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Review

Bioprocessing of Waste for Renewable Chemicals and Fuels to Promote Bioeconomy

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Abstract: The world's rising energy needs, and the depletion of fossil resources demand a shift from fossil-based feedstocks to organic waste to develop a competitive, resource-efficient, and low-carbon sustainable economy in the long run. It is well known that the production of fuels and chemicals via chemical routes is advantageous because it is a well-established technology with low production costs. However, the use of toxic/environmentally harmful and expensive catalysts generates toxic intermediates, making the process unsustainable. Alternatively, utilization of renewable resources for bioprocessing with a multi-product approach that aligns novel integration improves resource utilization and contributes to the "green economy". The present review discusses organic waste bioprocessing through the anaerobic fermentation (AF) process to produce biohydrogen (H_2), biomethane (CH_4), volatile fatty acids (VFAs) and medium chain fatty acids (MCFA). Furthermore, the roles of photosynthetic bacteria and microalgae for biofuel production are discussed. In addition, a roadmap to create a fermentative biorefinery approach in the framework of an AF-integrated bioprocessing format is deliberated, along with limitations and future scope. This novel bioprocessing approach significantly contributes to promoting the circular bioeconomy by launching complete carbon turnover practices in accordance with sustainable development goals.

Keywords: organic waste; biomethane; biohydrogen; waste biorefinery; volatile fatty acids

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1. Introduction

Our need for a waste-derived bioeconomy culminates from multiple areas of concern. These include, firstly, the well-documented non-renewability of our principal sources of energy and industrially important chemicals, i.e., petroleum-based products, and their effects on the environment and climate change [1]. Secondly, the drastic increase in waste production (50 million dry tons in the US alone in 2017) and unsustainable disposal strategies, such as landfilling or incineration [2]. Thirdly, to meet the increased demand for alternative renewable products and chemicals, it is important to develop sustainable methods and processes [3]. Taking a waste-to-treasure approach towards producing environmentally benign solutions can be sustainable only if an economy is modeled around it, with the potential to create a green world and solve problems, such as food security. Several types of organic waste that can be used as renewable feedstock include food waste, agricultural, forestry, and animal waste, and sludges [4]. The conversion of different kinds of biomass to produce energy has been known for a long time, but the biochemical conversion of waste for this purpose has gained importance in the last century [5,6]. Typically, wastes are categorized based on composition, source of production, targeted product recovery or consumption [7]. Organic wastes with a high transformation potential can be used in AF to produce liquid biofuels, gaseous fuels, and multiple renewable platform chemicals. Sugars, fats, and similar compounds in wastes can be directly converted to useful renewable chemicals because of their use in industrially important materials, such as paints, lubricants, adhesives, etc. Food-grade wastes are exploited for their use in flavoring and preservatives. Lignocellulosic materials, on the other hand, have been explored for their potential in biofuel production [8].

Anaerobic fermentation (AF), or anaerobic digestion of organic waste, produces biogas as a major product and contains 40–60% methane (CH_4). Due to the high feasibility of AF, biomethane can be produced from a variety of waste sources including crop residues, organic fractions of municipal solid waste, and wastewater sludge [9,10]. Anaerobic fermentation is also a practical feasible method for biohydrogen production from waste including food waste; food wastes are the most suitable because of their high degradability and rich carbohydrate content [11]. Biofuels are known to substitute conventional fuels. The European Directives stipulated that up to 10% of gasoline and diesel could be substituted by biofuels by 2020 [12]. Production of biofuels from municipal solid waste and the household and biomass fraction of industrial waste is an important part of the Sustainable Development Goals (SDGs) agreed upon by the UN in 2015. Lignocellulosic feedstock and edible waste are the most important sources being studied to produce liquid biofuels [13]. Bioethanol and biobutanol are the major candidates for the replacement of traditional fuels. Biobutanol is an excellent substitute for gasoline due to its high energy content, low volatility and high industrial use as a solvent [14]. Organic carbon derivatives from formic acid, acetic acid, and propionic acid to decanoic acid are called VFAs and are products of the acidification phase of AF [15,16]. These short and medium chain fatty acids can further be used as platform chemicals to produce plasticizers, fertilizers and so on [17]. Mainly produced through the fermentation of food and mixed organic wastes, the demand for these chemicals in the food, pharma, textile and other industries is significant with an average annual growth rate of 5% [6,18].

Waste collection, pre-treatment, bioprocessing, and purification or downstream processing of bioproducts/fuels are energy and cost-intensive, while traditional processes, such as incineration or composting, are more economically friendly. Optimization of these processes is an active area of research to enhance biobased products' marketability [19]. However, on a brighter note, a recent survey by the UK Government noted that the EU bioeconomy had already triggered a turnout of nearly 2 trillion euros, with an estimation of a 1:10 euro value addition by 2025. This not only accounted for 9% of total employment in the EU, but also forecasts great investment opportunities in the Green Investment sector, given the availability of waste feedstock. This clearly demonstrates that what has already been achieved in the sector holds great opportunities for the bioeconomy, and more focused efforts will ensure an active promotion of the same. In India, it was estimated that the solid waste produced would rise to 436 MT by 2050, which would be worth USD 13 billion by 2025 [20].

On the other hand, the global population will reach nine billion by 2050, which would require a 50% increase in both food and energy production, according to the United Nations report (EUSBSR, Five principles for a sustainable economy, 2017). Meeting fundamental necessities while reducing negative environmental effects is the key challenge. Bioprocessing of waste offers a suitable solution to find and utilize resources alternative to the conventional ones, while reducing the environmental impact and providing waste management solutions with the production of high-value products. Today, this field can integrate into a variety of industries, from energy, construction, biofuels, bioplastics, textiles, and food. However, it should also be noted that all bioeconomic processes are not sustainable. There are renewable sources that have already been overexploited, and their further use must be minimized. A sustainable bioeconomy, hence, requires that we find sustainable sources and build sustainable processes around them, i.e., develop technologies that maximize product recovery from waste and at every step contribute to a circular economy to reuse and recycle materials [21,22]. It also requires that we make decisions that are economically workable and contribute to the social, economic, and environmental upliftment of rural, urban, and global societies. This study emphasizes the potential of biogenic waste/wastewater as an alternative feedstock for renewable chemicals and fuels to establish a bioeconomy. The potential of organic waste-driven production for gaseous fuels (biohydrogen, biomethane and biopropane/hythane), and renewable chemicals (volatile fatty acids and medium chain fatty acids) is discussed. An exploration of the current state of the bioeconomy for each of these products, their diverse sources and productivity trends, is covered. Furthermore, the scope of biorefinery establishments along with limitations and challenges of waste bioprocessing that stand to build a sustainable biobased economy are deliberated.

2. Feedstock and Optimization Strategies

2.1. Organic Waste

According to the food and agricultural organization, one-third of global food waste is through losses in the supply chains. The EU countries alone produced 89 MT of food waste (FW) in 2012 [23]. These FW are improperly disposed, thereby increasing contributions to landfills or incineration, causing air pollution. Alternatively, FW could be subjected to AF to produce biogas and VFAs [24]. Though the composition of VFAs varies based on source and origin, food wastes are known to be rich in organic content along with required nitrogen and phosphorous contents. This makes them highly supportive of microbial growth, and hence, can be exploited for bioprocessing. Studies demonstrated the potential of FW as a substrate through its bioconversion to VFAs, with an excellent yield by yeast and acetic acid bacteria (AAB) fermentation [25]. Agricultural waste also falls under the category of mixed organic residues. These residues have been subjected to AF and extensively used in the European nations to recover multiple benefits, including biogas, renewable energy, and fertilizer. More than 15,000 units for biowaste conversion are operational in the EU today [26,27].

2.2. Optimization Strategies

As discussed above, various organic waste derived from agricultural, food, vegetable, or fruit and brewery can be a potential feedstock for biobased products via AF. AF is a series of interdependent processes that terminate with methanogenesis; biomethane has been the focus of many studies using organic waste as substrate (Figure 1). However, owing to the effect of methane on the global environment as a major greenhouse gas, the role of hydrogen and reaction intermediates, such as VFAs, have come into the limelight [28]. Since methane is a natural consequence of the fermentation process, obtaining VFA requires arresting the process at the acidogenesis stage of AF [1]. This involves the following stages: (i) choice of the substrate, (ii) mixed consortia vs. pure cultures and medium composition leading to different ratios of acidogenic products, (iii) non-specificity of products, i.e., selecting a product and maximizing its yield from multiple VFAs obtained, and (iv) product feedback inhibition. These stages are further described below.

