. A less acidic pH, a change from 5 to 6, stimulates the production of propionic acid and reduces that of valeric acid, regardless of the SRT used [77]. Other studies [81,82] use a different type of reactor, in this case, a continuous stirred tank reactor (CSTR) with an SRT of 48 h, also conclude that increasing the pH from 5.25 to 6 favors the production of propionic acid to the detriment of butyric acid. A distinct study was conducted by Yu and Fang [83], which showed that propionate is favored during the acidogenesis of dairy wastewater (simulated dairy wastewater, prepared from full-cream powdered milk) at pH 4.0–4.5.
- Organic loading rate (OLR). The organic loading rate indicates the amount of material used in the reactor feed, and can be expressed in terms of COD or volatile solids (VSs). Pérez Morales et al. [80], no clear trend was observed between changes in organic loading and VFA yield and production; Calero et al. [77] observed that an increase in organic loading had a negative effect on VFA production when whey was used as substrate. The increase in OLR from 3 to 12 g COD L^{-1} d^{-1} means a decrease in the acidification degree from 94% to 65%. Regarding the VFA profile, in the same study, it was concluded that a lower organic load improves the production of propionic and valeric acids; the highest ratio of both acids occurred at an OLR of 3 g COD L^{-1} d^{-1}. The effect of OLR on the distribution of the different VFA is illustrated in the figure below (Figure 2).
- Temperature. The mesophilic condition (35 °C) is considered the most efficient and economically favorable for VFA production [80]. However, the influence of temperature on the type of VFA produced is less than that of pH [84].

In conclusion, according to the literature reviewed, whey is a good raw material for VFA production due to its high content of fermentable organic matter. The SBR operating parameters such as pH, SRT, and OLR have a direct influence on the VFA distribution [77].

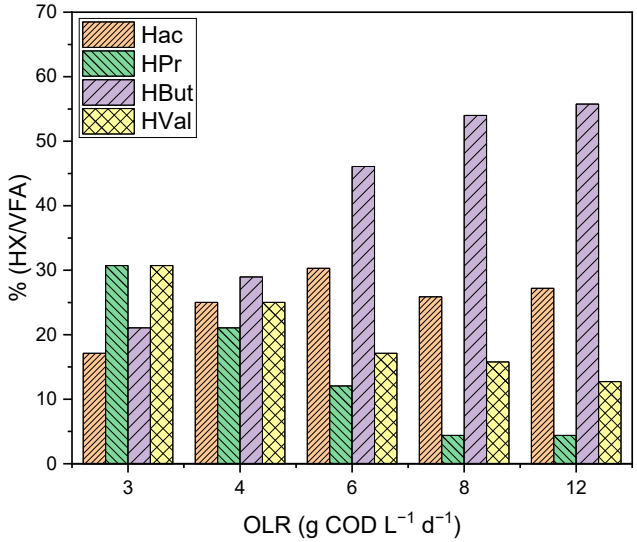

Figure 2. Effect of organic loading rate on VFA distribution. HAc = acetic acid, HPr = propionic acid, HBu = butiric acid, and HVal = valeric acid. Modified from Calero et al. [77].

2.2.2. Production of VFAs Rich in Valeric Acid and Propionic Acid from Low-Value-Added Starches

In the literature, different wastes have been used as starch sources. Some of the most relevant are reviewed below.

(a) Potato industry waste

Potato peelings can be included in this group of wastes. Potato (*Solanum tuberosum* L.) is one of the world's most important crops. According to statistics from the Food and Agriculture Organization of the United Nations (FAO), annual worldwide potato production exceeded 350 million tons in 2020 [85]. Liang et al. stated in their study [86] that potato peel contains the following components in dry weight: starch (34%), carbohydrates (63%), protein (17%), lipids (1.2%), and lignin and suberin complex, which are soluble and insoluble acids, and ash (21%). Due to the above composition, by-products of the potato industry are ideal as a carbon source for fermentation [87,88]. They can be used for the production of lactic acid by using mixed culture fermentation [86,87] as a culture medium for the production of bacterial cellulose [89]; as a feedstock for the production of biobutanol or bioethanol [90–92]; as a raw material for biodegradable films [93]; as a potential source for the extraction of steroidal alkaloids and starch [94,95]; as a precursor for biochar synthesis [96,97], and for biogas production by anaerobic digestion [86,98].

In addition to the above-mentioned forms of utilization, it is possible to recover potato waste by dark fermentation to produce VFA. In single-phase digesters utilizing this type of waste, the processes of hydrolysis and acidogenesis can occur, leading to the accumulation of VFAs and the inhibition of methanogenic microorganisms [99,100]. In this valorization process, the intermediate products resulting from VFAs can be more valuable than the final products (CH_4) [101]. The process of dark fermentation with mixed cultures of this type of waste is notable for its ability to proceed without the necessity for pretreatment, due to the ease with which the waste is degraded, and without the need for additional methanogenic inhibitors to prevent the conversion of VFAs to CH4 [102].

The composition of volatile fatty acids (VFAs) is a pivotal factor, as their regulation exerts a significant influence on the subsequent process [103]. In their study, Zhou et al. [84] concluded that when using potato peel waste to produce VFA, pH, organic loading time, and residence time affect the VFA produced. Similar results were obtained by Lu et al. [104]. In their studies, Lu et al. [102] evaluated the influence of pH adjustment as well as the

initial organic load on the composition and production of volatile fatty acids (VFAs) during the acidogenesis of potato peel waste. A series of tests were studied within a stirred tank reactor at a temperature of 37 °C. The working volume was set at 5 L, and the inoculum and residue were mixed at 8% (based on SV content). The operating conditions were as follows: 37 °C ± 0.5 °C and 300 rpm stirring speed; pH: 5.0, 7.0, and 11.0 during acidogenesis. The uncontrolled pH was used for comparison. In the study carried out by Lu et al. [104], the effect of the initial organic load on the production of VFAs from potato peel waste through acidogenic fermentation was studied. The results show that increasing the initial organic load enhances the concentration of VFAs, particularly butyric acid, but decreases the overall VFA yield. The optimal initial organic load for VFA production was identified as 71.5 g volatile solids/L, which accelerates acidogenesis and reduces hydrolysis time.

With regard to the composition of VFAs, the main results to be highlighted by Lu et al. [102] at the different pH levels tested were the following:

- Acetic acid was the main product treated at pH 7.0 and 11.0, representing 46–77% and 74–92% of the total VFAs, respectively, while butyric acid was the main product at pH 5.0 and uncontrolled pH, representing 11–75% and 38–82% of the VFA mixture, respectively.
- In the pH 7.0 treatment, the percentage of propionic acid increased as the fermentation progressed, while the acetic acid content decreased. The highest propionic acid production was obtained at pH 7.0. At this level, a favorable balance is achieved between the activity of acidogenic microorganisms and the production of propionates, while the production of other VFAs, which could predominate at lower or higher pH levels, is reduced.
- In particular, the percentage of butyric acid decreased with increasing pH. When treated at pH 5.0 and uncontrolled pH, the hexanoic acid content was about 20% of the total VFA at the end of fermentation.

In the same study, paying attention to the SRT, a prolonged SRT allows acidogenic bacteria to adapt and maximize fermentation, increasing the proportion of VFAs, particularly at near-neutral pH conditions. This provides time for microbial metabolism to favor the production of odd-chain acids such as propionic acid. In terms of organic loading, propionic acid production increases with moderate organic loading, as an excess can lead to acidification of the medium, inhibiting the production of certain VFA and favoring other acids such as butyric acid. Moderate levels allow efficient conversion of substrates to propionic acid without excessive accumulation of by-products [102].

(b) Beer industry waste

As for another type of low-value starch, beer bagasse, according to the recent publication of Liu et al. [105], the production of VFAs from beer bagasse is maximized by a synergistic pretreatment of ball milling followed by enzymatic hydrolysis. This process facilitates the breakdown of the lignocellulosic structure of beer bagasse, increasing the solubilization of the available carbohydrates, which enhances the production of VFAs.

Although using beer bagasse as a substrate in dark fermentation, valeric and propionic acids are not the main fatty acids obtained in a high proportion: Guarda et al. [106] recently found that it can be deduced that in order to maximize the production of valeric and propionic acids from beer bagasse, the conditions to be adjusted are again pH and organic load. The results showed that operating at a higher pH (around 6.0) and a high organic load (OL of 40 g COD/L) maximizes the diversity and concentration of organic acids. However, proportionally, valeric and propionic acids are more abundant compared to the remaining acids at 10 g COD/L compared to 40 g COD/L. These acids are produced as

part of a mixture of volatile fatty acids, which favors the proportion of odd-chain acids under these conditions.

