Waste-Derived Fuels and Renewable Chemicals for Bioeconomy Promotion: A Sustainable Approach

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Abstract
Bio-based fuels and chemicals through the biorefinery approach has gained significant interest as an alternative platform for the petroleum-derived processes as these biobased processes are noticed to have positive environmental and societal impacts. Decades of research was involved in understanding the diversity of microorganisms in different habitats that could synthesize various secondary metabolites that have functional potential as fuels, chemicals, nutraceuticals, food ingredients, and many more. Later, due to the substrate-related process economics, the diverse low-value, high-carbon feedstocks like lignocellulosic biomass, industrial byproducts, and waste streams were investigated to have greater potential. Among them, municipal solid wastes can be used as the source of substrates for the production of commercially viable gaseous and liquid fuels, as well as short-chain fattyacids and carboxylic acids. In this work, technologies and processes demanding the production of value-added products were explained in detail to understand and inculcate the value of municipal solid wastes and the economy, and it can provide to the biorefinery aspect.

Keywords Renewable · Biofuels · Carboxylic acids · Fatty acids · Biorefinery
Introduction

Sustainable waste management practices play a critical role in minimizing environmental pollution and also promote the transformation towards a green society [125, 126]. Conventional waste management practices eliminate the potential advantage of waste as feedstock and also emit greenhouse gases. So to switch towards environmental sustainability and a biobased economy efficient waste management practices needs to be developed embedded with resource recovery [18, 60]. Furthermore, various industrial and academic researchers are intensely involved in the valorization of this waste into value-added products. Various solid, liquid, and gaseous waste (CO₂ originating from municipal bodies, domestic (kitchen/food waste), and industrial could be used as a feedstock for biofuels and renewable chemicals synthesis [3]. Therefore, all major sectors, including environment expertise, industrialists, and economists, are pushing to recover and regain valuable products from waste resources [7]. It is important to explore individual and combined technologies to convert specific wastes to a wide spectrum of value-added products.

Renewable sugars and nutrient-rich hydrolysate extracted from organic solid waste could be considered an alternative and potential resource biobased industries (Kumar et al. 2018). Acidogenic fermentation is an emerging technology, which is compatible with various composite waste (high strength) biodegradation with concurrent production of biohydrogen (H₂) and volatile fatty acids (VFAs) or short-chain carboxylic acids [129]. VFAs are the soluble intermediate metabolic products of acidogenic fermentation, which are majorly composed of acetic acid (AA: C2), propionic acid (PA: C3), butyric acid (BA: C4), and valeric acid (IVA: C5) [131]. Further, VFAs are considered platform chemicals and act as building blocks for various high-value product synthesis including alcohols, ketones, esters, and medium-chain fatty acids (caproic/capric acid) [64]. Medium-chain fatty acids (MCFAs) are superior to VFAs as they have a longer hydrophobic carbon chain and low oxygen/carbon ratio, which increases the energy density and makes its separation simple [95, 96]. MCFAs are identified as C₆–C₁₂ acids namely, caproic acid (C₆), oenanthic acid (C₇), caprylic acid (C₈), pelargonic acid (C₉), and capric acid (C₁₀). Among these acids, the biological production of caproic acid from VFA and alcohols utilizing the chain elongation pathway is gaining perceptible interest.

Waste valorization is the process of transforming organic-rich substrate into valuable products like renewable chemicals, biofuels, and materials. The globe is tuning the magnitude of the waste management problems and has been working towards the development of advanced waste remediation technologies with resource recovery as the main goal [125, 126]. On the other hand, there is a platform that exists for the devotion of sustainable technologies that could follow the “trash to cash” concept by producing industrially important chemicals, materials, and fuels which will reduce the dependency on fossil-based fuels and products but also help in addressing the environmental sustainable remediation issues [14]. The concept of biorefinery analogous to today’s petroleum refineries is also showing interest. Petroleum or fossil fuel is a natural source that has been the greatest important synthesis substrate for energy fuel and biochemicals for periods. Nevertheless, they are non-renewable and hold ecological threat characteristics which resulted in atmospheric change by the discharge of greenhouse gases mostly CO₂ to the environment. These ecological matters have elevated the global alertness and thus a great number of investigations on carbon mitigation and adaptation. Shifting to a waste biorefinery concept from the fossil fuel–based refinery concept specifies a large effort on carbon management and greenhouse gas management. Biorefinery systems work by utilizing bio-based feedstock to produce a range of bio-products like fuel, platform chemicals, animal feeds, in a closed-loop approach [60, 91]. Municipal solid wastes, industrial side streams, and other biological wastes available are the potential feedstocks for the alternative bioenergy generation, and also the composition of these wastes provides the potential of valorizing them into value-added fuels and chemicals replacing the petroleum-derived substrates and processes.

In this perspective, the present review aimed to summarize waste as a potential resource for biofuels and renewable chemical production and biobased economy promotion. Initially, waste potential is an alternative resource for gaseous biofuels such as biohydrogen, biomethane, and biohythane. Additionally, the scope of liquid biofuels was also covered namely bioethanol, biodiesel, butanol, hexanol, etc. The scope of VFAs as platform chemicals and its contribution towards the role of the renewable chemical were deliberated. The role of these biofuels and renewable chemicals in biorefinery establishments along with the bioeconomy development are cohesively discussed.