(i) Choice of substrate: it is generally observed that substrates with high sugar content, for instance, brewery trub, show higher stoichiometric methane production, and hence, higher VFA production, than that of more complex fibers, such as fruit mass or tree waste [29]. A recent survey conducted on research into AF for VFA production between 2010 and 2020, showed that approximately 50% used sludge and food waste while 6.3% used lignocellulosic biomass as feedstocks [30]. Food wastes are considered the best substrates for VFA production as they are rich in materials indispensable for microbial metabolism, such as organic matter (15–20% total solids). Animal excrement was found to have a higher amount of nitrogen and phosphorus compared to carbohydrates [31].

Lignocellulosic biomass has good amounts of carbohydrates and is gaining importance as feedstock for biorefineries. To increase yield from lignocellulosic biomass, different optimization strategies have been suggested, one of the most important being pretreatment. The main goals are to remove useless inert material, reduction in substrate size, and extraction of simpler compounds via pretreatment by breaking lignin protection. Physical methods achieve these via the mechanical deconstruction of biomass such as milling, while chemical methods use solvents for the solubilization of complex fiber material. Biological methods are the most environmentally friendly as they use natural enzyme hydrolysis to achieve pretreatment, but their kinetics are terribly slow [1]. However, substrate overloading and product inhibition soon limit acidogenic yield. This is well-studied: cells in the broth are forced to balance the acidification of the broth and are drawn away from metabolism, which lowers yield. (ii) Mixed consortia are preferred as they digest different complex feeds and ensure a diversity of metabolic pathway utilization, opening up the possibility for co-fermentation [16]. (iii) Non-specificity of products, or using multiple substrates, helps maintain the C/N ratio which in turn can aid the growth of acidogenic bacteria [29,32]. Varying the pH was shown to improve yield in many cases [32]. (iv) Acidification of the medium results in process feedback inhibition because microorganisms are forced to maintain pH homeostasis, resulting in an acid shock [33].

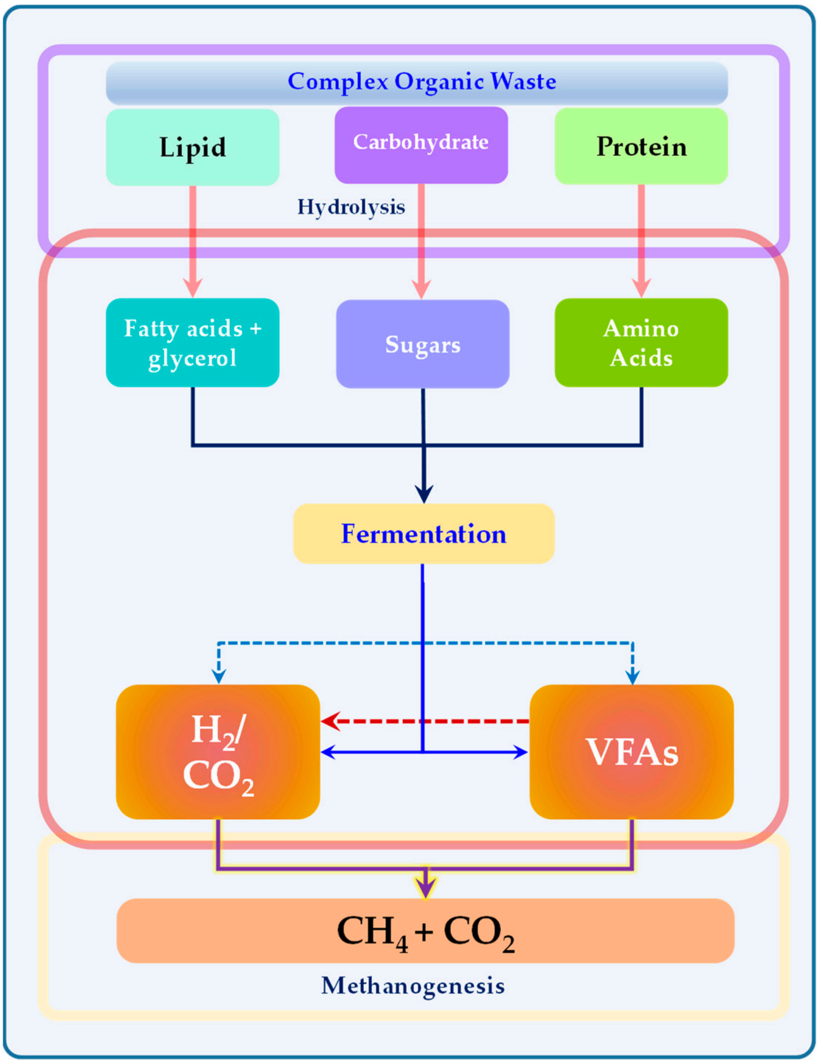

Figure 1. Schematic representation of anaerobic fermentation stages.

3. Anaerobic Fermentation or Dark Fermentation

3.1. Biohydrogen

A clean gaseous renewable fuel biohydrogen (bioH_2) with a high energy density (approximately 142 kJ/g) can be derived from biomass or organic waste (a renewable source) [33,34]. Biohydrogen is considered as one of the most promising alternative fuels. This renewable energy source has the potential to replace fossil-based oil, gas, and to a considerable measure, electricity [35]. In recent years, interest in the production of dark fermentative biohydrogen has increased by utilizing various feedstocks including biogenic waste/wastewater employing mixed and pure culture [36,37]. Other than biological processes, several methods have been employed to produce H_2, including water electrolysis, CH_4 reforming, coal gasification, and natural gas oxidations. However, these processes rely on the utilization of non-renewable resources and demand high temperatures (>700 °C), rendering them non-sustainable and inefficient. As a result, interest has grown in biological routes, such as photo and AF, and its integration with other processes to produce renewable hydrogen (biohydrogen) using inexpensive, inorganic and carbon-rich waste and wastewater as substrates [38]. Moreover, these methods have low operating temperatures and pressure requirements. Microorganisms are the key players in bioH_2 production [39]. Microorganisms in nature exist in communities that dynamically change and involve syntrophic interactions in a productive ecosystem. Both pure and mixed cultures have advantages and drawbacks. The bioprocess is limited to using pure culture systems in biotechnological applications [33,40]. Individual microorganisms' physiological and metabolic capabilities are constantly being explored using a range of methods that help regulate the bioprocesses that are performed by self-selecting microbiomes [41]. In this direction, the pretreatment of mixed culture plays a key role in targeting the product of interest. Mixed microbial cultures, in particular anaerobic sludge, are more practical and effective sources of inoculum. Mixed culture offers various advantages including capacity to endure harsh environmental conditions, availability in nature and flexibility to accommodate a variety of substrates [42,43]. A mixed culture is composed of both hydrogen-producing and consuming microorganisms (i.e., homo-acetogens and methanogens). Hydrogen-consuming microbes hamper the biohydrogen production process. Therefore, to increase biohydrogen production, it is necessary to suppress or inhibit hydrogen-consuming bacteria, particularly methanogens, in mixed cultures [5].

Targeting a higher yield of bioH_2, an effective inoculum pretreatment strategy was developed to suppress methanogens in the mixed culture. Different pretreatment methods, including chemical, physical, and others, are employed to suppress methanogens with simultaneous selective enrichment of bioH_2-producing bacteria in the mixed culture. It is crucial to employ an effective pretreatment method to enhance bioH_2 producers and reduce its consumer (methanogens) in the mixed culture. With this aim, several pretreatment methods are employed, including chemical (acidic, alkaline), physical (heat shock, ultrasonic, microwave), and others (enzymatic). Enriching phylogenetic groups of microbes in mixed culture applications can accelerate substrate uptake to produce metabolites. However, the challenge that must be overcome is the theoretical yield. To address this issue, the production of biohydrogen has been integrated with other processes in a biorefinery structure to maximize the system's energy output. Recent design and engineering of the synthetic microbial consortium have become a significant avenue in biotechnology [44,45]. A synthetic consortium could be composed of self-selecting microbiomes, pure cultures, genetically modified organisms, or wild-type organisms. The motivation to develop a synthetic microbial consortium is to overcome the physiological limitations that exist in the microorganisms currently used in the bioprocess [44–46].