2.2.3. Production of VFAs Rich in Valeric Acid and Propionic Acid from Low Value-Added Starches and Cheese Whey: Co-Fermentation

Sarkar et al. [107] investigated the co-fermentation of beer bagasse and cheese whey. Despite the fact that a complete fermentation process was employed, rather than a dark fermentation process whose primary objective is not the production of VFAs, an increase in their synthesis was observed as a result of the methodology utilized. The study was published in 2022, and it was carried out in two phases (P-I and P-II), and three different conditions where the brewery spent grains fed (BSG) was set at 35 g VS and three different cheese whey loads of 20, 30, and 40 g COD/L were established. In the second phase (P-II), the biogas (H_2 + CO_2) produced during the acidogenic fermentation (P-I) was recirculated to provide a source of inorganic carbon (CO_2) and an electron donor (H_2) for the homoacetogens in the mixed culture.

Propionic acid was synthesized in a lower concentration than the other acids and was only detected from the 16th day onward. As the COD fed increased, the production of propionic acid also increased, owing to the greater availability of amino acids. Conversely, a decline in propionic acid was observed, suggesting its transformation into valeric and caproic acids, along with acetic and butyric acids. In a mixed microbial culture of BSG, the increase in the concentration of these acids and their transformation into longer chain molecules indicates that the hydrolysis of the residue is being efficient, which translates into a continuous flow of fermentable sugars. The onset of valeric acid production was observed on day 32. The initial values, which were dependent on the COD fed, were low and increased over time, reaching a maximum on day 56.

In Phase II, the previously produced biogas was recirculated to evaluate the effect of H_2 and CO_2 on carboxylic acid production. The result was an increase in the production of carboxylic acids compared to those produced in P-I. In the case of valeric acid, production increased and was earliest at day 24 (day 32 in P-I). The increases were 37.7%, 11.3%, and 9.37%, respectively, compared to P-I. However, in the case of propionic acid, gas recirculation did not have a significant effect, as it remained relatively low and only increased when the operating COD concentration was high.

2.2.4. Production of VFAs Rich in Valeric Acid and Propionic Acid from Expired Juices

In the context of other waste products typical of the agri-food industry, such as expired juices, the potential for biohydrogen production through acidogenic fermentation has also been the subject of investigation. The findings indicated by González del Campo et al. [108] in 2014 show that the biohydrogen produced comprised 55% H_2 and 45% CO_2 by volume. Moreover, in that study, the gas mixture was fed directly into a fuel cell without undergoing any purification step. The generation of VFAs was not subject to monitoring in the course of this study. Although the objective of the study was not the production of VFAs, it can be inferred from the results that acidogenic fermentation to generate VFAs from these waste materials is a viable process. In this case, a real effluent of fruit juices with a sugar concentration of 9 g/L was used, comprising 5.4 g/L glucose, 1.9 g/L fructose, and 1.8 g/L sucrose.

2.2.5. Production of VFAs Rich in Valeric Acid and Propionic Acid from Non-Agri-Food Waste

In this case, two main studies, dating from 2009 and 2020, promoting the production of these acids from non-agri-food waste, are reviewed below. They are notable for their

strategies for the generation of VFAs, which are rich in the acids of interest and could be exported to dark fermentation with the agri-food waste that could be valorized.

In the context of valeric acid generation, research has been conducted by Shi et al. [109] to assess the potential of incorporating riboflavin into the fermentation process as a means of producing valeric acid from waste-activated sludge. Furthermore, the potential for solids reduction was explored. The results indicated that the addition of riboflavin (0.5 mM) led to a significant increase in VFA production, with the most abundant acid being valeric. An increase in riboflavin doses from 0.05 to 5 mM resulted in a notable rise in the DOC fraction of valeric acid in relation to total VFAs, reaching 62.8%. This is a higher proportion than that observed with other chemical supplements. Furthermore, the addition of riboflavin resulted in an enhanced reduction in mixed liquor volatile suspended solids (MLVSSs). The application of a riboflavin dose of 0.2 mM resulted in the maximum reduction in MLVSS, which reached 47.4% compared to the control without riboflavin, which demonstrated a reduction of 33.9%. Riboflavin may, therefore, be an option as a cost-effective chemical agent for the enhancement of fermentative valeric acid production from waste-activated sludge, in conjunction with solid reduction.

In the case of propionic acid, a number of strategies have been investigated with a view to increasing its production. Two examples are provided below for reference:

A number of studies have demonstrated that the selection of the appropriate microorganism is a critical factor in the formation of propionic acid. The utilization of bacteria belonging to the genus *Propionibacterium*, such as *Propionibacterium acidipropionici*, is of paramount importance due to their exceptional efficiency in propionic acid production [110–114].

In the literature, the transformation of an anaerobic activated sludge (WAS) to VFAs was enhanced by the addition of alkylpolyglucose (APG) [115]. The APG significantly enhanced the production of short-chain fatty acids (SCFAs), particularly propionic acid. This was achieved by accelerating solubilization and hydrolysis, improving acidification, inhibiting methanogenesis and balancing the C/N ratio of the substrate. Furthermore, the operational lifespan was diminished. The results demonstrated that the yield of SCFA with 0.3 g of APG per gram of total suspended solids (TSSs) in 4 days was 2988 $\pm$ 60 milligrams of COD per liter, a significantly higher value than those obtained with WAS alone or WAS alone plus APG alone. The corresponding propionic acid yield was 1312 $\pm$ 25 mg COD/L, which is 7.9 times higher than that of WAS alone. The investigation demonstrated that during anaerobic treatment of WAS in the presence of APG, solubilization was accelerated, while hydrolysis and acidification were enhanced, and methanogenesis was inhibited. Furthermore, the activities of pivotal enzymes engaged in WAS hydrolysis and acidification were augmented by the presence of APG. It is of greater significance that by maintaining equilibrium in the C/N mass ratio of the substrate, the production of propionic acid was enhanced. A comparative analysis of the activities of pivotal enzymes and the prevalence of anaerobic instrumental microorganisms in sludge hydrolysis and SCFA production, with and without APG, revealed that the stimulation of SCFA accumulation, particularly propionic acid, was predominantly attributable to biological processes.

Table 1 summarizes the different results reported in Section 2, where the more suitable agri-food waste for their valorization to specific fatty acids are reviewed, and the conditions for their transformation. The table shows the kind of waste to be transformed to VFA, the operating conditions (pH, T, OLR, SRT, and additives), and the VFA yields obtained.

Table 1. Summary of the operating conditions (pH, T[a], OLR, STR) and other considerations for the production of a VFA-rich solution in valeric and propionic acids by dark fermentation of the different wastes mentioned above.

Waste	pH	T (°C)	OLR	SRT (days = d)	Additives and Other Considerations	VFA Concentration	Valeric and Propionic Acid Yield (%)
Whey [77]	6 (just for propionic acid)	35	Low: 3 g COD/(L·d)	STR = 10	-	-	-Propionic: 36 (pH = 6, STR = 10 d) -Valeric: 25 (pH = 5, STR = 10 d)
Potato peel [102]	7 for propionic acid	37	-	5 d (propionic acid)	-	-Propionic: 180 mg COD/gVS_{fed} -Acetic: 289.5 mg COD/g$VS_{fed.}$ -Butyric: 157.2 mg COD/gVS_{fed} Hexanoic: 89.4 mg COD/gVS_{fed}	-
Bagasse [106]	6	30	10 g COD/(L·d)	7 d	Pretreatment of hydrolysis to BSG	-	-Propionic: 1,2% COD basis -Valeric: 2% COD basis
Whey and bagasse [107]	6–6.5	35	40 g COD/(L·d)	48 d (propionic acid) 56 d (valeric acid)	Recirculation of CO_2 and H_2 generated that increased propionic concentration	-Propionic: 3.85 g COD/L (d 48). -Acetic: 10.56 g COD/L (d 48). -Butyric: 20.42 g COD/L (d 56). -Valeric: 3.77 g COD/L (d 56). -Caproic: 13.02 g COD/L (d 56). -with CO_2 recirculation.	-
Activated Sludge [109]	Nearly 9	35	13.4 g/(L·d) of MLVSS	21 d	Rivoflavin	-	Valeric acid: 62.8% with a riboflavin dose of 5 mM
Activated Sludge [115]	No pH control. Initial pH was 6.8 ± 2	25	-	8 d	Alkylpolyglucose	Propionic: 1,3 g COD/L	Propionic acid:43,9% at AOG of 0.3 g/g TSS

3. Production of Bioplastics from Volatile Fatty Acids

As mentioned above, VFA can be produced by dark fermentation from various sources of agro-industrial waste. Once produced, they serve as a substrate for various microorganisms in the synthesis of bioplastics. VFAs can be assimilated by a range of microorganisms [116–118]: bacteria, heterotrophic microalgae, and yeasts, as evidenced by Figure 3 and this allows for the production of a variety of bioproducts.