Waste as an alternative resource for energy

A wide range of bioenergy crops serves as the feedstock for the synthesis of various chemicals. For bioethanol production, corn and sugarcane are used in the production of bioethanol in North America and Brazil [44]. In 2018, Li et al. discussed the utilization of protein waste into biofuels. It was found that the production of vegetable oil and
biodiesel with oil crops will result in the protein content (nearly 40 and 60% (w/w)) in waste streams. Through the alkali or acid-based precipitation method or by the ammonia fiber expansion method, the protein will be recovered [66]. The microwave-assisted process has the features of reducing the processing time and less energy cost for the improved product quality and yield. During the hydrothermal liquefaction process, the catalytic conversion of lignocellulosic biomass to value-added products will take place [37]. Municipal sewage sludge with a high lipid profile is a potential feedstock because of its low cost and availability [19]. Various lignocellulosic biomass was obtained from agricultural crop residues and mill wastes, and garden residues were used for the conversion process. The crops wheat, maize, rice, and sugarcane which were produced globally were used as the lignocellulosic biomass in the biorefinery process. A sum of nearly 5350 million tonnes of dry biomass per year is obtained from the abovementioned four crops [12]. Sugar released from agricultural feedstock and solid wastes was also used by the biorefinery approach to produce value-added products. Other than these resources, municipal solid wastes, animal and food processing industrial waste, and green waste were also used. The rate of energy is produced through the waste biomass which were mainly from wood and wood wastes, then municipal solid wastes, agricultural waste, and landfill gases. Agricultural biomass includes the edible parts of crops (corn, fruits) and non-edible portions (leaves, stalks, rice straw, rice husk), grass waste, and animal wastes [93]. Cellulose, hemicellulose, and lignin are the major components of lignocellulosic biomass and for the efficient utilization of these feedstock, pre-treatment is required in order to release the components [61].

**Biofuels**

The innovative developments of energy efficient bioproceses are vital to transform biomass into value-added products including biofuels for the effective implementation of the biorefinery concept [70, 101, 132]. Biomass is the only renewable energy source that can be transformed into a variety of fuel types, including solid, liquid, and gaseous fuels [104]. Biomass with a high hemicellulose and cellulose concentration produces more bio-oil and syngas, whereas biomass with greater lignin content promotes the generation of gaseous biochar [4, 57, 89]. The urge for biofuel production is increasing day by day because of the myriad raise of pollution especially CO₂ emissions from fossil fuel–driven vehicles [1, 74]. The shift from petroleum products to biofuels can also boost the crop production, and effective utilization of agro residues helps in a direct support to rural economy and as a whole to the overall techno-economy of both developed and developing countries.

**Gaseous fuels**

Gaseous fuels are crucial transition fuels, and their relevance will grow even more now that they can be ramped up and down in a flexible manner. When a high proportion of variable renewable energy is attained, this is extremely crucial for grid balancing [48]. Gaseous fuels are used in steam boilers or turbines, particularly in high-efficiency combined heat and power (CHP) cycles. Biogas and syngas are the most often utilized alternative fuels in stationary applications such as CHP [116]. Pyrolysis, gasification, and anaerobic digestion are all methods for obtaining them. Methane is the primary component of gaseous fuel, although it also contains significant amounts of CO₂, CO, H₂, and other higher hydrocarbons [81]. The fundamental disadvantage of such types of fuels is that their heating value is inconsistent and inferior (11–35 MJ/kg) when compared to natural gas (20–21 MJ/kg) [43]. Hydrogen is one of the most common gaseous fuel for automobile and aviation applications, and is already used in vehicles in some developed countries [8]. In the gaseous phase, ammonia can be co-fired with similar gas fuels to improve combustion performance and to overcome problems related to liquid ammonia [116]. Different types of gaseous fuels are discussed in detail in Fig. 1.

**Biohydrogen**

Biohydrogen combustion produces just water as a byproduct, making it the cleanest biofuel. But, in the current scenario, hydrogen is producing from non-renewable resources making the whole process unsustainable. As a result, the use of lignocellulosic biomasses (LBs) for biohydrogen production via anaerobic conditions using microbial catalysts is gaining popularity [13, 16, 90]. The methods for producing biohydrogen may fundamentally be divided into two groups: thermochemical and biochemical conversion routes. The first route relies on high-temperature processes to decompose biomass wastes into biohydrogen, with the types and conditions of feedstocks employed having a significant impact on the product’s output. The physical characteristics of the media and the sort of catalysts utilized are more important in the biochemical conversion process [24]. Numerous advanced techniques for producing biohydrogen have been deployed, including photo fermentation, biophotolysis, and dark fermentation, the latter of which has gained favor since it is light-independent and can be used with a variety of LBs. In the absence of sunlight, dark fermentation is the most effective method of acidogenic degradation of LBs by anaerobic bacteria, but it indicated the presence of hydrogen-consuming bacteria such as methanogens and homoacetogens, as well as hydrogen production–inhibiting bacteria such as lactic acid bacteria [21]. Therefore, some genetic engineering techniques are to be employed to suppress these
types of bacteria to promote biohydrogen production. For instance, several hydrogenase enzymes are used to catalyze biohydrogen production in dark fermentation to achieve the better reduction of LBs to monomers. The presence of iron and nickel at the enzyme’s active sites revealed that both metals had a significant impact on the fermentation pathway, increasing biohydrogen yields. Biohydrogen generation may be made more cost-effective and sustainable by using nanomaterials to some extent, both in the lab and in the industry [115]. Nonetheless, combining the usage of LBs as a cheap and widely available feedstock with nanomaterials is predicted to contribute in the design of efficient, cost-effective, and sustainable biohydrogen production processes [114].