Apart from these processes, microbial electrolysis cells (MEC) is the latest innovative technology developed for biohydrogen production where the electrochemical components of cells are combined with fixed-biomass anaerobic bioreactors [47,48]. In MEC, organic matter is decomposed to form protons, electrons, and CO_2 by biofilm formed on a solid electrode by electrochemically active bacteria. Transfer of electrons to the cathode from the anode is achieved, while protons are allowed to migrate to the catholyte from the anolyte to produce biohydrogen on the cathode through the reduction of protons in the catholyte and electrons on the cathode [49,50]. As this process is not spontaneous in nature, external power is supplied throughout the process. Recently, technological advancements have enabled application of bioengineering, genomics, and computational tools for enhancing biohydrogen production [51]. Strategies such as use of nano catalysts, integration of processes (physical + chemical + biological), and application of ultrasound irradiation during pretreatment process significantly improve the yield of bioH_2.

3.2. Biomethane

Biomethane is a well-known renewable natural gas with distinct names and comes from organic waste bioconversion through anaerobic digestion (AD). AD is a biological process that occurs through four steps and produces biomethane as an end product [52,53]. The process begins with the breakdown of complex organic polymers into monomers, such as amino acids, fatty acids, and sugars. Further, these monomers are transformed into VFAs (acetate, butyrate, and propionate) by fermentative bacteria (acidogens). Finally, VFAs are converted to biomethane (CH_4) by methanogens. The AD process can potentially break down a variety of feedstocks, including lignocellulosic feedstocks, food waste, and agricultural and livestock wastes to produce biomethane. However, the methane content in the biogas that evolves during AD greatly varies with respect to the nature of the substrate and operating conditions being employed. For instance, compared to lignocellulosic biomass which yields 330 mL CH_4/g VS (volatile solids), a higher methane yield of 450 mL CH_4/g VS can be produced from a substrate rich in sugar and starch [54]. A relatively lower biomethane output is due to the complex structure of lignocellulosic biomass, which makes it particularly resistant to anaerobic breakdown. Due to the biomass's recalcitrant structure, commercial production of biomethane from lignocellulose is eventually constrained. Increasing surface area, removing lignin, and reducing cellulose crystallinity are necessary pretreatments for lignocellulose biomass to overcome this barrier. Various pretreatment methods have been developed to overcome the limitations caused by the recalcitrant structure of biomass. Any feedstock that contains organic matter has good potential for biogas production. Apart from lignocellulosic (including energy crops) and industrial biogenic waste, sludge and settling wastewater can be used as renewable feedstock. Using these as feedstocks rather than leaving them as waste has benefits for both the economy and the environment. Renewable natural gases emit less CO_2 compared to fossil-derived natural gas. This is because the CO_2 is either restored using energy crop plants or it is CO_2 that would otherwise be emitted by waste. However, from an environmental perspective, renewable natural gas (biomethane) poses the same environmental risks as fossil-based natural gas. Upon burning, it emits particulate matter, carbon monoxide, sulfur dioxide, nitrogen oxide, and hydrogen sulfide into the environment, which are all long-lived greenhouse gases. Despite the environmental risks, biogas (biomethane) is currently being produced at a large scale, which has significant advantages for distribution and consumption in the grid infrastructure and for appliances already in place, making it a promising alternative heat and energy source that does not require initial capital investment from consumers. Other advantages include the easy transportation of gases over long distances with minimal energy requirements. For example, areas with cheap, plentiful biomass may readily be connected to industrial and residential demands. In one study, it was found that biosolids in US wastewater alone could provide feedstock for enough biogas to meet 12% of the country's national demand for electricity [55]. It should be emphasized that biogas must first be purified to be utilized as fuel. Gas upgrading is the process of removing traces of water, carbon dioxide, hydrogen sulfide, and other substances to transform the gas closer to fossil-based natural gas. Biogas upgradation significantly increases the methane content to at least 90%, enabling the gas to be distributed to customers using existing infrastructure and everyday appliances. Moreover, electricity generated from high quality biogas is extremely advantageous for the development and preservation of the environment [56,57].

3.3. Bio-LPG (Bio-Propane)

Bio-propane, an analog of bio-LPG (bio-liquid petroleum gas) is a sustainable alternative to its fossil fuel counterpart [58]. With a low carbon-to-hydrogen ratio compared to coal and oil, LPG burns clean and emits significantly less CO_2 per unit of heat produced. This results in significant carbon savings [59]. Mainly used for domestic consumption and transportation, LPG consists of propane as its chief component, occupying third place worldwide for its use as a transportation fuel [60]. Propane is attractive due to its easy transitions between the gaseous and liquid phases at ambient conditions. This feature makes it simple to separate from the liquid-based biotechnological process as a gas [61]. Bio-propane can be produced in massive quantities from waste feedstocks, such as food waste, farm waste, and sewage, by integrating different processes in a biorefinery approach. Biomass-derived fermentation originated from long-chain fatty acids and VFAs can be precursor molecules to produce both liquid and gaseous hydrocarbons using a variety of chemistries. The use of these biobased precursor molecules will become more significant when separated from the mixture/fermenting media. The separation procedure, however, is challenging and increases production costs by up to 40% [29,62].

Bio-propane is produced during the manufacturing of biodiesel as a by-product. Bio-propane is a drop-in biofuel of fossil propane, an advantageous aspect for entirely replacing fossil propane with sustainable bio-propane [58]. Initially combined with a mixture of low-value fuel gases due to being a byproduct, the full potential of using bio-LPG/bio-propane was realized in 2017 when Finland-headquartered Neste extracted Hydrogenated Vegetable Oil (HVO) bio-propane from its HVO plant in Rotterdam, Netherlands [58]. At present, two promising methods of bio-LPG production as a product are known, namely, hydrotreatment of bio-oil and gaseous conversion and synthesis of cellulosic organic wastes, of which the bio-oil method has been commercialized, while the latter is in the demonstration stage.

While microbes can produce C_2 and C_3 hydrocarbons, their yield and concentration can be higher with naturally occurring microbes due to their better environmental adaptation. The production of propane in marine sediments is a result of microbial synthesis, indicating microorganisms' capability for utilizing various substrates with different approaches [30,59]. A new avenue to bio-LPG has just been offered via synthetic biology. Even though earlier genetically modified bacteria produced a significant amount of propane, the toxicity induced by high propane concentrations faced substantial difficulties for industrial biotechnology [31,32]. A naturally occurring propane-biosynthesizing bacterium (*Photobacterium* sp. FC4.9) was isolated from sediment. In addition, several genes inside this strain's genome were found to possibly be part of the pathway for propane production [59]. Engineering a synthetic metabolic pathway is another way to produce renewable propane. In *Escherichia coli*, the process that converts fatty acids into cell membranes was interrupted and directed toward the production of propane. A pathway with three essential enzymes was engineered to produce propane: (i) thioesterase to produce butyric acid, (ii) a carboxylic acid reductase to convert butyric acid into butyraldehyde, and (iii) aldehyde-deformylating oxygenase (ADO) [61]. The propane titer can be enhanced by eliminating competing routes, adding a developed version with improved specificity towards short-chain substrates, and integrating a ferredoxin-based electron supply system [32]. Upon using these fuels in a range extender engine, the carbon emissions can be decreased by 10% when using LPG, 20% when using CNG, and 99% when using renewable biomethane (in place of CNG) and bio-propane (in place of LPG). Aiming to scale up the process, Neste invested EUR 60 million towards a bio-LPG (bio-propane) production and storage facility in Rotterdam, targeting a production capacity of 30 to 40 k tons of fuel per year [63]. Compared to fossil-based LPG, bio-propane produced via catalytic hydrothermal decarboxylation of butyric acid derived from biomass can be found at affordable prices. Onwudili and Nouwe Edou found that the selling price of bio-propane excluding CO_2 was USD 2.51/kg; further, the price can be significantly reduced to USD 0.98/kg (less than USD 1.25/kg, the current price of fossil LPG) by incorporating the UK's renewable energy subsidies [64].

4. Photo Fermentation

4.1. Photosynthetic Bacteria

Fundamental research has shown that algae and bacteria can produce molecular hydrogen. PF offers several benefits, including stabilizing the organic substrate source with the production of a significant amount of hydrogen (over 90%) in biogas. PF is a light-dependent process driven by phototrophic purple-non-sulfur-bacteria (PNSB) that can effectively convert a wide range of organic substrates (especially short-chain organic acids) into electron donors to produce molecular hydrogen, with greater conversion efficiency under anaerobic conditions. PNSB is one of the first photosynthetic organisms to appear on Earth and are red or purple-colored oxygenic and anoxygenic bacteria. In PNSB, electron and proton transfer reactions transform light energy into biochemically usable energy that meets their energy needs to survive. Light-harvesting pigments absorb light to initiate photosynthesis, followed by the transfer of electronic excitation energy to the reaction center protein [65].