As seen in Figure 3, VFAs can be transformed into more than just PHAs by utilizing different bacteria, microalgae, and yeast. Depending on the type of microorganism employed, Omega-3-rich oil or single-cell oil can also be obtained. The following paragraphs briefly describe VFA transformation by microalgae and yeast. Microalgae are considered photoautotrophic organisms; however, several species have heterotrophic metabolism [119]. Oleaginous microorganisms can thrive in heterotrophic cultures using VFAs as a carbon source, accumulating significant amounts of valuable products like omega-3 fatty acids [120]. Acetic acid, an intermediate in anaerobic digestion, frequently accumulates

during dark fermentation processes and can be converted by microalgae into acetyl-CoA, the primary precursor for lipid synthesis [121]. There are two pathways for the metabolic oxidation of acetyl-CoA:

1. In the glyoxysomes, the glyoxylate cycle converts acetyl-CoA to malate.
2. In the mitochondria, the tricarboxylic acid (TCA) cycle converts acetyl-CoA to citrate [122,123].

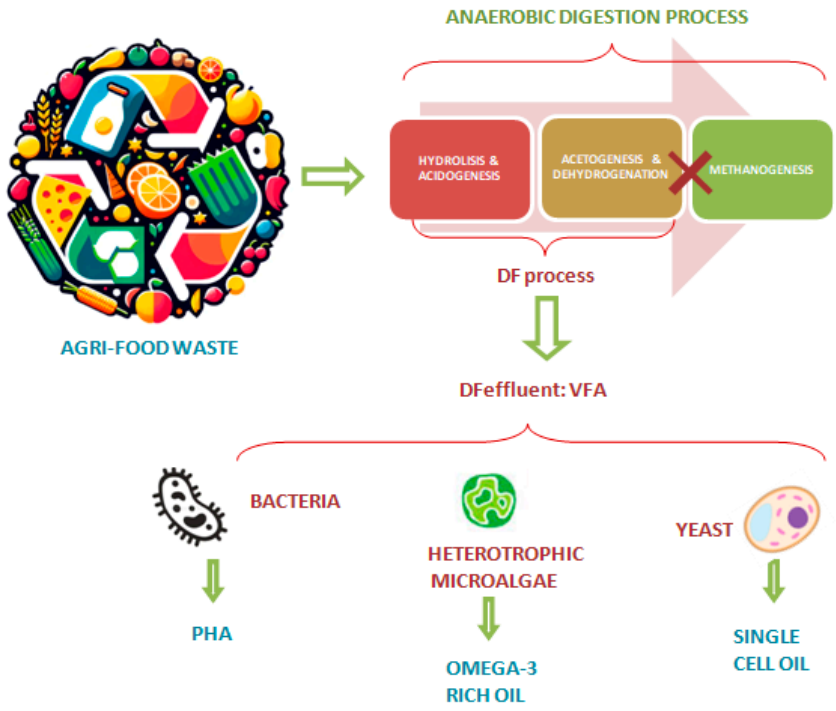

Figure 3. Schematic overview of the dark fermentation process and production of VFAs that can be consumed by different microorganisms to produce different bioproducts. Adapted from Chalima et al. [32].

Several species of algae can carry out this biosynthesis with different VFAs as a carbon sources, such as *Chlorella sorokiniana* (CCAP 211/8K), which uses acetate and butyrate [124]; *Micractinium inermum* F014, which uses acetic, propionic, and butyric acids [125], and *Chlorella protothecoides* FACHB-3, which can use a mixture of VFAs [126].

Additionally, in the case of yeasts, VFAs are regarded as a prospective hydrocarbon source for lipid production, offering a viable alternative to traditional hydrocarbon sources such as glucose. This is attributed to their transient metabolic pathways and elevated theoretical conversion efficiency [127]. Acetic acid can be converted into lipids by oleaginous yeasts and is related to acetyl-CoA metabolism. The formation of new fatty acids is contingent upon the uninterrupted provision of acetyl-CoA, which can be achieved by the cultivation of oleaginous yeasts on acetic acid as a carbon source [128]. Following the uptake of the acid, it is converted to acetyl-CoA, with the surplus being utilized for intracellular lipid accumulation. The oily yeast genera include *Yarrowia*, *Candida*, *Rhodotorula*, *Rhodosporidium*, *Cryptococcus*, *Trichosporon*, and *Lipomyces* [129].

The Section 3.1 addresses the bacterial production of bioplastics, from VFAs as carbon source, but mainly focuses on PHA production.

3.1. Microorganisms Responsible for the Transformation of VFA into PHA

3.1.1. Phosphorus-Accumulating Organisms

Phosphorus accumulating bacteria, or Phosphorus-Accumulating Organisms (PAOs), are a specialized group of microorganisms that are capable of storing significant quantities

of phosphorus intracellularly, predominantly in the form of polyphosphates. Consequently, in wastewater treatment systems, PAOs play a pivotal role in the biological phosphorus removal process (BPRS), assisting in the reduction of phosphorus content in the final effluent and the prevention of its discharge into water bodies [130,131].

PAOs operate within a specific anaerobic-aerobic cycle. The anaerobic phase is characterized by the absence of oxygen. PAOs release phosphorus into water by decomposing their polyphosphate reserves and, concurrently, assimilate volatile fatty acids, which they subsequently store as polyhydroxyalkanoates [132,133] in the subsequent aerobic phase. In the presence of oxygen, PAOs utilize PHAs as an energy source, thereby recovering phosphorus from the medium and rebuilding their intracellular polyphosphate reserves. This cycle enables the net accumulation of phosphorus in the system and its removal from the sludge in water treatment [134]. The optimal pH and temperature range for PAOs is near neutral (6.5–8.0) and moderate (15–30 °C) [118]. The growth of PAO and their PHA storage capacity is dependent on volatile fatty acids such as acetic and propionic acid. This enables efficient phosphorus processing [131,135].

It is evident that these phosphorus-accumulating bacteria play a pivotal role in the removal of phosphorus in wastewater treatment systems. Additionally, they have the capacity to function as PHA producers from volatile fatty acids. PAO bacteria have metabolic characteristics and the ability to adapt to specific conditions that make them of great interest for use in PHA production processes:

- PAO can utilize volatile fatty acids, such as acetic acid and propionic acid, found in sewage and other organic wastes. This allows the use of low-cost materials, creating a more economical and sustainable PHA production process, rather than relying on purified carbon sources such as glucose. This capability contributes to the circular economy concept by enabling the valorization of waste [133,134].
- PHA production in an anaerobic-aerobic cycle. Under anaerobic conditions, storage cells integrate PHAs using VFAs as a carbon source and store it in their cells as an energy reserve. In the aerobic phase, they consume this PHA for phosphorus accumulation, a process specific to PAOs. This anaerobic-aerobic cycle has the advantage that PHA production does not require continuous aeration, thus reducing energy consumption compared to other microorganisms that produce PHAs only under aerobic conditions [132].
- Flexibility in the production of different types of PHA. PAOs can produce different types of PHA, such as poly(3-hydroxybutyrate) (PHB) or poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) [135]. This flexibility in the type of PHA allows the mechanical and thermal properties of the bioplastic to be tailored to specific applications, such as biodegradable packaging or medical materials products [136].
- Compatibility with wastewater treatment. Already found in biological wastewater treatment systems due to their role in phosphorus removal, PHA production systems could be integrated into water treatment facilities, making use of existing infrastructure and eliminating the need for separating production facilities. This would allow simultaneous nutrient removal and bioplastic production, maximizing system efficiency [137].

3.1.2. Mechanism of PHA Accumulation. Accumulating Microorganisms

The mechanism of PHA accumulation has been extensively studied. There are various naturally occurring pathways for PHA formation. Numerous genetic studies have been conducted to investigate the regulatory mechanisms that control PHA formation in response to different growth conditions. Several studies using PHA mutants with alterations in genes other than the p b genes have provided insights into the fundamental role of cell

physiology and central metabolism. These studies not only provide important knowledge for the design and engineering of recombinant organisms for PHA production [135].

Figure 4 [138] illustrates the different pathways (A-G) to produce short-chain-length PHA (scl-PHA) using glucose as the carbon source:

A: Represents the tricarboxylic acid cycle.

B: Synthetic pathway to produce acetyl-CoA monomers. In this pathway, LDH refers to lactate dehydrogenase and PCT to propionyl-CoA transferase.