**Biomethane**

Biogas is a combination of methane and carbon dioxide that is produced from biomass by biochemical or thermochemical processes [4]. Methane is widely employed, not only in the chemical sector, but also in transportation as compressed natural gas, which is considered a cleaner energy source compared to other fuels. Biomethane is a feasible alternative to fossil-derived natural gas that is created by processing biogas to yield about 97% methane. Different pre-treatment procedures, such as chemical, thermal, mechanical, and biological processes, may be required for anaerobic digestion (AD) of LBs [6]. Gasification and pyrolysis are two innovative thermochemical techniques for transforming LBs to syngas, which may later be converted to biomethane [128]. Pyrolysis produces bio-oils, biochar, and non-condensable biogases at a moderate temperature range of 400–800°C within a short hot vapor processing time. Gasification, on the other hand, produces gaseous fuels at extremely high temperatures of 600–1200°C and a longer vapor contact time [88]. When comparing the two processes, pyrolysis has lower investment costs and produces more energy [65]. AD currently generates biomethane, which is commercially viable and has great environmental performance throughout the consumption. However, the thermochemical strategy is the less explored one, which entails gasification of semi-dry and dry biomasses followed by syngas purification, methanation, and final upgrading [9].

**Biohythane**

Biohythane, a two-stage fermentation product including biohydrogen and biomethane, is a potentially high-value alternative for the valorization of waste biomass resources and a feasible alternative to fossil-based hythane [46]. Hythane is one of the valuable fuels associated with achieving the switchover of technological models from a fossil fuel–dependent society to a terminal hydrogen-dependent society because it combines the advantages of biohydrogen and biomethane. Hythane gas is a more valuable gas than biogas, and it could be stored and transferred using existing natural gas infrastructure. Hythane-fueled cars are being marketed in the USA and India because of their better performance, and have drawn the attention of major automotive manufacturers. Dark fermentation of waste compost, such as sludge, animal dung, and landfill, produces the methane utilized in hythane gas. When utilized as a source for hythane,
the high CO₂ level decreases the heat value of biogas and necessitates extra treatment [62].

Conventional biogas production techniques, including such water washing or alkaline treatments, waste a lot of chemicals and energy while producing little value-added hythane products. As a result, biohythane is now produced by a two-step anaerobic digestion in which the initial fermentation step produces hydrogen, which is subsequently followed by the methane production stage. The two-step method has difficulty maintaining a good H₂:CH₄ ratio, and the production rate is low and unstable. Gottardo and coworkers reported the production of stable hythane gas from food waste by combining thermophilic dark fermentation with anaerobic digestion, with the addition of about 5–10% of H₂ of rich CH₄-containing biogas which enhances the quality and purity of hythane with reduced emission of CO₂ [39]. Recently, Luo et al. reported the high yield production of biohythane using dual-chamber microbial electrolysis cells. This dual-chamber approach might maintain a steady biohythane composition in the long run, ensuring energy recovery [73].

Syngas

Syngas generation from biomass thermochemical conversion is a potential approach for maximizing renewable energy consumption. The Fischer–Tropsch reaction mechanism might be used to turn the syngas generated by gasification into value-added compounds [97]. Renewable energy may be converted into transportable and high-density energy using syngas and CO₂ methanation. However, tar formation and catalyst deactivation are the most pressing concerns during gasification and methanation. The development of techniques incorporating tar-cracked removal and innovative catalyst usage will be critical in order to increase this high-efficiency cleaner operation. Syngas was produced using a two-stage method that combined biomass catalytic pyrolysis and gasification processes. The effects of pyrolysis and gasification temperatures on gas generation were examined in the presence of several nickel-based catalysts. In the pyrolysis stage, more high-quality syngas and char could be created at a temperature of 750 °C, whereas in the gasification stage, pyrolysis char (made at 750 °C) interacted with steam and the highest yield of syngas was obtained at 850 °C [134]. Biomass gasification using a dual fluidized bed gasifier (DFBG) has taken a major step in enhancing the yield and purity of syngas produced. With steam as the gasification agent, indirect DFBGs generate a high percentage of syngas with a heating value of 15–20 MJ/nm³ [38].