Organic acid degradation by PNSB yields 4–10 mol H_2/mol of substrate [66]. The nitrogenase (MoFe), catalyzes the synthesis of ammonium, and plays a key role in the production of hydrogen by PNSB (Equation (1)). Reduction of protons to molecular hydrogen is helped by nitrogenase occurring in the PNSB (Equation (2)).

$$N_2 + 16\ ATP + 8e^- + 8H^+ \rightarrow 2NH_3 + 16\ ADP + 16Pi + H_2 \tag{1}$$

$$8H^+ + 8e^- + 16\ ATP \rightarrow 4H_2 + 16\ ADP + 16P_i \tag{2}$$

The primary metabolic routes of PNSB include the Calvin–Benson cycle followed by glyoxylic acid cycle, Embden–Meyerhof–Parnas pathway, and tricarboxylic acid cycle [67]. In addition to producing molecular hydrogen, PNSB can also biosynthesize various biochemicals, such as a-aminolaevulinic acid, bacteriochlorophylls a and b and biodegradable thermo-polymers, exhibiting several competitive metabolic pathways [25,26]. GAC is a PNSB-specific metabolic pathway that majorly contributes towards the breakdown of VFAs for biomass production. PF-based bioahydrogen production has been developed and improved significantly with the aid of biotechnology. The production of photo-fermentative hydrogen is influenced by multiple biotic and abiotic factors, including illumination regime, immobilization methods, the use of photo-luminating nanomaterials, genetic engineering, and other techniques. These strategies improve the system performance to produce biohydrogen by PNSB. Further, in a biorefinery approach, the organic acids produced during AF can be used as feedstock to produce biohydrogen by photo-fermentation [68]. This approach aids in overcoming the toxicity caused by the change in pH of the fermenting media towards acidic. The single-stage co-culture technology can also be helpful because it shortens fermentation times and boosts hydrogen productivity [69]. Different studies proposed the integration of dark and photo-fermentation for biohydrogen production. Moreira et al. [70] studied single-stage photo-fermentation co-culturing acidogenic and photosynthetic bacteria of *Enterobacter cloacae* and *Rhodobacter capsulatus* with a bioH_2 evolution rate of 262.77 mmol H_2/L/day. The single-stage study proved advantageous for reduced fermentation duration, making simple handling and improving yields [71].

4.2. Microalgae

Photosynthesis is a natural mechanism that plays a crucial role in keeping life on Earth. By using the sun's energy, algae and plants produce biomass and sugar through photosynthesis, releasing oxygen in the process [71,72]. Microalgae can grow faster than higher plants, supplying a platform for both industrial and academic research. The two photosynthetic complexes, known as photosystems-I and II, function under light with different wavelengths. Importantly, the conversion of light energy into chemical energy is powered by the intake of light energy into photosystems I and II, allowing electrons into the photosynthetic machine [73,74]. During this process, electrons are transmitted to the ferredoxin protein. In green algae, molecular hydrogen is produced when ferredoxin sends electrons to an enzyme hydrogenase during photosynthesis. Thus, the production of this renewable molecular hydrogen (H_2) is light-dependent, and can be a potential source of energy in the future. Recently, researchers demonstrated the possibility of two photosystem-I monomers in plants joining together to form a dimer, further characterizing the chemical structure of this novel type of molecular machine [73].

Synthesis of microalgal metabolites proceeds in a complex metabolic process. Compared to bacteria, fungi, and higher plants, the specific molecular mechanisms or strategies in microalgae are still poorly understood and functionally uncharacterized. However, recent developments in genome sequencing and strain development technologies motivate advanced research on microalgae. Improving the metabolism through genetic engineering can aid to achieve enhanced hydrogen production through microbial photosynthetic pathways with simultaneous microbial bioconversion of organic feedstock [73]. For better understanding, several potential strains, including *Scenedesmus obliquus*, *Chlamydomonas reinhardtiim*, *Chlorella fusca*, *Platymonas subcordiformis*, and *Chlorella vulgaris*, have been evaluated for biohydrogen generation. *Chlamydomonas reinhardtii* and *Chlorella pyrenoidosa* are two common model species known for their strong hydrogenase activity, quick growth, simple cultivation, and clear genetic information [72]. On the other hand, the atmospheric and room-temperature plasma (ARTP), a whole-cell mutagenesis method developed with functions based on helium radio-frequency atmospheric-pressure glow discharge plasma, is considered more beneficial than conventional UV radiation or chemical mutagens. For many bacterial, fungal, and algal species, ARTP has been successfully employed to increase biomass and metabolite productivity [75,76]. The bioH_2 production by mutant *Chlamydomonas reinhardtii* was enhanced up to 1.8–5.2 times greater than the wild type by reducing the size of the chlorophyll [76]. Although photo-hydrogen production through algae is one of the most promising methods to produce green hydrogen energy due to the algae's high efficiency in harvesting light and converting it into energy, more research is needed at the lab and semi-pilot scale for large-scale commercial production.

5. Renewable Chemicals

5.1. Volatile Fatty Acids

VFAs, or short chain fatty acids (SVFAs), are aliphatic monocarboxylate compounds with two to six carbon atoms. Formic (C_1), acetic (C_2), propionic (C_3), butyric (C_4) and valeric (C_5) acids are the most common VFAs and are produced naturally in the guts of higher organisms through the AF of carbohydrates [6,77] (Figure 2). Biological production of VFAs has increasing market demand because of the cost-effectiveness and environmentally friendly approaches [37,78]. Food waste, waste-activated sludge and lignocellulosic biomass have been considered suitable sources for VFA production. AF of these typically produces biogas, but VFA is formed as an intermediate after the hydrolytic and acidogenic stages. This process is optimized at the reaction level by arresting further methanogenesis through inhibiting methanogens using non-genetical methods with knowingly high organic load operation, heat pretreatment and BESA (2-bromoethanesulfonic acid) pretreatment. The factors that affect the production of VFAs include hydraulic retention time, pH, temperature, substrate composition, and inoculum to substrate ratio. An important challenge in this process is the recovery of VFAs which is made difficult by the formation of azeotropic mixture with water. In addition, immediate purification or conversion of VFAs into value-added products is crucial. It is important to note the diversity of products that can be retrieved by using VFAs as starting material. One such instance is the usage of VFAs produced from biomass as feedstock for the cultivation of lipogenic microalgae and yeasts in the context of biodiesel production.

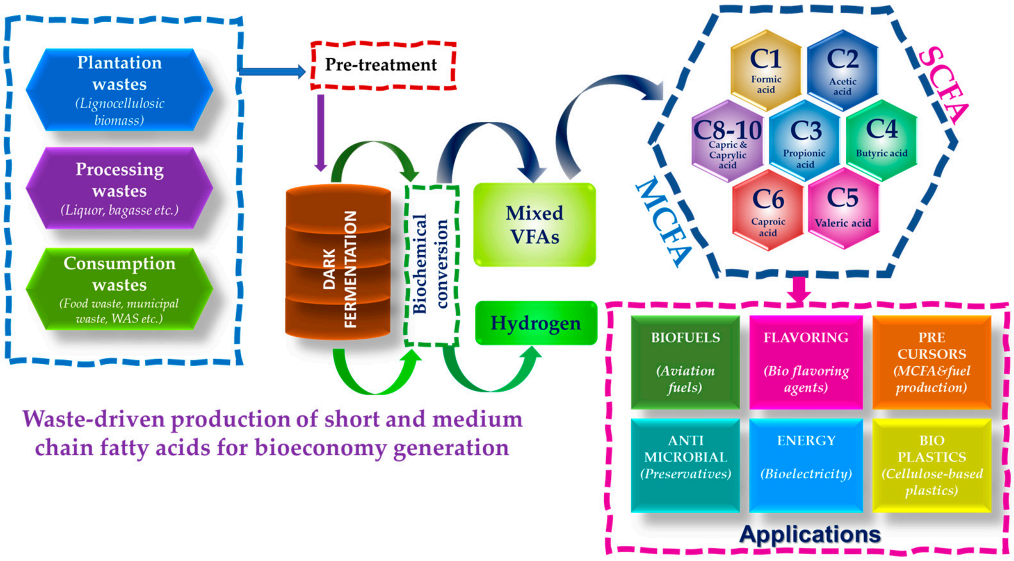

Figure 2. Fermentative organic waste bioconversion into biobased products.