C: Pathways derived to produce 3-hydroxybutyryl-CoA (3HB-CoA) from *Ralstoniaeutropha* for., PhaA (ketothiolase), and PhaB (ketoreductase) are involved.

D: Pathway for the formation of 3-hydroxyvaleryl-CoA (3HV-CoA) involving IlvA (threonine deaminase) and BktB (ketothiolase).

E: 3HB-CoA pathway production from fatty acid biosynthesis. Key enzymes are AccA (acetyl-CoA carboxylase), FabD (malonyl-CoA:ACPtransacylase), FabH (3-ketoacyl-CoA-CoA synthase III), and FabG (3-ketoacyl-CoA-CoA reductase).

F: Alternative pathway for 3HV synthesis involving the enzymes Sbm (bella dormant mutase), YgfG (methylmalonyl-CoA decarboxylase), and BktB (ketothiolase).

G: The 4-hydroxybutyryl-CoA production pathway involving SucD (succinate dehydrogenase), 4HbD (4-hydroxybutyrate dehydrogenase), and the transferases Cat2 and Cat1 (4-hydroxybutyrate transferase).

The study by Madison and Huisman [135] provided a comprehensive account of the mechanism of polyhydroxyalkanoate synthesis in bacteria, with a particular focus on poly(3-hydroxybutyrate) (PHB) and other short- and medium-chain PHAs. The synthesis process of scl-PHA can be summarized as follows: The synthesis process commences with the generation of precursors derived from acetyl-CoA. This metabolite is essential and has its origin in a variety of carbon sources, including sugars, fatty acids (of which VFA is a prominent example), and other organic compounds. In circumstances where specific nutrients (such as nitrogen or phosphorus) are scarce, but carbon is plentiful, bacteria redirect surplus acetyl-CoA toward PHA synthesis as a means of storing energy and carbon. The initial stage of PHB biosynthesis entails the condensation of two acetyl-CoA molecules, resulting in the formation of acetoacetyl-CoA. The enzyme β-ketoacyl-CoA thiolase is responsible for catalyzing this step, which is a common process in many bacteria and marks the commencement of the PHA production pathway. This enzyme plays a pivotal role in the regulation of substrate allocation toward PHA synthesis, rather than other metabolic pathways. Subsequently, the formation of 3-hydroxybutyryl-CoA is catalyzed by the enzyme acetoacetyl-CoA reductase, which is dependent on the cofactor NADPH (nicotinamide adenine dinucleotid phosphate (reduced form). This is a pivotal stage, as the reduction determines the structure of the monomer unit that will be incorporated into the PHA polymer. It is a selective step for the formation of 3-hydroxybutyrate (3HB) monomers, which constitute the fundamental building block of PHB. The availability of NADPH is crucial for this reaction, indicating that the cellular environment must possess sufficient NADPH regeneration capacity to sustain the process. Subsequently, the polymerization of 3-hydroxybutyryl-CoA into a PHA chain occurs and is catalyzed by a key enzyme: PHA polymerase. This enzyme binds to the 3-hydroxybutyryl-CoA monomer and catalyzes the formation of ester bonds, resulting in the linear polymerization of the monomer and the formation of a very long chain. It is crucial to emphasize that PHA polymerase is specific to each bacterial species, thereby determining the type of PHA that is produced (PHB or copolymers such as PHBV). In the case of PHBV, the incorporation of 3-hydroxyvalerate (3HV) units into the polymeric chain is achieved through the introduction of precursors, such as propionic acid or valeric acid, into the culture medium.

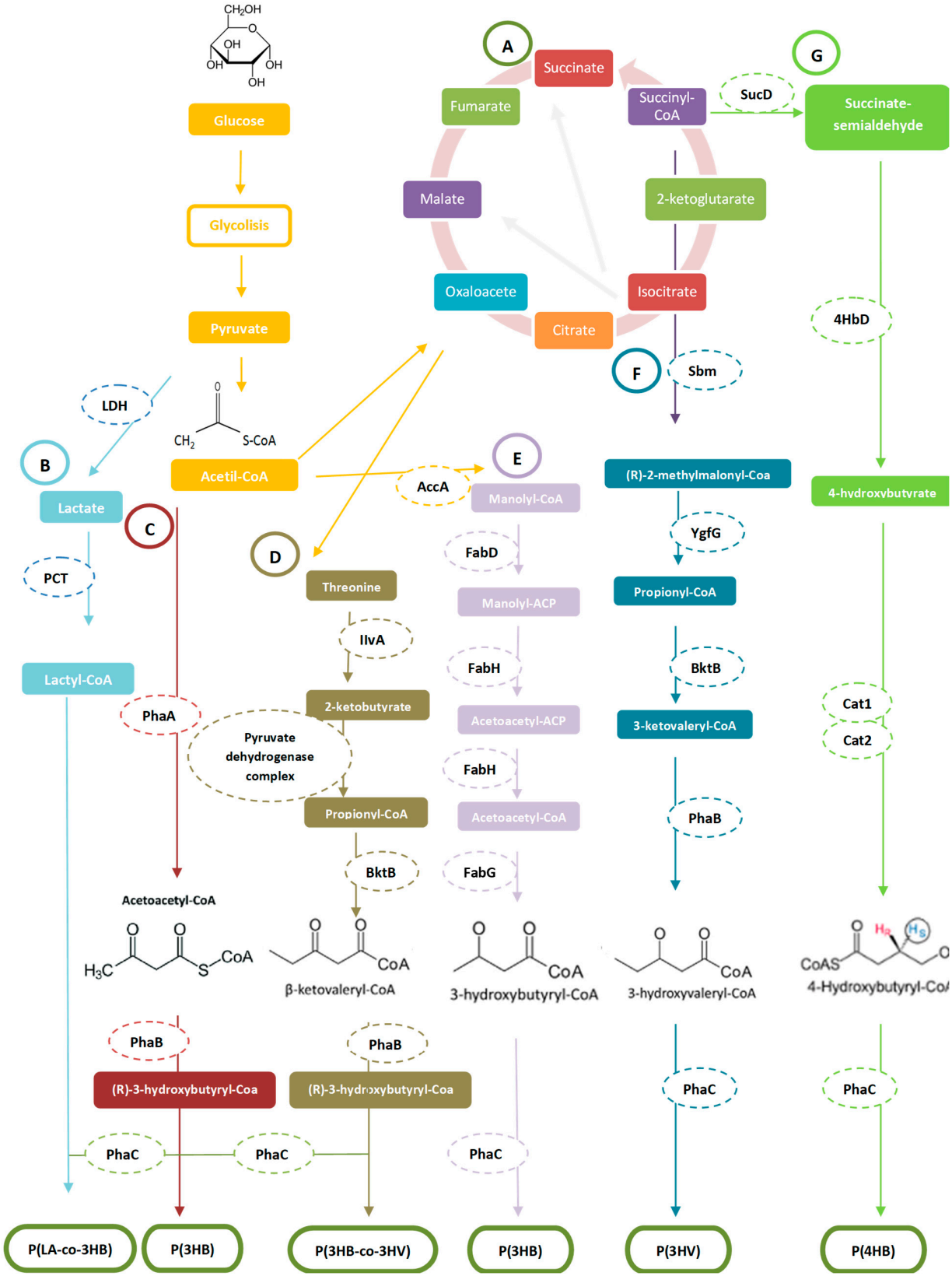

Figure 4. Scl-PHA production pathway using glucose as the carbon source. PhaC is the PHA synthase enzyme in all pathways and catalyzes the polymerization of monomers to PHA polymers. Modified from Lu et al. [138].

With regard to the intracellular accumulation of the polymer, it is synthesized and subsequently accumulates in the cytoplasm of the bacterium in the form of PHA granules.

The granules are encased in a layer of proteins and phospholipids, which regulate their size and structure [135].

The production of copolymers such as PHBV necessitates the utilization of particular precursors (including propionic acid and valeric acid) within the culture medium. These acids are incorporated into the metabolic pathway as alternative substrates that PHA synthase polymerizes into 3HV units. The ratio of 3HB to 3HV in the final PHBV can be modified by controlling the relative concentration of these acids in the medium, thereby allowing the properties of the bioplastic to be tailored to suit specific applications [135].

The regulation of gene expressions in PHA-producing bacteria is encoded in several genes, including phaA, phaB, and phaC. These genes encode the enzymes β-ketoacyl-CoA thiolase, acetoacetyl-CoA reductase, and PHA polymerase, respectively. These genes are organized in an operon (the pha operon), and their expression is controlled by regulatory factors that respond to the availability of nutrients and carbon sources [135].

Table 2 provides a list of the PHA-producing bacteria, ordered according to the substrate used for synthesis.