Another route for the production of syngas is through solid oxide fuel cells (SOFC) with biomass gasification techniques to create a single, highly efficient system that combines the benefits of renewable energy sources and hydrogen energy systems. Household combined heat and power (CHP) is extremely efficient up to >90%. Micro CHP for space heating has already been proven popular in Europe and Japan, utilizing natural gas as a fuel. The SOFC is a promising contender for green renewable energy because of its wide range of fuels, silent operation, zero emissions, and great efficiency. Intending to reduce heat consumption, SOFCs are more appealing for usage in intermediate working temperatures of 400–700 °C [92].

Liquid fuels

Liquid fuels play a central role in global transportation. The renewable energy policy network 2020 reported the dependency of human life on fossil fuels. According to total final energy consumption (2019), we are still majorly dependent on fossil fuel with 80% of total energy usage followed by 18% of renewable energy, and 2% of nuclear energy [98]. In 2020, a 5% decline in global biofuel production was observed on transport energy demand due to the impacts of the COVID-19 pandemic. The global ethanol volumes faced a sharp decline in 2020 while biodiesel production and use have been reported steady. The global ethanol production declined from 115 to 105 billion liters (8.6%), with an 11% drop reported in the US ethanol production—the major producer. On the other hand, biodiesel production from hydrogenated vegetable oil increased 15.3%, i.e., from 6.5 to 7.5 billion liters, while FAME biodiesel production faced a decline of 4.8% from 41 to 39 billion liters [99].

For sustainable usage of fuels and meeting future transportation, liquid fuel needs various biomass feedstocks that can directly be converted into liquid fuels. Blending ethanol to gasoline and converting vegetable/waste oil to biodiesel has the potential to substitute petroleum-based fuels because of their comparable properties and readiness to be used in internal combustion engines. Biofuels are typically categorized into sugar alcohols obtained after fermentation, and fatty acid methyl esters or hydrocarbons from biomass lipids/oils. The most common biofuels, for instance, bioethanol and biodiesel, have been already implemented commercially in most parts around the globe. However, more alternatives are needed to produce a similar amount of energy as compared to gasoline; hence, investigations are still ongoing to include new feedstocks, especially non-food feedstocks, and improving their properties in internal combustion engines [23, 106]. Improvements and advancements on sustainability issues are critical for the growth of the international biofuels market.

Bioethanol

Bioethanol is one of the most crucial renewable energy which can be produced from any feedstock rich in starch or
polysaccharides containing fermentable sugars. Starch and polysaccharides in different biomass are hydrolyzed using enzymes to obtain monosaccharides that are conveniently convertible into ethyl alcohol on fermentation. The production of ethanol from biomass is categorized into four generations (Fig. 2) [76]. First-generation bioethanol production utilizes the starch/sugar contained in food crops such as corn, sugar beet, sugarcane, wheat, and barley as the major source of fermentable sugar that is directly fermented to ethanol [111]. On the other hand, second-generation bioethanol production uses complex polysaccharides in lignocellulosic biomass for fermentation. Ethanol production from lignocellulosic biomass requires pretreatment of biomass, hydrolysis of polysaccharides using enzymes into fermentable monosaccharides, fermentation, and recovery of ethanol. Since grains are a possible competition for food, the lignocellulosic biomass is considered the most promising and low-cost feedstock for commercial bioethanol production. However, the production cost for second-generation ethanol production is very high and research efforts are underway to make it competitive with first-generation ethanol [30]. Besides, seaweed and microalgae-based third-generation bioethanol production has shown potential as viable feedstock over first- and second-generation bioethanol. The advantages of using microalgae include its non-requirement of agricultural land or freshwater for cultivation, significantly higher growth rate as compared to crops even under poor nutritional conditions, usage of unutilized water bodies (oceans and seas) for sustainable cultivation, and their ability to capture solar energy to convert into chemical energy more efficiently than land crops [29, 118].

The advancements in synthetic biology and biotechnology have come up with metabolically engineered organisms and bioenergy crops for enhancing biofuel yields. Bioethanol produced from genetically modified organisms/biomasses is referred to as fourth-generation bioethanol [76]. The fourth-generation microorganisms have displayed an increased rate of carbon dioxide intake during photosynthesis that creates an artificial carbon sink and enhances the conversion and accumulation of solar energy and carbon dioxide into chemical energy. In addition, the genetically modified lignocellulosic feedstocks can accumulate energy-rich molecules,
i.e., triacylglycerides in their vegetative tissues; hence, both bioethanol and biodiesel can be produced from the same raw material [86, 123, 136].

Currently, future research in the bioethanol field is directed to address the suitable methods and their efficiencies for pretreatment of various feedstocks, microbial engineering to produce microorganisms with superior qualities for fermentation, design a consolidated bioprocess to combine the process with existing commercial methods, and investigate the technical and economic aspects of the process to speed the commercialization [72, 102].