Integration of VFAs into other sustainable processes has revealed that VFAs are promising substrates for microbial electricity production and bioplastics, such as polyhydroxyalkanoates (PHA), hydroxybutyrate, and hydroxy valerate. Some bacteria are known to synthesize hydrogen with VFAs as an energy source. The ever-expanding markets are now becoming more receptive to these sustainable alternatives and researchers are focusing on developing an integrated bioeconomy around these chemicals. For example, the market size of VFAs produced via AF of biomass was calculated to increase to 18,500 kilo tons by 2020 because of economic growth. An analysis in 2018 revealed that VFA production from food wastes showed a profit of 296 USD/ton-VS, as opposed to the 9 USD/ton-VS obtained from methane production. VFA has the additional advantage of easy storage, compared to methane [11]. This points towards a tangible market potential for the chemicals to integrate with or to replace conventional chemicals and the scope for better waste management, a circularized economy.

5.1.1. Acetic Acid

Acetic acid (AA) is a two-carbon molecule that is ubiquitous in the biosphere. It is an important part of animal, plant, and microbial metabolism. Its industrial applications range from the food industry to complementing petrochemical reagents. The Asia-Pacific regions are the largest consumer of acetic acid because of the increasing demand for acetic acid-derived essentials in the paint and textile industries, such as VAM, purified terephthalic acid, and ethyl acetate. Further predictions assign a considerable rise in demand, which increases the need for more sources of production and purification of acetic acid. Conventionally, AA could be derived by chemical catalysis via carbonylation of methanol or oxidation of acetaldehyde and ethylene. However, fermentation-based production of AA has gained importance as a potential alternative to chemical catalysis (Figure 3 and Table 1). AA can be produced from the oxidation of ethanol by 19 different genera of gram-negative bacteria [79]. Another particularly important mode of biobased AA production is via AF by homoacetogens. These anaerobes ferment sugar to produce an overall fermentation yield of 85% (w/w) of acetate and are hence preferred for industry use. Some of the most common acetogen phyla include *Spirochaetes*, *Firmicutes* (e.g., *Clostridium*), *Chloroflexi*, and *Proteobacteria*, out of a prospective 100 species and more than 20 genera [80]. *Acetobacterium* and *Clostridium* are the most extensively investigated homoacetogens which can utilize various substrates, such as CO_2, CO, sugars, formate, methanol, pyruvate, and lactate [16]. Applications of acetic acid in the food industry include its role as a flavoring agent, preservative, and acidity regulator. In the chemical industry, it is a key component to produce various acetate compounds that are important in paint, plastic, and synthetic fiber production [6,33,81].

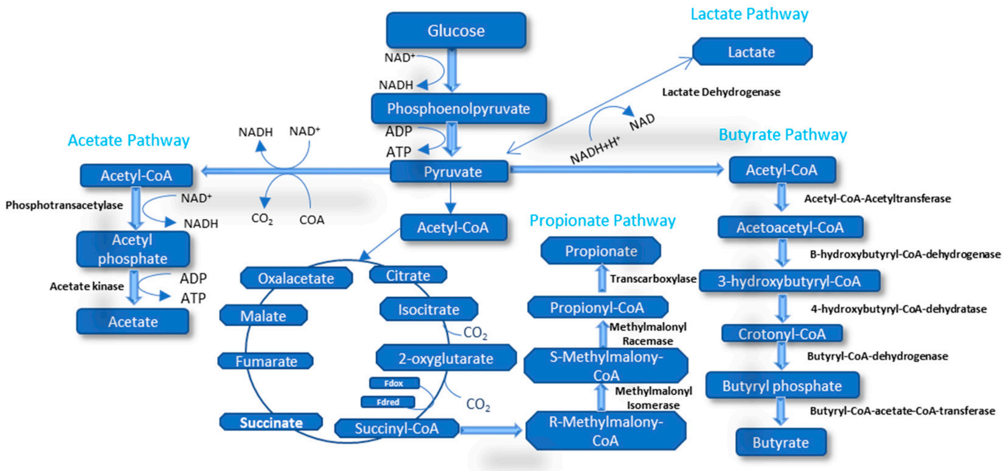

Figure 3. Volatile fatty acid production mechanism from glucose.

Various feedstock rich in carbohydrates have been evaluated to produce both mixed acid and pure AA employing *Acetobacter aceti.* This process involves sugar fermentation to produce biogas where VFA are intermediate products. Aerobic bacteria, such as *Acetobacter* and *Glucanacetobacter*, are extensively used for their aerobic production of food-grade vinegar in the industry. Production of acetic acid from biomass without microbial fermentation is being investigated where solvent extraction is used. It has been shown that mild solvents, such as super and subcritical water, can be used for this purpose. A Brazil-based company called Braskem has patented the anaerobic co-production of acetic acid along with other high-value materials which seem to greatly improve yield [82]. Pretreated straw and grape pomace comprised 78% cellulose and hemicellulose, which were utilized to produce ethanol and acetic acid [83]. Further, steam-treated lignocellulosic biomass derived from wheat straw, forest residue, switch grass, and sugarcane straw were fermented to acetic acid along with 5-hydroxymethyl furfural using the *Moorella thermoacetica* strain. This bacterium was reported to have completely consumed xylose and glucose and achieved an average of 50% of mannose, arabinose, and galactose within 72 h of fermentation, producing 71% of the theoretical yield [84]. Acetic acid production has also been reported from the pyrolysis oil of lignocellulosic biomass [85].

Table 1. Microbial production of acetic acid.

Culture	Substrate/Fermentation Conditions	Production (g/L)	References
Acetobacter aceti	Cheese whey, 30 L Integrated Fermenter, pH 2–11	96.9	[86]
Clostridium acetium	Mixed gas (163 mL Glass Serum bottle), pH 7.08–7.27	1.3	[87]
Clostridium lentocellum SG6	Paddy straw, 120 mL serum vials, pH 7.2	30.9	[88]
Moorella thermoacetica	Sugarcane straw hydrolysate, 1.3 L Flask, pH 6.8	17.2	[84]
Saccharomyces cerevisiae + Acetobacter pasteurianus	Glucose, 10 L Fed batch	66.0	[89]
Streptococcus lactis and Clostridium formicoaceticum	Whey lactose, 5 L Fermenter, pH 6.4	30	[90]
Acetobacterium woodii	Corn Stover, 3 L sterilized fermenter Bioaugmented with *A. woodii*, pH 6.5	30.8	[91]
Kluyveromyces fragilis	Whey, 500 mL Shake flask, pH 8.5	25.85	[92]
Acetobacterium BR-446	Carbon dioxide (CO_2), BR-446 batch cultivation, pH 7.3	51	[93]