Table 2. Adapted from [139]. A summary of the substrates and the microorganisms that synthesize PHA. P3HHx = poly(3-hydroxylhexanoate); P3HO = poly(3-hydroxyoctoate); P3HD = poly(3-hydroxydodecanoate); P3HB = poly(3-hydroxybutyrate); P3HV = poly(3-hydroxyvalerate). "Co" is used to indicate the copolymer.

Substrate	Bacteria Involved	Type of PHA
Simple sugar	*Alcaligenes latus*, *Ralstonia eutropha*, *Haloferax mediterranei*, *Azotobacter vinelandii*	-P3HB -Adding organic acids: P(3HB-3HV), P(3HB-4HB)
	Pseudomonas putida, *Pseudomonas citronellolis*	-P3HHx, P3HO, and other medium chain PHA (mcl-PHA)
	Aeromonas hydrophila, *Aeromona scaviae*, *Rhodospirillum rubrum*	-Adding organic acids or alcohols: P(3HB-co-3HHx), P(3HB-co-3HO) and other scl-mcl copolymers.
	Bacillus megatherium [140]	-PHB
	Bacillus thuringiensis [141]	-PHBV
Tryacylglycerols	*Aeromonas hydrophila*	-P3HB-3HHx
	Pseudomonas oleovroans, *Pseudomonas stutzeri*, *Pseudomonas citronellolis*	-P3HHx, P3HO and other mcl-PHA.
	Cupravidus necator [142]	-P3HB, P(3HB-3HV)
Hydrocarbons	*Pseudomonas oleovorans*, *Pseudomonas citronellolis*	-P3HHx, P3HO, P3HD and other mcl-PHA.

3.2. Accumulation of PHA Fermentation Conditions

The fermentation conditions will vary depending on the specific microorganism involved, the composition of the fermentation medium, and the type of PHA being produced. This section focuses on *Cupravidus necator*, a bacterium that is used for the synthesis of PHBV from volatile fatty acids [132].

Cupriavidus necator (previously known as *Wautersiaeutropha*, *Ralstoniaeutropha*, and *Alcaligenes eutrophus*) is a Gram-negative bacterium that belongs to the Burkholderiaceae family [143].

The wild-type *C. necator is* capable of producing PHBV from an artificial mixture of VFA plus CO_2 and H_2, as well as VFAs from digestate [144].

Furthermore, an additional variant of *C. necator* has been identified by Venkata Mohan et al. [122]., which is recombinant or modified and capable of utilizing an alternative

carbon source to produce PHBV. Schlegel et al. [145] found that to facilitate the production of PHBV by using *C. necator*, it is essential to establish fermentation conditions that are conducive to this process. It is important to note that PHBV accumulation is a consequence of nutritional stress, whereby the accumulation of granules occurs when other nutrients are in short supply. For this accumulation to occur, a carbon source must remain available, and nutrients, such as nitrogen or phosphate, must be in short supply [146].

Vu et al. [147] delineate the culture conditions employed in their investigation of PHBV production utilizing *C. necator* as the producing microorganism. The strain employed was DSM 545, and the culture medium was a mixture of volatile fatty acids produced by anaerobic fermentation in a semi-continuous membrane reactor from food waste. The primary variables to be monitored and regulated were pH, C/N ratio, aeration, and nitrogen sources. The pH was maintained at 7, which is considered optimal for bacterial growth. The C/N ratio that was identified as optimal was 6, as this resulted in the greatest extent of bacterial growth and PHBV accumulation. However, a ratio of 12 was also tested, but this was ultimately excluded due to the lower biomass production, which consequently led to a reduction in the overall PHBV accumulation. The effect of aeration on the culture was also investigated, and a value of 1 vvm (volume of air per volume of medium per minute) was identified as the optimal condition. Finally, two nitrogen sources, ammonium sulfate, and urea, were tested, and no significant differences in biomass production or PHBV accumulation were observed between them. The maximum PHA accumulation and PHA yield on biomass were 1.5 g/L and 56%, respectively. The accumulated PHA was found to be PHBV, with the percentage of hydroxybutyrate ranging from 91–96%.

It is also noteworthy that PHA can be obtained through biological methods, although the carbon source can be synthetic (such as glucose) or derived from residual waste or by-products. For instance, as Kant et al. [148] observed, in the case of lignocellulosic materials intended for PHA synthesis, pretreatments (physical, chemical, or biological) are necessary to eliminate lignin and render cellulose and hemicellulose accessible for the subsequent saccharification process. Furthermore, the generation of by-products, including furfural, vanillin, hydroxymethylfurfural (HMF), and acetate, during pretreatment has been observed to exert an inhibitory effect on microbial fermentation, particularly on cell growth and PHA production.

In the same vein, Saratale and Oh [149] observed that higher biomass accumulation and PHB yields occurred when glucose was used as a carbon source as opposed to xylose and arabinose, and that yields were higher when pure glucose was used than mixed sugars.

Rodrigues et al. [150] found that in the case of other wastes (fruit pulp waste), it has been demonstrated that the use of real waste as a substrate can result in the presence of impurities that are more difficult to remove from PHA.

However, from an environmental, technological, and economic point of view, Naranjo [151] stated that the use of agro-industrial waste in the production of PHA is positive, as it creates an alternative to the use of a by-product which in many cases has a high environmental impact or requires high economic investment for its treatment. It also promotes green technologies in the biopolymer industry, particularly PHB, by reducing production costs and adding value to a polluting raw material.

In addition to *C. necator*, other microorganisms have been shown to synthesize PHAs For instance, *Bacillus megaterium* has been found to possess a robust expression system and a lipopolysaccharide-deficient cell wall, making it an excellent microorganism for this purpose [152].

Martinez et al. [153] recently described the production of PHBV, with this bacterium using biogas digestate as the fermentation substrate. In this study, the Colombian bacterium strain *B. megaterium* LVN01 was utilized for fermentation in bioreactors with a working

volume of 3 L and agitation of 400 rpm, operated in batch mode. The pH was adjusted to 7.0 ± 0.2, adjusted with HCl or NaOH 1M as needed. The temperature was 30.8 °C, and the fermentation time was 60 h. The optimal PHB yield was produced at 16 h, yielding 2.7 g PHB/g cell and a DCW (dry cell weight) of 0.133 g/L. However, the maximum DCW values were reached at 60 h, at 0.563 g/L, although the highest PHB production value was attained at 16 h, at 360 mg PHBV/L. The utilization of biogas digestate as a substrate resulted in an enhancement of accumulation efficiency during the initial phases (16 h), which can be ascribed to the stress conditions imposed by the complexity of the substrate [154]. In the context of such substrates, *B. megaterium* experiences a prolonged acclimatization period prior to attaining optimal growth. This adaptation time must be taken into account when designing and optimizing fermentation processes, as it impacts the productivity and efficiency of the process [155]. In this study, *B. megaterium* LVN01 has demonstrated its efficiency in producing PHBV from biogas digestate in a short fermentation period.

Another PHA-producing microorganism is *Haloferax mediterranei*, an extremely halophilic marine archaeon. In the study by Susiana et al. [156], an experiment was carried out in which the concentration of the phosphorus source was varied to see how this affected the accumulation of PHAs by this microorganism. Monobasic potassium phosphate (KH_2PO_4) was used as the phosphorus source. Shake flasks of 500 mL containing 100 mL of culture inoculated with 10% (*v*/*v*) inoculum from a previous inoculum growth stage were used. They were incubated at 37 °C for one week. The concentrations of KH2PO4 tested were 0.5, 0.25, and 0.00375 g/L. In this study, the best result was obtained with 0.5 g/L KH_2PO_4, the accumulation being 0.95 g/L with 15.6% dry biomass.

Pseudomonas oleovorans has also been used for PHA synthesis by Chmelová et al. [157], as it is able to synthesize mcl-PHA in culture conditions with carbon excess and nitrogen deficiency. Chmelová describes how a yield of 1.17 g/L biomass was achieved with a synthetic medium (8.4 g/L glucose, 5.7 g/L sodium ammonium phosphate, and 35.4 mM phosphate buffer). The results were satisfactory since, as described by the authors, a biomass yield 1.7 times higher than with the conventional medium was obtained after 48 h of culture. In this case, the *P. oleovorans* strain used was DSM 1045 in a culture incubated for 48 h at 30 °C under shaking conditions (150 rpm).