**Biodiesel**

Like bioethanol, biodiesel presents a green and renewable alternative to conventional diesel. The primary feedstock used for the commercial production of biodiesel is oilseeds [32]. The quality of biodiesel obtained from oilseeds meets the specifications set by ASTM (American Society of Testing and Materials) motor fuel. B100 represents pure biodiesel and is rarely used for existing diesel engines. Pure biodiesel is blended with fossil fuel in certain proportions to make it suitable for different automobiles. By 2025, the value of biodiesel in the global market is expected to surpass approximately 50 billion US dollars [2]. The growing prominence of biodiesel would require alternative sources of non-feed raw materials that can meet the continuous growing demand. Oleaginous microorganisms such as bacteria, yeasts, microalgae, and fungi (molds) present an alternative source with a similar composition of lipids. In recent path-breaking research, metabolically engineered transgenic lignocellulosic biomass has been developed that accumulates energy-rich triacylglyceride molecules in their vegetative tissues [86, 123, 124, 136]. Transgenic lignocellulosic biomass which is metabolically engineered for the accumulation of triacylglycerides can be a promising non-oilseed alternative for biodiesel production. However, the research for alternative sources is underway and would take a substantial amount of time to establish itself at the commercial level.

To this end, several advancements in process technology have been implemented to improve yield and the environmental impact of biodiesel production. The introduction of biobased processing methods for the conversion of lipids into biodiesel like enzyme-based transesterification and biomass-derived catalyst would further reduce the chemical waste produced during the process. The bio-based processes use less hazardous chemicals and require mild operating conditions and the recovery steps are simple [13]. The use of heterogeneous catalysts derived from waste oil sources along with continuous flow reactor technologies has made biodiesel synthesis economical. Continuous reverse flow helical coil reactor system allows high conversion yield and requires less catalyst compared to the conventional batch reactor. It can be used for both homogeneous and heterogeneous catalysts [42].

Utilizing waste and non-edible oils from animal fats, algae, or transgenic bioenergy crops is a promising approach for biodiesel production. Furthermore, the process of biodiesel production could be economical by integrating the processes for by-product recovery such as bioethanol. This can be achieved by using transgenic bioenergy crops with hyper-accumulated energy-rich triacylglycerides (Fig. 3) [45].

**Butanol**

The lower vaporization enthalpy and higher energy density of butanol are suitable to be used as both fuels for internal combustion engines and/or as oxygenating agents for blends with gasoline. Biobutanol is produced through ABE (acetone-butanol-ethanol) fermentation process using *Clostridium* genera from biomass feedstock [58]. Production of butanol from biomass such as corn and lignocellulosic biomass presents the potential to be used as a biofuel. However, the process used for the production of biobutanol influences the isomer of butanol, i.e., n-butanol, t-butanol, and isobutanol, that is produced. Only n- and isobutanol fit the criteria of biofuel. t-Butanol has slow environmental degradation, hence unfit to be used as biofuel [130]. ABE fermentation of lignocellulosic hydrolysates produces concentrations of acetone, butanol, and ethanol in approximately 24%:72%:4% ratio in ABE solvent of fermentation liquor, respectively. Noteworthy, it was observed that fermenting only glucose from the mixture of sugars in hydrolysates increases the ratio of the concentrations of acetone, butanol, and ethanol in ABE solvent [15]. However, more detailed experimentation on the effect of various pretreatments of lignocellulosic biomass on ABE fermentation, type of butanol isomer produced, and the development of toxic tolerant organisms are needed to successfully use lignocellulosic biomass for the production of biobutanol.

**Hexanol**

Industrial interest in hexanol has increased as an alternative fuel. Hexanol is higher carbon alcohol, characterized by a higher energy content like butanol, and non-toxic at low concentrations. Evaluation of the blends of hexanol with biodiesel and gasoline has shown its potential to be used as biofuel [75]. Recently, a novel HBE (hexanol-butanol-ethanol) fermentation has been introduced as a promising alternative similar to existing ABE fermentation for the production of three major biofuel candidates. HBE fermentation is carried out by acetogenic bacteria, mainly belonging to the genus *clostridium* [33]. Acetogens can grow on an array of substrates, for instance, C6, C2, and C1 compounds, and can
produce acetate from CO₂ via the Wood-Ljungdahl pathway. Therefore, acetogens can use a mixture of gases (syngas) primarily carbon monoxide, hydrogen, and carbon dioxide during the fermentation process to produce organic acids and alcohols [78]. Production of valuable biofuels using inexpensive syngas could be a cost-effective bioprocess. Unlike ABE and ethanol fermentation, HBE fermentation can use a wide variety of abundant renewable carbon source. HBE fermentation allows the use of waste gases from industrial processes, agricultural residues, and lignocellulosic biomass for the production of value-added products [33]. However, strategic research and improved process technologies are needed to improve the yields by reducing or avoiding the inhibitory effects of end products, downstream processing to recover the desired compounds, and improving the mass transfer of CO, CO₂, and H₂ gas during the fermentation.

Renewable chemicals

Short-chain fatty acids (C₂–C₅)

Short-chain fatty acids (SCFAs) are valuable products produced from organic waste through anaerobic fermentation. SCFAs can be recovered from many sources as food waste, waste-activated sludge, agricultural waste, etc. through dark fermentation [73, 103, 138] (Table 1). These SCFAs can be derived from different sources and production methods but are mainly derived from fossil sources. SCFAs could be produced using renewable sources or waste biomass and biological methods which is a pivotal aspect in circular bioeconomy [68, 107]. In this section, different types of SCFAs derived from renewable resources and different processes are discussed in detail.