5.1.2. Propionic Acid

Propionic acid (PA) is a three-carbon carboxylic acid that has industrial importance as an intermediate chemical. Conventionally, it is produced through the Reppe and Larson processes which involve catalytic conversion of ethanol and carbon monoxide into propionates, or alternatively the oxidation of propionaldehyde [94]. PA has extensive applications as an antimicrobial in the pharmaceutical industry and as a component in the manufacture of cellulose-derived plastics, such as textiles, membranes for reverse osmosis, air filters, etc. PA, in its salt form, is also used as a preservative, as an artificial fruit flavor, and as a key ingredient for vitamin E production. It is also used for fragrances, synthetic fibers, and environmentally friendly solvents. Global production of propionic acid was approximately ~450,000 tons per year with a 2.7% growth rate and a price ranging between 2–3 USD/kg. The global PA market size was estimated at USD 1.2 billion in 2020, with a compound annual growth rate of over 6% in the next six years [95]. Hence, it has become more important to look for an alternative, especially sustainable sources, for the production of this compound. Biologically, PA is synthesized via fermentative, biosynthetic, and amino acid catalytic processes (Table 2). Extensive production of PA has been studied in bacteria of the *Propionibacterium* spp. and includes various strains *P. acidipropionici*, *P. freudenreichii*, *P. shermanii*, *P. thoeni*, etc., using various substrates such as glucose and lactose [96]. Other interesting substrates for PA production include crude glycerol and sugarcane molasses. *Propionibacteria*, gram-positive facultative anaerobes, use the Wood–Werkman pathway to produce propionate and are the best biocatalysts for this process at an industrial scale. Anaerobic conditions are preferred in the industry, but product recovery, cleaning, and adaptation of reactor design remain major constraints. The benchmark for economically feasible fermentation (set in 2020) of 0.6 g/g can be overcome with suitable optimization of pH, nutrients, biomass immobilization, and metabolic engineering [80]. PA was produced for a long time from lactose-based sources. However, this process was deemed too slow to be of industrial importance. Recent research demonstrates the possibilities of the production of PA from different substrates other than lactose. For example, PA production was demonstrated from sugar cane molasses and waste in plant fibrous-bed bioreactors employing *Propionibacterium freudenreichii*. Fermenting molasses in a stirred fermentation, PA production of 12.69 g/L was achieved in 120 h, whereas 79.81 g/L was produced from hydrolyzed molasses in PFB after 302 h [97]. Demonstrating the potential of xylose as a substrate, PA production was achieved from maize cob molasses with an output of 71.8 g/L, representing a productivity of 0.28 g/L/h. In another case, glycerol from biodiesel production was used as feedstock for genetically engineered strains of *Propionibacterium* which improved the yield. In a limiting metabolite condition, a mutant strain of *Propionibacterium acidipropionici* synthesized more propionic acid [98]. High carbohydrate content waste, such as food and kitchen wastes, can be a potential feedstock for PA production. Adopting a novel strategy, an enhanced PA production was shown from food waste and sludge in a two-stage fermentation process where, in the first stage, production of lactic acid improved the PA biosynthesis in the later stage of fermentation [99].

Table 2. Microbial production of propionic acid.

Culture	Substrate/Fermentation Conditions	Concentration (g/L)	References
Propionibacterium acidipropionici (ATCC 4965)	Lactate, glycerol and sugarcane molasses, 1 L Glass Flask, Batch Fermenter, pH 6.87	15.1	[100]
Propionibacterium acidipropionici (CGMCC 1.223)	Glycerol, 7 L Fed-Batch Fermenter, pH 7.0	44.6	[101]
Propionibacterium acidipropionici (CGMCC 1.223)	Hemicellulose hydrolysate, 2 L Batch fermenter, pH 6.8	18.0	[102]

Table 2. *Cont.*

Culture	Substrate/Fermentation Conditions	Concentration (g/L)	References
Propionibacterium acidipropionici (ATCC 4875)	Cheese whey, 6 L Continuous Fermentation, pH 6.5	19.7	[103]
Propionibacterium freudenreichii CCTCC M207015	Glucose, 7.5 L Multi-point fibrous-bed (MFB) bioreactor, pH 6.9	67.1	[104]
Propionibacterium freudenreichii spp. *shermanii*	Glycerol, 1.2 L Batch Fermenter, pH 7.0	9.0	[105]
Acetobacterium ruminis	Corn stover, 3 L sterilized fermenter, Bioaugmentation with A. ruminis, pH 6.5	30.8	[91]
Propionibacterium zeae (CCT 5329)	Sugarcane molasses, Submerged Fermentation, pH 7.0	6.83	[106]
Propionibacterium jensenii	Lactate, 1 L Submerged Fermentation, pH 6.83	16.31	[107]
Propionibacterium acidipropionici	Flour hydrolysate, 2.5 L Fed-Batch Fermentation, pH 6.0	30	[108]

5.1.3. Butyric Acid

Butyric acid (BA) is a carboxylic compound with four carbons that is an industrially useful chemical. With multiple applications, BA is considered a precursor molecule in the synthesis of biofuels, making it a significant renewable chemical. The market for butyric acid was valued at USD 124.6 million in 2014 and is said to have an annual compound growth rate of at least 5% in the next few years. BA is a major biodiesel source and an excellent choice for animal feedstock. Additionally, it is known to have antipathogenic and anticancer effects. Not only useful in cellulose-based plastic production, it is also known for its capability to induce cell differentiation, and is thus significant in anticancer therapies. BA is used to produce other value-added compounds such as biobutanol, polyhydroxybutyrate (PHB), and cellulose acetate butyrate. Much like propionic acid, BA is mostly obtained by catalytic oxidation of the respective aldehyde. The chemical process has a low production cost and easily available raw materials, but due to increased market preference towards organic and environmental products, biobased methods are being developed. The anaerobic strains of *Clostridia* are so far the most productive and high-yielding biocatalysts for butyrate production (Table 3). Industrially, *C. butyricum*, *C. tyrobutyricum* and *C. thermobutyricum* are the most significant as they are capable of high yields while withstanding high concentrations of the product. *C. butyricum* can ferment many carbon sources including hexoses, pentoses, glycerol, lignocellulose, molasses, potato starch, and cheese-whey permeate [109]. Much like the other VFA, product recovery is an important constraint. The pH affects not only the process, but also the final product concentration, and the presence of hydrogen gas is known to affect the final concentration [80]. Efforts are being made to reduce the dependence on commercial sugars as substrates and focus on more carbon-rich and economical alternatives.

The preferred organism employed for the biosynthesis of BA is *Clostridium tyrobutyricum* through carbohydrate fermentation. Fed-batch fermentation holding immobilized bacteria was known to show a good yield of 55.2 g/L of BA from pretreated molasses containing sugars (glucose, fructose, and sucrose). The fermentation yield was 0.46 g/g and the productivity was 3.22 g/L/h. Typical lignocellulosic sources for the production of butyrate that have been reported are sugarcane bagasse hydrolysate, wheat straw hydrolysate, sweet sorghum stalks and beet molasses, corn fiber, sorghum bagasse, switch straw, and corn stover. *C. tyrobytyricum* was used in most of these cases and reported yields were between 0.2 to 0.52 g/g of feedstock [110–112]. Shahb et al. [113] used microbial consortia where a fungus is used to break down lignocellulose from beechwood to simple sugars, which are converted to lactic acid by aerobic bacteria; anaerobic bacteria from the consortium then converts this into butyrate. They also produced acetic and propionic acid as intermediates using an obligate anaerobe *Veilonella criceti*. In another study, lignocellulosic corn husk hydrolysate was used in batch fermenters to produce butyrate with the biocatalyst *C. tyrobutyricum* with a lesser yield of 0.39 g/g [114]. Food waste is a popular and rich source of sustainable biomass and has been used in the production of butyric acid. Stein et al. [115] used food waste to maximize the production of BA at thermophilic conditions.

Table 3. Microbial production of butyric acid.

Culture	Substrate and Fermentation Conditions	Concentration (g/L)	References
Clostridium butyricum S21	Sucrose, 500 mL Pertractive fed-batch fermentation, pH 5.2	20.0	[116]
Clostridium butyricum ZJUCB	Glucose, 5 L Fed-batch fermentation, pH 6.5	16.7	[109]
Clostridium thermobutyricum JW171K	Glucose, 500 mL Rotary fermenter, pH 7.1	18.4	[117]
Clostridium tyrobutyricum	Sugarcane Bagasse Hydrolysate, 5 L Batch fermentation, pH 5.0	20.9	[118]
Acetobacterium woodii	Corn Stover, 3 L sterilized fermenter Bioaugmentation with *A. woodii*, pH 6.5	49.31	[91]
Clostridium tyrobutyricum	Cane Molasses, 5 L Fed-batch/Immobilized. Fibrous bed bioreactor, pH 6.0	55.52	[119]
Clostridium thermobutyricum	Corn Stalk, Immobilized continuous reactor, pH 6.0	15.82	[120]
Clostridium tyrobutyricum	Jerusalem artichoke, 5 L Fed-batch/Immobilized fibrous-bed bioreactor, pH 6.0	27.5	[121]

5.2. Medium Chain Fatty Acids

Medium chain fatty acids (MCFAs) are saturated fatty acids with 6–12 carbons. They are known for their use in biofuel and alkane fuel production as precursors, antimicrobials, and corrosion inhibitors [122,123]. These are usually found in nature in mammalian milk, animal and plant oils and petroleum. The market value for MCFAs was 600 million USD in 2017. As can be expected, the ease of production of MCFAs depends on two factors: (i) hydrolysis and transport of complex organic substrates into the biocatalyst, and (ii) diversion of AF towards chain elongation of VFA [124]. The latter involves the formation of butyric acid and further elongation via the β-oxidation pathway and often, ethanol and lactic acid serve as good additives to ease production. Ethanol could be added in its chemical form or in organic form [122,125]. It not only aids chain elongation, but itself participates in the conversion of VFAs into MCFAs through the process of chain elongation. One of the most viable sources for MCFA production is reported to be CO_2 in the bio-electrochemical scenario, where electro-autotrophic bacteria are used such as *Clostridium ljungdhalii* [124].