Some *Aeromonas* species are also used to produce PHA due to their simple and robust growth and their ability to synthesize homopolymers, copolymers, and terpolymers with unique material properties [158]. For example, *A.hydrophila*, using sodium gluconate as substrate and with phosphorus limitation, is able to generate a biomass concentration of 4.63 g/L with a P(3HB) content of 35.1% [159]. Another example would be the *A. hydrophila* 4AK4 strain that, with phosphorus limitation, achieves a biomass concentration of 16.2 g/L with a P(3HB-co-HHx) content of 51.5; using, in this case, lauric acid and glucose as substrate [160]. In addition, from these PHAs, *A. hydrophila* 4AK4 is also able to synthesize P(3HV) from an undecanoic acid medium, achieving yields of 5.01 g/L biomass with 45.2% PHA accumulation [161]. As can be deduced, the variability of the type of PHA accumulated, as well as the yield with *Aeromonas* will depend on the strain used, the substrate, and fermentation conditions such as the limiting nutrient.

Table 3 summarizes the main fermentation conditions, the yields and the type of PHA obtained with each one of the reviewed microorganisms.

As shown in this section, there are many types of PHA-producing microorganisms, and each requires a different medium and fermentation conditions. The use of one or the other will depend on the objective, the type of PHA sought, and the type of waste to be recovered (in the case of using a waste medium, such as biogas digestate, for example).

Table 3. Summary of microorganisms producing different types of PHA, fermentation conditions, and yields achieved.

Strain	Fermentation Conditions	Yield	Type
Cupravidus necator DSM 545 [147]	-Mix of volatile fatty acids. -pH 7 -C/N 6	1.5 g/L of biomass and 56% of PHA accumulation	PHBV with 91–96% of hidroxybutyrate content.
Bacillus megaterium LVN01 [153]	-Biogas digestate. -pH 7 -30.8 °C	0.360 g/L of PHA and 0.133 g/L of DCW.	PHBV
Haloferaxmediterranei [156]	-Phosphate limitation (KH_2PO_4). -37 °C	0.95 g/Lwith 15.6% dry biomass	PHBV
Pseudomonas oleovorans DSM 1045 [157]	-Synthetic medium (8.4 g/L glucose + 5.7 g/L sodium ammonium phosphate +35.44 mM phosphate buffer) -30 °C	1.7 g/L of biomass	mcl-PHA
Aeromonas hydrophila 4AK4 [158–161]	-Sodium gluconate -P limitation	4.63 g/L of biomass with 35.1% of PHA	P(3HB)
	-Lauric acid + glucose -P limitation	16.2 g/L of biomass with 51.5% of PHA	P(3HB-co-HHx)
	-Undecanoic acid	5.01 g/L of biomass with 45.2% of PHA	P(3HV)

3.3. Physico-Chemical Properties of Bioplastics and Their Applications

PHA biopolymer is the focus of this section; nevertheless, it is essential to mention other bioplastics for its suitable classification. Bioplastics can be classified into distinct categories based on their synthesis, which can be microbiological or involve a synthetic polymerization process. This classification is represented in Figure 5.

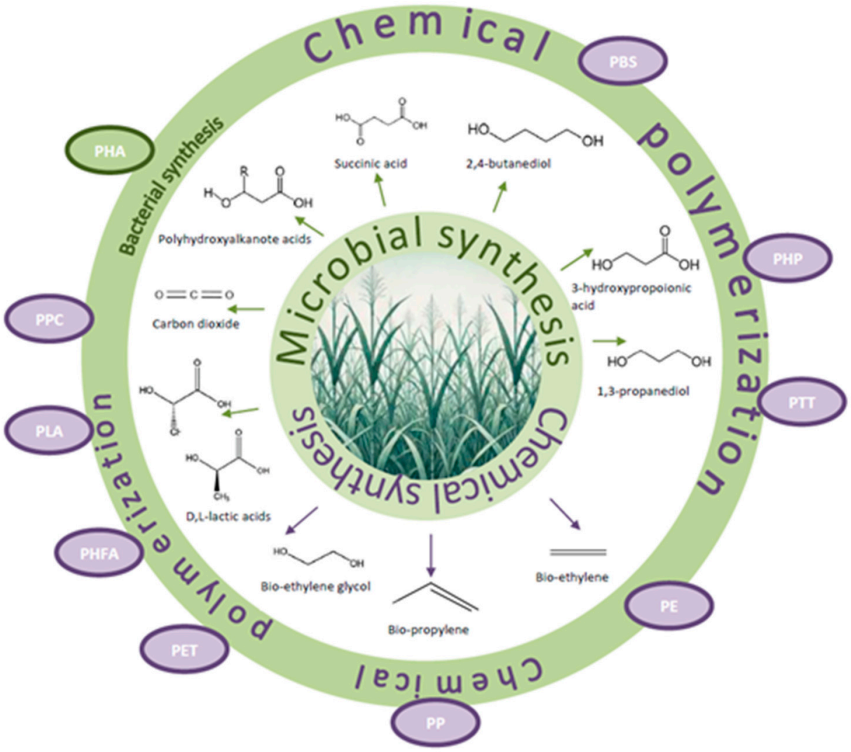

Figure 5. Bioplastic polymers, and their monomers, produced by microbial fermentation combined with chemical synthesis. Modified from Chen and Patel [162].

These monomers have been used to produce a range of bio-based plastics, including polyhydroxyalkanoates (PHAs), polylactic acid (PLA), poly(butylene succinate) (PBS), polyethylene (PE), polyethylene terephthalate (PET), polypropylene (PP), poly(propylene carbonate) (PPC), and poly(trimethylene terephthalate) (PTT) [163,164]. Apart from PE, PP, PTT, PET, and bio-based polyamides, all the other bio-based polymers mentioned above are biodegradable to varying degrees. Moreover, PHA is a unique biopolymer that can be fully obtained from the biological transformation of a residual carbon source, i.e., other biopolymers require a chemical synthesis step.

Another bioplastic not shown in Figure 5 is biopolyurethane, which can be synthesized from the bioproduced precursor 2,3-butanediol. Nowadays, the biological conversion of renewable carbon sources with bacteria, such as *Klebsiella pneumoniae* or yeast is a sustainable method to produce 2,3-BDO. Different carbon sources, such as glucose, glycerol, molasses, and lignocellulose hydrolysate, have been used [165]. Furthermore, their biosynthesis is currently being investigated as part of the European PROMOFER project [28].

Because they are bio-based and biodegradable, PBS, PHA, PLA, and PPC have been proposed as environmentally friendly, sustainable, less fossil-fuel-dependent, and low-carbon fingerprint bioplastics for future applications [164,165]. The physicochemical properties of each bio-based and biodegradable one are described in detail below.

3.3.1. Polyhydroxyalkanoates (PHAs)

Polyhydroxyalkanoates (PHAs) are a family of polymers that predominantly consist of linear polyesters derived from 3-hydroxy fatty acid monomers. In these polymers, the carboxyl group of one monomer forms an ester linkage with the hydroxyl group of another. The diversity of PHA polymers and their wide range of applications stem from variations in chain length and composition, as well as the potential to modify their reactive substituents. Within the PHA family, poly(3-hydroxybutyrate) [P(3HB)] has been the most extensively studied due to its widespread occurrence. Additionally, P(3HB) copolymers can be synthesized by co-functionalizing substrates, incorporating monomers such as 3-hydroxyvalerate (3HV) or 4-hydroxybutyrate (4HB) into the polymer chain. This enhances the material's properties and broadens its applications [135].

PHAs can be classified based on the number of carbon atoms in the monomer, resulting in the categories of scl-PHA, medium-chain-length PHA (mcl-PHA), and long-chain-length PHA (lcl-PHA). These correspond to 3–5, 6–14, and 15 or more carbon atoms, respectively [166].

To date, more than 90 distinct types of PHAs, comprising a variety of monomer units, have been identified and documented [167]. The following table (Table 4) provides an overview of the main types of PHAs that have been the subject of study, showing their main physio-chemical properties, applications, and other considerations such as their biodegradability.

Table 4. Overview of some types of PHAs that have been studied, together with a description of their characteristics and main applications.

PHA Type	Description	Physio-Chemical Properties	Applications	Other Considerations
scl-PHA (Short-chain-length PHA)	PHA with monomers of 3 to 5 carbon atoms [168].	The monomer, P(3HB) is highly crystalline [169] brittle and high melting temperature [135].	Packaging, fiber, biomedical [168].	High biodegradability [168].