Lactic acid

Lactic acid (LA) is an organic acid, which finds huge applications in several industries such as food and beverages, drugs and pharmaceutical, chemicals, and textile [84]. It can be produced by chemical synthesis or by fermentation of simple carbohydrates such as sugars and starch. Industrially, it has been traditionally produced by lactic acid bacteria by cultivating them either on pure sugars such as sucrose or polymers such as starch or on sugar-rich byproducts such as molasses and whey [49, 52]. Fermentative production of LA offers several advantages, including mainly the cheaper production cost as the process usually involves waste residues as source of energy and carbon, e.g., molasses. LA produced by fermentation is generally a racemic mixture of d and l forms. However, there have been huge efforts to produce d- or l-lactic acid through specially designed microbial processes as these forms separately find very interesting and effective applications in the food and pharmaceutical sectors. For example, l-lactic acid can be polymerized to produce polylactides which is the biodegradable and biocompatible polymer and finds several applications such as to develop...
packaging and fibers to foams for food products and in biomedical appliances.

In recent years, there has been a surge in usage of different kinds of biowastes such as lignocellulosic biomass for the production of fuels and chemicals, especially working on the principles of biorefinery [51, 55]. Such processes are considered “green” and potentially beneficial for energy and environmental sustainability [83]. Use of genetically modified lactic acid bacteria offers the potential to utilize selective carbon spectrum for increasing the substrate utilization efficiency [50, 127]. Tools of metabolic engineering too have been proved highly efficient to increase bacterial efficiency and carbon spectrum utilization [110]. Food waste is yet another organic rich feedstock that has been exploited for the production of lactic acid [113]. Disposal and management of food waste is a serious environmental issue because if not managed properly and left in the environment without treatment, it poses health hazards for humans, apart from polluting the environment.

In a sustainable production and application development based on lactic acid, several important aspects must be considered which include producer microorganisms and its metabolic pathway, physico-chemical parameters of fermentation, and isolation and purification of the product (i.e., LA) from the fermentation broth and treatment and management of industrial effluent generated.

**Acetic acid**

Acetic acid (AA) is one of the most important and commercially valuable volatile SCFAs and it is commonly produced in the industry by oxidizing ethanol and acetaldehyde. It has huge applications in food, pharmaceuticals, medical, cosmetics, and detergents [5]. AA can be produced from different waste streams. Food waste (cafeteria waste) was utilized for the production of AA by yeast and acetic acid bacteria through the micro-aerobic fermentation process. The total yield of AA was achieved at 25.88 gL⁻¹ [69]. Protein-rich substrate (tofu and egg white) were studied by Shen et al. [108] for AA production through acidogenic fermentation. Proteins have complex structure, and lower hydrolysis efficiency which affects the AA productivity.

| Substrate | Type of SCFA | Concentration | Microorganism | Process | References |
|-----------|--------------|---------------|---------------|---------|------------|
| Food wastes (cafeteria waste) | AA | 25.88 g/L | Accharomyces cerevisiae and acetic acid bacteria | Micro-aerobic fermentation | Li et al. [69] |
| protein-rich substrates (tofu and egg) | AA | 0.46 g/g (from tofu); 0.26 g/g (from egg white) | Leuconostoc and Lactobacillus | Acidogenic fermentation | Shen et al. [108] |
| Cheese whey | AA | 0.3–0.4 g/gCOD | Mixed microbes Propionibacterium freudenreichii ssp. Shermanii | Anaerobic fermentation | Silva et al. [109] |
| Industrial waste (glycerol and whey lactose) | PA | 22.57 g/L (whey lactose); 24.47 g/L (whey lactose with pure glycerol); 24.80 g/L (whey lactose with crude glycerol) | Lactobacillus | Batch fermentation | Kosmider et al. [59] |
| Dog food waste | PA | 10 g/L (untreated substrate); 26.5 g/L (treated substrate) | Mixed bacterial culture | Batch fermentation | Ali et al. [5] |
| liquid of sewage sludge and food waste | PA | – | Propionibacterium acidipropionici | Fermentation | Li et al. [67] |
| municipal solid waste | LA | 0.65 g/ghydrocarbon | Lactobacillus delbrueckii | Fermentation | Tsapokos et al. [121] |
| Food wastes (canteen waste) | LA | 0.46 g/gTS | Lactobacillus | Fermentation | Tang et al. [119] |
| Methanogenic sludge, fresh food waste, and anaerobic activated sludge | LA | 28.4 g/L | Lactobacillus | Fermentation | Tang et al. [120] |
| Vegetable waste | BA | – | Acidogenic bacteria Clostridium tyrobutyricum | Anaerobic fermentation | Zhang et al. [137] |
| Corn husk hydrolysate | BA | 50.37 ± 0.04 g/L | Clostridium tyrobutyricum | Fermentation | Xiao et al. [133] |