A suitable way to develop a bioeconomy through the straightforward process that largely revolves around conventional AF is to choose systems that have been well-studied and showed stability and yield. Common sources include waste effluents and similar complex substrates, such as organic municipal waste, food waste, lignocellulosic biomass, wine and dairy effluents, and manure [126]. *Rhodospirillum rubrum* and *Clostridium kluyveri* are well-established biocatalysts for MCFA production and both pure and mixed cultures were used for experimentation over the years. Another unique challenge in the production of MCFAs is the extent of control on terminal product length which could partially be resolved by timely product removal from media. Enzyme-specific uses were also found [127]. Caproic (C_6), caprylic (C_8) and capric acids (C_{10}) are the common MCFAs produced during AF with an industrial value. The typical production cycle starts from mixed organic feed subjected to fermentation, specifically acidogenesis, chain elongation, and then product recovery. Caproic acid has uses as an antimicrobial and plant growth promoter. It is also known to have inflammatory properties. It is usually derived from plants directly for industrial use, but the low yield is a challenge.

MCFA production from waste could potentially replace extraction methods from coconut or palm. The process is currently not economically friendly, but as research progresses, it is expected to drop. Possibilities to transform MCFAs into alkanes for use as a transportation fuel has previously been proven. Other potential applications as feedstock and nutritional supplements are also being explored [128,129]. MCFAs are naturally more energy-dense, and hence, have more economic value than methane or VFAs. In addition, since MCFAs are less water soluble, they demonstrate good separation and significantly reduce the downstream separation cost [129]. One of the most important applications of VFAs is that they are used in producing extensive quantities of caproate as the major product of acidogenesis, with acetate and butyrate as the principal intermediates [130,131]. A recent venture into utilizing this process resulted in a pilot-scale system for economically viable production of caproate from mixed organic waste and ethanol by the company ChainCraft B.V. based in Amsterdam [127]. The organic fraction of municipal solid waste (OFMSW) can be an excellent substrate for caproate production aided by ethanol production yielding up to 12.6 g/L [132]. An interesting application of membrane electrolysis was utilized in the fermentation of grass to lactic acid, which in turn was used to produce caproate, which gave an overall yield of 10.92 $\pm$ 0.62 g/L [133].

As a development on the earlier two-phase anaerobic system, without the addition of electron donors, another group achieved a caproate yield as high as 21.86 $\pm$ 0.57 g/L using leach bed reactors through dilution and recirculation of leachate before every run. This study also demonstrated that the high yield need not be associated with standard caproate producers such as *C. kluyveri*, but is rather a product of mixed consortia which exhibit extreme similarities with the former [134]. A similar study, but with acidified food waste as the source, with a higher hydraulic retention time, gave one of the highest yields of caproate, i.e., 25.7 g/L along with a two-fold decrease in ethanol consumption [135]. Another unique study proposed that lactate could serve as an alternate electron donor for caproate production, and the microbiome produced a yield as high as 23.42 g/L, almost 83% higher compared to ethanol-based production. Chinese strong-flavor liquor was used as the source for the process [136].

These studies demonstrate that the knowledge gap for viable caproate production, reducing the use of environmentally harmful solvents such as ethanol, can be bridged through the exploration of consortia and known waste sources. The use of lactate along with common liquor waste and similar wastes shows potential for the design of bioeconomic solutions for this valuable chemical [16,78]. A very recent study proves this very statement: investigation into the fermentation of Baijiu, a popular fermented product in China, resulted in the discovery of a novel yeast, *Clavispora lusitaniae*, which could produce an extensive yield of 62.0 mg/L of ethyl caproate from sorghum hydrolysate and sugar medium. This not only improves the quality of Baijiu commercial production, but also shows the economic value of caproate [137]. Interestingly, since MCFAs are obtained together, their presence in natural foods can be enhanced by biocatalytic modification. Sengupta et al. (2015) used mustard oil as a solvent and three immobilized biocatalysts, *Thermomyces lanuginosus, Rhizomucor miehei* and *Candida antarctica*, to improve the concentration of MCFAs in the substrate, paving a potential use of microbial fermentation for nutraceutical applications [138]. Another leap in the production of MCFAs was in terms of improving the tolerance of cells to high amounts of MCFAs and this was achieved over genetic engineering of two main fatty acid synthases of *S. cerevisiae*, coupled with the directed evolution of the membrane transporter which resulted up to 1.7 $\pm$ 0.2-fold increase in MCFA yield [139].

6. Biorefinery Approach for Biofuels and Renewable Chemicals

The first step in developing a sustainable bioeconomy is to develop a strategy for substituting traditional feedstocks to produce important chemicals with more environmentally friendly sources, while trying to combine this with technology that can reduce the negative impact on the environment [3,140]. Biorefineries enable the creation of an alternative production chain to produce biofuels and biochemicals utilizing biomass-replacing oils or petrochemicals [141,142] (Figure 4). A biorefinery is analogous to a petroleum refinery but serves as a facility to utilize sustainable biomass to produce transportation fuels, power, and chemicals. Since most biofuel and biochemical production cycles are unintegrated, we need to explore technologies to weave these into the biorefinery concept and reduce dependence on feedstock such as commercial sugars, which stand in competition with the food and feed industry. Biorefinery enables us to identify sources such as lignocellulosic crops, which are grown specially to function as feedstocks. Carbohydrates and lignin, triglycerides, and mixed organic residues are the three classes of biomass feedstocks, while the main products of a biorefinery are broadly categorized into two—material products and energy products [3,143]. Materials and energy are the output of biorefinery, apart from multiple other low-value products. A biorefinery must be created in conjunction with the natural cycles of chemicals and their interdependencies, the system should be periodically evaluated, and impacts must be calculated using Life Cycle Assessment [23].

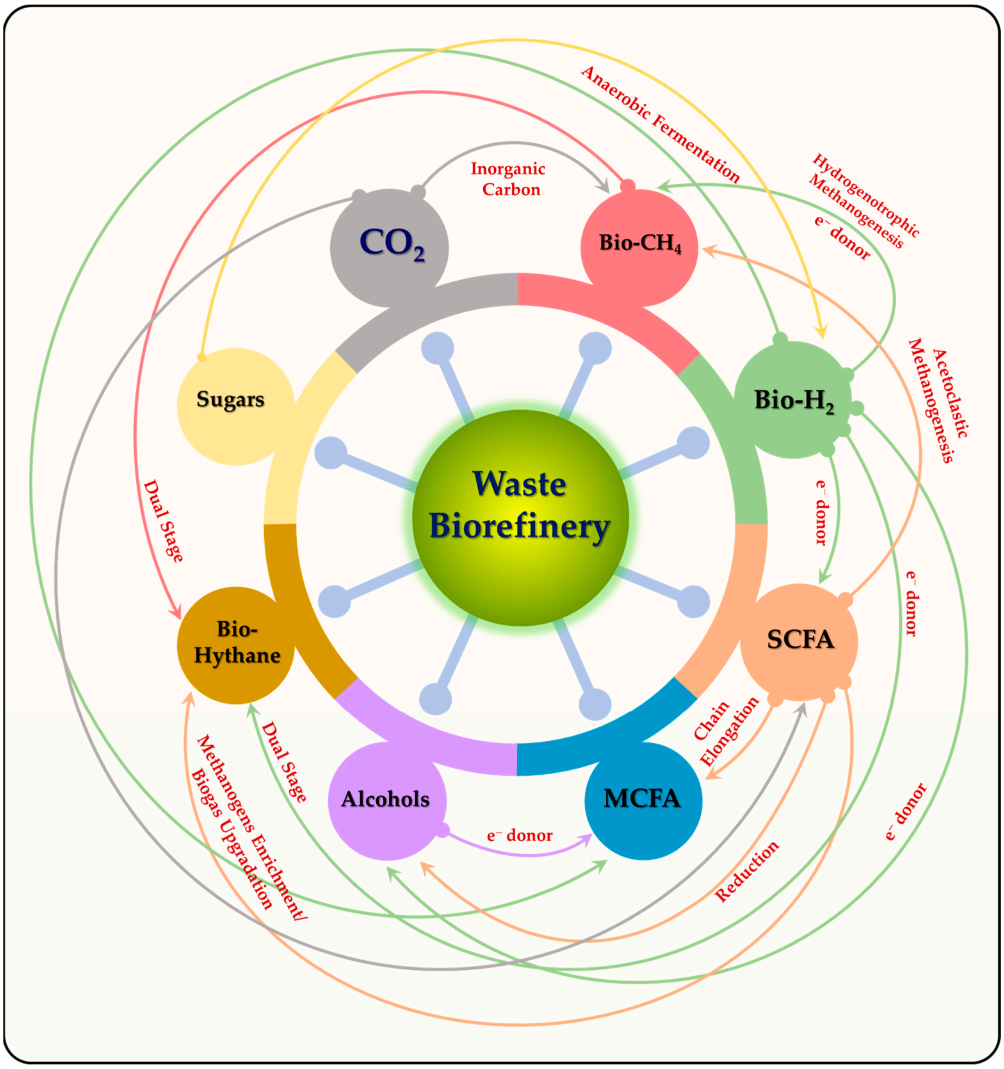

Figure 4. Waste biorefinery model integrated with multiple processes.