Table 4. *Cont.*

PHA Type	Description	Physio-Chemical Properties	Applications	Other Considerations
mcl-PHA (Medium-chain length PHA)	PHA with monomers of 6 to 14 carbon atoms [168].	In general, are flexible [136] Mechanical strength due to their crystalline parts [170].	Due to their flexibility, they are suitable for food packaging and tissue engineering [136].	Biodegradable and biocompatible [136].
PHB (Polyhydroxibutirate)	PHA homopolymer [162].	Hight crystallinity. Stiffness. Fragile at low temperatures. Sensitive to thermal degradation [171].	Biomedical applications such as matrix for in vitro cell growth, implant patches or sutures [171].	Biodegradable and biocompatible [171,172].
PHBV (Poly(3-hydroxybutyrate-co-3-hydroxyvalerate))	Copolymer. It results from the incorporation of 3 units of 3-hydroxyvalerate (HV) into PHB. [173].	Compared to PHB, it has a lower melting temperature and higher viscosity and flexibility [173].	Tissue engineering [173–177] Disposable items: bags, packaging. Food packaging [178,179].	Biodegradable and biocompatible. Reduced cytotoxicity [180].
PHBH (Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate)	Copolymer resulting from the incorporation of mcl-PHA monomer (poly(3-hydroxyhexnoate)) into poly(3-hydroxybutyrate) [181].	High elasticity, low crystallinity, high elongation at break [181].	Packaging materials [182], coffee capsules, straws, cutlery, shopping bags, fishery items [183].	Biodegradable and non-toxic [183].
PHBVH (Poly(3-hydroxybutyrate-co-3-hydroxyvalerate-co-3-hydroxyhexanoate)	Copolymer that can be produced by recombinant *Aeromonas hydrophila* [184].	Rougher surface and higher hydrophobicity than poly (L-lactic acid) and PHBH. High thermal degradation temperature [184].	Tissue engineering [184].	Biocompatible for several cells: fibroblast [185], chondrocytes [186], osteoblasts [187].
PHP (Poly (3-hydroxypropionate)	scl-PHA [188].	High flexibility, low rigidity [188].	Drug capsules [189,190].	Biodegradable and biocompatible [189,190].

Scl-PHA exhibits a wide range of properties depending on their monomer composition. For example, poly(3-hydroxybutyrate) [P(3HB)] is highly crystalline, stiff, and brittle, with a tensile strength like polypropylene [191]. In contrast, poly(4-hydroxybutyrate) [P(4HB)] is a flexible thermoplastic with tensile strength comparable to polyethylene [191]. Structurally, P(3HB) forms a compact levorotatory helix and is optically active due to the R-configuration of the chiral center in its monomer unit. Its mechanical properties, such as tensile strength and Young's modulus, are like those of polypropylene [192].

Despite the considerable diversity of PHAs and the resulting heterogeneity of their properties, the following table (Table 5) illustrates a comparison of the physical properties of selected PHAs and non-biobased plastics, such as polypropylene (PP) and low-density polyethylene (LDPE), with data gained from references [161,193–196].

Table 5. Comparison of the physical properties of different polymers. LDPE: low-density polyethylene; Tg: glass transition temperature; ME: modulus of elasticity; EF: elongation at fracture; E: elongation at break.

Polymer	Melting Point (°C)	Tg (°C)	ME (GPa)	EF (MPa)	E (%)	Biodegradation
P(3HB)	180	4	3.5	40	5	High rate
P(3HB-co-20 mol% 3HV)	145	−1	0.8	20	50	High rate
P(3HB-co-6 mol% 3HV)	133	−8	0.2	17	680	High rate
P(3HV)	103	−15.8	-	-	-	High rate
P(75.3% 3HB-co-13.1% 3HV-co-11.7% 3HHx)	102.3	−1.8	-	-	-	High rate
P(73.8% 3HB-co-7.6% 4HB-co-18.6% 3HHx)	-	−11.7	0.003	-	143	High rate
Polypropylene	176	−10	1.7	38	400	Slow rate
LDPE	130	−30	0.2	10	620	Slow rate

One of the possible substitutes to avoid dependence on fossil fuels in the manufacture of plastics is PHA, but PHA is currently not cost-competitive with fossil products [197]. PHA polymers have analogous physical and chemical properties to those of common petroleum-based plastics, such as PP or LDPE [193], as shown in Table 5.

P(3HB) was the first PHA to be isolated and characterized. Compared to other synthetic polymers, it has a higher barrier permeability than PE and PP. It is also stiffer and less flexible than PP. It has also good permeability barrier properties compared to polyethylene terephthalate (PET) and polyvinyl chloride (PVC). All these properties make it advantageous for use in various packaging applications compared to conventional polymers [198].

Comparing other properties, PHB shows a better barrier to moisture and oxygen gas than PP and PET, respectively [199]. In general, the properties of PHAs, such as processability, mechanical properties, and UV resistance, are like those of conventional fossil-based polymers such as PP and polystyrene (PS). Depending on the composition of their monomers, the properties and functionalities of PHA vary [200]. Some of the various applications of the different types of PHA are shown in Table 4 of this document.

In terms of biodegradability, P3(HB) is a biopolymer that degrades in a reasonable time when in contact with microorganisms in biologically active environments such as soil, freshwater, etc. Therefore, it is a sustainable alternative to synthetic polymers with which it is compatible [201]. Although PHAs are biodegradable, as indicated in Table 5, it has recently been shown that the biodegradability of P3HB and P3HB/valerate copolymers is highly dependent on molecular weight, processing conditions, and crystallinity [202].

This biodegradability is an advantage over plastics of fossil origin, such as PE, PP, and nylon, which are xenobiotic. The release of these plastics into the environment causes pollution, and their mechanical degradation into microplastics is also an additional problem [203,204]. As mentioned above, PHA can be used in packaging. Most traditional plastics used in packaging are non-biodegradable, such as PE, PP, PS, PVC, or PET. These non-biodegradable plastics are the main source of plastic waste, causing a serious environmental pollution problem. This is a serious global environmental problem known as 'white pollution' [205,206].

However, despite recent advances in bio-based and biodegradable polymers, more research is needed before these biopolymers can fully replace petroleum-based plastics [207].

3.3.2. Other Bioplastics

(a) Poly(lactic acid) (PLA)

PLA can be produced from renewable resources. The carbohydrates extracted from plants (lignocellulosic biomass [208]) or waste materials (brewer's spent grain [209]) are subjected to fermentation, resulting in the production of lactic acid [210]. Polysaccharides from the cell wall of lignocellulosic materials can be converted to fermentable sugars after going through pretreatment and hydrolysis steps [211]. For example, lactic acid can be produced from the fermentation of dextrose, which can be derived from plant starch by bacteria. Examples of agricultural products that are employed in the preparation of PLA include sugar cane, corn, and sugar beet [212]. Also, in their study, Rojas et al. obtained lactic acid from whey under controlled fermentation conditions, achieving lactose consumption levels of 94.6% [213].

It is semi-crystalline if the proportion of enantiomerically pure monomers exceeds 85–88%. At lower purities, the material is amorphous and exhibits a reduced melting temperature. Semi-crystalline PLA exhibits a melting temperature between 170 and 180 °C, with a glass transition temperature between 55 and 60 °C. Furthermore, the properties of PLA are contingent upon its molar mass. In accordance with their respective properties, amorphous, low-molecular-weight DL-PLA is employed in medical applications that necessitate drug release, where good degradability is a requisite. In contrast, high-molecular-weight L-PLA (>100,000 g/mol) is utilized in packaging applications where superior thermomechanical properties are paramount [214,215]. In recent years, research has been conducted as part of the European InnOREX project with the objective of investigating its potential as a substitute for polypropylene [216].

Lactic acid, the monomer which is employed in the polymerization of PLA, can be obtained through either a chemical or a biotechnological process. The former is based on the reaction of acetaldehyde with hydrocyanic acid (HCN) to give lactonitrile, which can be hydrolyzed to lactic acid. Another type of reaction is based on the high-pressure reaction of acetaldehyde with carbon monoxide and water in the presence of sulphuric acid as a catalyst. This method of production has the disadvantage that the lactic acid produced is a mixture of D and L, optically inactive lactic acids [217,218].

In contrast, biotechnological production is based on the fermentation of carbohydrate-rich substrates by microorganisms, resulting in the formation of optically active D(+) or L(+) enantiomers, which is an advantage over chemical production. The microorganisms employed are preferably thermophilic, capable of rapid and complete fermentation of inexpensive substrates with minimal nitrogenous nutrient supplementation. They thrive in conditions of low pH, exhibit minimal biomass production, and generate negligible by-products. The most utilized bacterial genera for production are *Lactobacillus*, *Carnobacterium*, *Leuconostoc*, *Pediococcus*, *Streptococcus*, *Tetragenococcoccus*, *Lactococcus*, *Vagococcoccus*, *Enterococcus*, and *Aerococcoccus*. However, it is also possible to employ fungal strains such as Rhizopus that are capable of producing L(+) lactic acid [219].

(b) Poly(butylene succinate) (PBS).