“–” not mentioned
Propionic acid

Propionic acid (PA) production via anaerobic digestion (AD) is easy and has a lot of potential. PA recovery and separation from fermented media may enhance its production cost; numerous techniques including extraction, membrane systems, electrodialysis, adsorption, and distillation are in trend for the recovery of PA to make the process cost-effective. Substrate is also a big issue for PA production, to cut down the production cost of PA; researchers are focused to utilize the renewable resources. Lab-scale batch fermentation of food waste was carried out by Ali et al. [5] for PA production. Selected inoculum was consist of bacterial consortium, milk, and soft goat cheese and maximum 26.5 gL−1 PA was obtained using food waste as substrate. Results showed that at optimal process conditions, sufficient quantity of PA can be produced from food waste. In other study, Kosmider et al. [59] utilized industrial waste (glycerol and whey lactose) for PA production by Propionibacterium freudenreichii ssp. Shermanii through batch fermentation process. The maximum PA (24.80 gL−1) was obtained using whey lactose with crude glycerol as substrate. It concluded that industrial waste has an excellent capacity to be used as a substrate of PA production. Liquid of sewage sludge and food waste was also utilized by Propionibacterium acidipropionic as carbon source for PA production through fermentation process [67].

Butyric acid

Butyric acid (BA) production from vegetable wastes is a cost-effective and resource-recovery method. Composition of organic matter and downstream processing may influence the yield and cost of desired product. Unlike pure sugars, various wastes like potato peels, carrots, celery, and Chinese cabbage were investigated by Zhan et al. [137] to see the effect of type of vegetable wastes on the production of BA in an anaerobic fermentation. The highest volatile fatty acid yield was observed in potato peels and maximum BA produced using carrot. Acid hydrolysate of corn husk was utilized by Clostridium tyrobutyricum carbon source for the production of BA via fermentation. Results found that corn husk hydrolysate by C. tyrobutyricum gave 42.6 and 53.0% higher BA in comparison to glucose and xylose, respectively [133]. Corn husk can be an another economical substrate for BA production.

Medium-chain fatty acids (C₆–C₁₀)

Medium-chain fatty acids (or MCFAs) exhibit high energy density with high hydrophobicity. MCFAs can be further converted into biofuels and chemicals after secondary fermentation [112]. MCFAs can be converted from SCFAs through chain elongation process (Fig. 4) under anaerobic conditions. This process involves the addition of one or two carbon atoms to the SCFA backbone, resulting in the production of MCFAs.

Fig. 4 Chain elongation process and associated pathway for the generation medium chain fatty acids with representative example of caproic acid production.
conditions utilizing various waste streams (Table 2). This section discusses the latest advancements in the production of caproic, caprylic, and capric acids.

**Caproic acid**

Caproic acid is a platform chemical that can be used as a precursor for fragrances, pharmaceuticals, paint additives, and lubricants as well as in feed additives, plant growth promoters, flavor additive, and antimicrobials [28]. Although caproic acid is produced from food crops, novel substrates such as mixed organic waste obtained directly from industries are quickly gaining popularity due to high productivity and lower cost of production [25, 26]. Moreover, the utilization of microbial co-cultures over pure cultures is now in consideration as it can perform more effectively in challenging process environments [71]. The co-digestion between cheese whey and sewage sludge has been explored for caproic acid production which showed 44% acidification with a 10-day hydrolytic retention time and 2 feeding cycles per day [47]. In another investigation, the co-digestion of sewage sludge with organic waste in a long-term operation under semi-continuous model produced caproic acid which contributed to 55% of the total volatile fatty acids produced [82]. Carbohydrate-rich waste streams can also be fermented to lactic acid that can be further fermented to produce caproic acid through chain elongation. In chain elongation, electron acceptors (SCFAs) and electron donors (lactic acid, ethanol, etc.) participate in a redox reaction that elongates the carbon chain through a reverse β-oxidation [112]. However, the chain elongators can compete with other bacterial groups over lactic acid and therefore, it is essential to critically control the driving parameters for medium-chain fatty acid production. In this regard, it has been reported that Caproiciproducens when used under a pH of 6 produces caproic acid due to movement of the microbial community towards chain elongation [22]. Fruit wastes have also been utilized for the generation of caproic acid. Reddy and Chang [94] reported that bacteria-incubated pumpkin waste comprising of pumpkin pulp and skin waste could produce 6.1 g/L of caproic acid as compared to 1.2 g/L when apple waste was used. Caproic acid has also been produced without an external electron donor through mesophilic chain elongation generating productivity of 0.07 g/L/h [135]. The production of caproic acid in this case was supported by a thermophilic conversion of acid whey (a waste stream from the Greek yoghurt industry) to lactic acid. Bioaugmented culture containing bacteria belonging to Clostridia, Desulfbacteraceae, Bacillus, and Sphingobacteriales could produce 8.1 g/L of caproic acid from food waste [95, 96].