Multiple production strategies have been developed to utilize different sustainable sources for its production. The implementation of biorefineries to produce acetic acid will be discussed based on the two categories of feedstocks. The concept of the biorefinery is an important device in environmental management as it facilitates the conversion of waste materials, by-products, and other output from linear processes, into value-added bioproducts such as renewable chemicals and biofuels [144]. Typical organic sources to produce renewable chemicals include food wastes, waste-activated sludge (WAS), lignocellulosic biomass, agricultural wastes, etc. In addition, a range of organic wastes is utilized as a renewable feedstock to produce renewable platform chemicals including 5-hydroxymethylfurfural (5-HMF), levulinic acid, sugar alcohols, lactic acid, succinic acid, and phenols. The typical process includes catalytic conversion of biomass into the respective chemical, and then a scaling and optimization process where production can be performed at an industrial scale, either from scratch or from a given platform material. The most effective process for producing a specific value-added product from biomass should be used in a biorefinery. As a result, various optimization strategies are usually applied to improve production cost and product recovery, decreasing any dependence on toxic chemicals and using alternative materials to increase overall efficiency.

7. Road Map for Waste Derived Bioeconomy Promotion

Natural resource consumption by humankind can be expressed as a quantity called "Earth's capacity" which is proportional to the population (P) of its inhabitants, their average consumption (C), and the amount of this converted into environmental burden (B), i.e., $EC = P \times C \times B$. It is more sustainable to address variables B rather than P and C, as they are population metrics. To cater to the environmental burden issue, we have two routes—dematerialization and trans materialization; the former refers to reducing consumption, while the latter deals with the substitution of traditional raw materials and energy sources at all levels of input and output [145].

The latter is a more sustainable and practical approach to the world's energy demand, which is increasing every day. Conventional, i.e., fossil-based refineries, produce chemicals and energy from crude oil and natural gas. Biorefineries utilize biomass to produce biobased fuels and platform chemicals. Biorefineries are primarily reliant upon feedstock, and efforts are underway to integrate a gate-to-gate approach to reduce the environmental footprint of substances and processes via the biorefinery concept. The advantages of biobased energy and chemical generation can be realized when it is deployed on a large scale. There is a need for intervention on the interdisciplinary level, including estimation of feedstock, yield, supply chain, and hence, economic performance, to judge the performance and sustainability of biorefineries at a large scale. This evaluation is not restricted to the process or plant parameters, but also includes scaling of the supply chain between the source of feedstock and biorefinery, distribution of the products to different consumers, and regulation of market prices of raw materials and products (both main and by-products) [146]. Many industrially important platform chemicals, including ethanol, butanol, lactic acid, succinic acid, and VFAs, are produced at a large scale and commercialized by industries such as DuPont. Though these could be produced in an isolated biorefinery, it is useful to explore the integration of these processes into a Phase III biorefinery, to enable a circular economy [147]. Highlighting the importance of integration as mentioned in the above review, we focused on the different biofuels and platform chemicals that can be helpful in setting up a waste-derived bioeconomy. Gaseous and liquid biofuels can be industrially produced from waste, followed by renewable VFAs and MCFAs from some main building blocks, such as alcohols, carboxylic and fatty acids, polyhydroxyalkanoates, etc. A major portion of this waste comes from the forest industry, followed by food waste and other complex organic residues. A significant challenge in the process is the valorization of lignocellulosic feedstock into these building blocks. Chemical and enzymatic methods along with some novel pretreatment methods are known to improve yield in these cases, as they help in the conversion of these complex chemicals into fermentable sugars [147,148]. After pretreatment, this can be subjected to fermentation based on the type of desired product.

The bio-based part is an essential module and is crucial for achieving sustainability in terms of resources and the environment. Known drivers for a biobased economy are policy framework, systems thinking, industry acceptability, sustainable production, and consumption, and zero discharge [149]. Materials and processes with a biological origin that imitate or use natural mechanisms to produce a resource-efficient design are accounted for by the bioeconomy [149]. Hence, it is predicted that the bio-waste valorization strategy will be essential in introducing circularity to the bioeconomy. Resource valorization will also be significantly influenced by the biotechnological valorization of non-bio-derived materials. Government aid, as well as scientific community initiatives, are required for improved research and technology endeavors in this field. To supply a context on the yield, typically 1 kg of food waste has 120–300 kg of COD, which in turn can produce 350 L and 466 L of methane and hydrogen, respectively. The gap between theoretical and practical yield is to be bridged for large-scale production while ensuring economic sustainability. Although worldwide efforts have resulted in a change in basic assumptions from petroleum-based to biobased refineries, there is still a need for the realization of optimal technological support for commercialization and economic feasibility. Brazilian companies which adopted biobased processes for ethanol production still face challenges to reduce costs. So far, biodiesel, bioethanol, and green gasoline have been declared most compatible with existing supply chains [149].

Artificial intelligence (AI) is also being explored for sustainable control of processes. In 2019, the World Economic Forum awarded Marc Zornes, the founder of Winnow Solutions, a Tech Disruptor Award for their use of AI to measure food waste in commercial kitchens. Their technology uses image detection to recognize waste items based on the menu and puts a monetary and environmental value on waste based on weight detection. This helps chefs and the management to monitor waste and make decisions to tackle overproduction or consider reuse. This system is in place in over 40 countries and allegedly saves 3–8% on food costs in not only Winnow Solutions, but also internationally renowned companies such as IKEA, Compass Group, and AccorHotels. This is an excellent example of how employing AI methods helps in quantifying and regulating waste at a practical level. Similar usage of imaging techniques could also be used in fermentation processes to detect growth changes by obtaining on-line cell count and cluster via microscopy. CelloScope is one such novel example of a microscopy device equipped with a software system that uses multiple algorithms for speedy and smart image detection. These helped in the correlation of cell size with growth and insulin production detection, and hence, have the scope to improve the process. Integration of AI helps in better decision-making and process control. Waste-driven bioeconomy is a potential solution to the global conflict of resource management and meeting energy demand. However, this involves commercial and political imperatives which currently aim to reduce structural changes to set up systems, hence, the development of substances such as 'drop-in' fuels which can be readily integrated and used [150,151]. Global organizations must also aim at equalizing the gap between resources and technology available in different countries.

8. Conclusions

Biorefineries have the potential scope to replace fossil-derived fuels and chemicals, simultaneously promoting a bioeconomy. This review focused on the roles and applications of fermentation-based renewable fuels and chemicals derived from organic waste, highlighting their importance in integrating bioprocess development and promoting bioeconomy. Fermentation technology enables the production of biofuels and biochemicals from organic waste, while concurrently addressing waste remediation. Acidogenic VFAs are the building blocks for the chemical industry and appear as one of the important alternatives to fossil based VFAs. Acidogenic VFAs have attracted attention due to their cost-effective production, increasing VFAs' market, sustainability, and environmentally friendly characteristics. In turn, biogas from AF could be used as a bioenergy source and liquid rich VFAs integrated into secondary fuels or medium chain fatty acids production to establish the complete carbon turnover into biobased chemicals/fuels. This technology provides a new platform to maximize the value of organic-rich waste to value-added products promoting carbon neutrality, which is much prioritized in maintaining the long-term sustainability of our society and driving the transition of the chemical and energy industries towards renewable feedstocks.

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