PBS is predominantly produced by polycondensation of succinic acid (SA) and 1,4-butanediol (BDO). It can be produced either by monomers derived from petroleum sources or by biological (bacterial) fermentation [220]. Regarding biological synthesis, BioAmber Inc. started the commercialization of bio-based succinic acid in 2010. Then, in 2016, Novamont S.p.A. started the production of 1,4-butanediol from renewable resources [221].

PBS is a semi-crystalline polymer that exists in two crystalline forms, designated α and β. The α-form is the most prevalent and forms under unstressed conditions, whereas the β-form emerges under stressed conditions and can revert to the α-form when the stress is

removed [222–226]. Its melting point is between 90 and 120 degrees Celsius. Furthermore, it exhibits excellent thermal stability, enabling processing in extrusion and injection molding applications across a temperature range of 160 to 200 °C [227].

In terms of applications, bio-based polybutylene succinate (PBS) has a wide range of potential uses in various fields, including:

- Agricultural mulch and packaging films: Its biodegradability and flexibility make it suitable for use in agricultural and packaging applications [228–230].
- Disposable tableware and utensils, including tableware [231].
- Drug encapsulation and orthopedic applications [232,233].

Their use has been compared to that of plastics derived from fossil fuels. Aliotta et al. [234] investigated PLA/PBS-based blends both in the laboratory and on a semi-industrial scale and showed subsequent plasticization migration [234,235]. The films produced showed higher flexibility, elongation at break, and tear strength than pure PLA, and their performance was competitive with fossil-based polyolefins. PBS has a broad temperature range and can be processed similarly to polyolefins within the range of 160 °C to 200 °C [236].

(c) Poly(propylene carbonate) (PPC)

PPC is a copolymer of carbon dioxide (CO_2) and propylene oxide (PO). It is a thermoplastic aliphatic polymer with high barrier properties. Also, it is flexible and biocompatible [237]. Its thermal stability is low [238], and it is an amorphous polymer with low intermolecular forces, so its mechanical properties are poor [239]. In fact, in the literature, several studies have been carried out to enhance the thermal and mechanical properties of the PPC by physical or chemical means, resulting in modified PPC composites with improved properties [240].

Current applications include packaging films, foams and controlled drug release systems, high barrier materials including cryogenic packaging applications, and agricultural films [241,242].

3.4. Economic Aspects and Technology Barriers

Biodegradable bio-based polymers are potential candidates for the replacement of traditional fossil-based polymers, due to the consideration of pollution and sustainability [243].

The production of polyhydroxyalkanoates (PHAs) from waste originating from the agri-food industry and through various microorganisms is a promising and sustainable alternative to petroleum-derived plastics [244]. However, a significant challenge confronting the widespread adoption of these biopolymers is the high cost associated with their production. A recent study by Pérez et al. [245] revealed that PHA can be produced from biogas at a competitive market price (8.6–8.8 €/kg PHA) in medium-sized waste treatment plants, irrespective of the economy of scale and technological readiness level. The study also revealed that the optimal scenario for the valorization of biogas within a waste treatment plant involves the use of cogeneration units powered by biogas, which would result in lowering PHA market prices by almost half (4.2–4.6 €/kg PHA). Bioplastics have also been shown to exhibit a reduced energy consumption of 57 MJ/kg for their production compared to traditional plastics (77 MJ/kg) [246]. However, as previously referenced, the manufacturing costs of bioplastics remain high. It is estimated that the price of biopolymers is between 2 and 5 times higher than that of conventional plastics [15,247], ranging from EUR 2 to 6 per kg (depending on the quantity) compared to EUR 1–2 per kg for traditional plastics [248–250]. The production cost of PHA depends on three main factors, as reported by Raza et al. [203]: (1) the cost of the fermentation substrate; (2) the

volumetric productivity of the process (g/L/h); and (3) the percentage of PHA content in the cell. It is estimated that at a scale of 100 kt, production costs range between EUR 2.5 and 6.5 per kg, depending on the microorganism that produces the PHA [251]. However, it is notable that the production costs of certain plastics, such as polyethylene (PE), are less than EUR 1 per kg [203].

The economic viability of current PHA production remains a significant challenge when compared to fossil fuel-derived plastics, which are typically used in high-volume, low-cost applications. Given that raw materials for the manufacture of PHAs constitute a key component of costs, waste, or low-value substrates acquire great relevance and continue to be the main focus of numerous studies and development initiatives around PHAs. Areas for improvement have been identified in the fermentation processes, the scalability of these processes, and the subsequent processing [252]. The utilization of waste materials such as milk, wine, wood, and beet molasses as substrates for the fermentation of microorganisms capable of synthesizing PHAs has been demonstrated to reduce costs and minimize the environmental impact through the reuse of waste products [244].

The production of bioplastics from food loss and waste (FLW) is a viable alternative. However, the assessment of FLW is currently limited by its low technological maturity and significant logistical challenges. This requires a tailored approach to process design and implementation, considering regional specificities, feedstock availability, and regulatory and infrastructural frameworks.

A commendable example of strategies that aspire to rectify economic bottlenecks for PHA commercialization is evident in the PROMOFER project [28], funded by the EU Commission. The objective of the project is to optimize the fabrication of bioplastics by utilizing waste as a primary constituent and by boosting pretreatment and extraction processes to maximize the yield of polyhydroxybutyrate (PHB) production. The PHB obtained will be utilized in flexible packaging as biodegradable coatings with specific properties, and in agriculture as biodegradable geotextile nets.

From a regulatory perspective, the use of FLW to produce bioplastics is complex as it is necessary to establish clear end-of-waste criteria for its application. This highlights the importance of further research to ensure that the valorization of FLW is a sustainable, safe, and transformative initiative capable of revolutionizing both the food system and the plastics economy without contributing to the problem of plastic pollution [253].

The Directive (EU) 2019/904 of 5 June 2019 on the reduction in the impact of certain plastic products on the environment [254] advocates for plastic recycling and the reuse of plastics. Thus, starting in 2025, beverage bottles must contain at least 25% recycled plastic, and the amount of waste from single-use plastic products equal to 77% of such single-use plastic products placed on the market must be recycled. Nevertheless, the directive points out the prohibition of single-use plastics on the market by Member States. The directive also relates to the biodegradability of plastics but does not mention the introduction of bioplastics on the market.

4. Conclusions

The generation of agri-food waste is a major global problem with significant environmental and economic impacts. Nowadays, European and international project initiatives play a key role in developing technologies for the valorization of agri-food waste and contribute to the circular economy model. The biotransformation potential of these wastes into volatile fatty acids (VFAs) and bioplastics has been reviewed, with special attention given to poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV), a potential polyhydroxyalkanoate (PHA) bioproduct with mechanical properties analogous to those of current fossil-based plastics.

Waste such as whey, potato peels, and brewery bagasse have demonstrated viability as sources for their valorization into a tailor-made VFA solution rich in valeric and propionic acids. Co-digestion of different wastes can also enhance the production of these specific fatty acids. High transformation yields under controlled fermentation conditions can be achieved, especially for whey, which can reach 36% and 25% yields of propionic and valeric acids, respectively, under common dark fermentation conditions (pH = 6, T = 35 °C, OLR = 3 g COD/(L-d), and SRT = 10 d). The use of additives, such as riboflavin and alkylpolyglucoside, can further improve the concentrations of propionic and valeric acids in the VFA solution. Efforts must, therefore, be made to produce a tailor-made VFA solution as an intermediate carbon source, which is a critical factor in its biopolymerization into PHBV, a biopolymer with improved mechanical and thermal properties.

Biopolymerization of PHA family polymers can be achieved with various microorganisms. However, one type of PHA can also be produced by different microorganisms. In the case of PHBV, *Cupriavidus necator* seems to achieve better yields in terms of PHBV accumulation and concentration (1.5 g/L of biomass and 56% PHA accumulation).

Polyhydroxyalkanoates are a promising alternative to conventional plastics and other bioplastics because they have a unique versatility in terms of mechanical and thermal properties. They can be tuned by polymerization with different co-substrates, allowing PHAs to be tailored to the required application. Furthermore, they are the only biopolymer that can be obtained entirely from the biological transformation of a residual carbon source. This biopolymer already shows better biodegradability, impermeability, and oxygen gas barrier properties than conventional plastics.

Future work should focus on reducing the cost of bioplastic production by improving process efficiency, developing more accessible technologies, and promoting the integration of these waste valorization systems into a wider industrial network. Bioplastics require less energy consumption than non-biobased plastics for their production; however, the price of biopolymers ranges between two and five times that of conventional plastics. Administrations may also promote the introduction of bioplastics on the market through their directives. This would reduce the economic constraints associated with fossil-based plastics and make bioplastics more affordable for the market. Overall, this will maximize positive environmental impacts and create new economic opportunities.

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