| Substrate | Type of MCFA | Concentration | Inoculum | Processes | References |
|-----------|--------------|---------------|----------|-----------|------------|
| Organic fraction waste (municipal solid waste and supermarket food waste) | Caproic acid | – | – | Chain elongation | [25, 26] |
| Lignocellulosic biomass (grass) | Caproic acid | 4.09 ± 0.54 g/L | *Clostridium* and *Lactobacillus* spp. | Microbial hydrolysis and acidification | Khor et al. [56] |
| Potato waste | Caproic acid | 110 mg/g | Anaerobic sludge as inoculum | Anaerobic digestion | Parawira et al. [87] |
| Influent waste from a full-scale organic waste treatment facility | Caproic acid | 12.6 g/L | Acetate and ethanol consuming consortium | Microbial hydrolysis and acidification | Grootscholten et al. [41] |
| Food waste from homes | Caproic, caprylic acid | 8.6 g/L; 0.23 g/L | Anaerobic bacteria, *C. kluyveri* | Microbial hydrolysis and acidification | [95, 96] |
| Corn beer | n-Caproic and n-caprylic acid | 0.638 g COD g−1 COD | Digestate from first phase of full-scale silage digester | – | Urban et al. [122] |
| Yogurt acid whey | n-Caproic and n-caprylic acid | 111 mmol C L−1 day−1 | Lab-scale food waste fermentation | Microbial hydrolysis and acidification | [135] |
| Maize silage | Caproic and caprylic acid | 3.6 g/L; 0.5 g/L | Fermented broth | Fermentation | Braune et al. [20] |
| Maize silage | Caproic and caprylic acid | 6.12 g/L; 1.83 g/L | Acidogenic percolate and methanogenic digestate | Digestion | Lambrecht et al. [63] |

“–” not mentioned

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Caprylic acid

Caprylic acid is small sized, highly digestible, and less water solubility MCFA which is known for its nutritional and medicinal benefits [31]. Different waste substrates have been evaluated for the production of caprylic acid using diverse microbial species. The administration of oleaginous yeast isolates on rice straw has been reposted to produce 75–90% caprylic acid–rich oils [31]. Bioaugmentation with Clostridium acetobutylicum ATCC 824 on granular sludge has also shown promising results for enhancing the production of caprylic acid [27]. Mixed microbial communities in fed-batch reactors have been reported to produce 0.32 g/L of caprylic acid from acetic acid in a fed-batch reactor [117] while 0.9 g/L caprylic acid can be produced in an elongation reaction using an upflow anaerobic filter with acetic acid and ethanol [40]. Increased concentrations of ethanol (100 mM) with bioaugmented chain elongation produced caprylic acid up to 1.7 g/L [27]. However, the most promising species so far for caprylic as well as caproic acid production has been identified as Clostridium kluyveri [95, 96].

Capric acid

The production of capric acid involves the oxidation of decanol under acidic conditions using a potent oxidant (such as CrO₃). Capric acid naturally occurs in palm and coconut oil and in the milk of mammals. Currently, capric acid production from waste substrates has not been fully investigated and may have been produced only in trace amounts [95, 96]. The waste streams from the oil and dairy processing industries could be potential sources for the production of capric acid that could have further applications in flavor, perfume, nutritional, and pharmaceutical industry [11].

Role of renewable chemicals and fuels in bioeconomy promotion

As a consequence of the linear economy, increasing population, and growing resource utilization, humanity is extremely dared by the accumulation of waste in huge amounts from several sectors. Organic, animal, and municipal waste signify the major category of waste produced by these areas. The decision of using various organic waste sources as feedstock for synthesizing both energy and bio-products is denoted to as biorefineries. The particular integrated approach has acknowledged substantial attention in current years as a sustainable and eco-friendly substitute to petroleum refineries, and take advantage of bio-waste for synthesizing high value materials and chemicals [10].

Waste-derived biorefineries are attaining large interest owing to their potential for the synthesis of fuel and biochemicals. Interestingly, waste biorefineries are an environmental-friendly form of biorefinery in which a large range of important products can be attained through several bioprocesses from waste biomass like agro-industrial wastes, as raw materials.

Waste biorefinery concept comprises in the execution of a eco-friendly circular bioeconomy based on the viewpoint of remanufacturing, recycling, and maintaining by changing from a linear economy according to the principle of take, manufacture, and dispose [36, 53].

Bioprocess techniques applying waste resources which comprise of solid, liquid, and municipal waste to synthesize value-added fuel and chemical regarded as waste-to-wealth have attained growing consideration as the products synthesized are renewable and exhibit eco-friendly benign biodegradable properties. The biological conversion of waste biorefinery on the synthesis of fuel and chemicals does not only aim the energy and ecological security concerns; in fact, it implies an improved management of waste streams. It is an environment-sustainable and economically viable model as the carbon source is eco-friendly and economical [125, 126]. Several types of waste materials such as food waste, waste stream from industries, agro-industrial waste, agriculture and forest waste, and lignocellulosic biomass waste as well as wastewat or sludge have been proficiently converted into beneficial and economical biofuels and chemicals [34, 35].

The entire procedure is recycled with special focus on the reduction of waste, to keep the sustainable nature of the process. The technology follows the laws of circular economy, where not only the waste valorisation but also the efficient usage or transformation of 2°/residual streams to valued bioproducts is promoted [126]. The value-added materials of waste biorefinery can be divided into major categories like (i) biomaterials like biopolymers, fertilizers, and active pharmaceutical ingredients and (ii) biofuels.

Furthermore, the ideal usage of waste biorefineries is related to a shift from a linear bioeconomy to a circular bioeconomy for a sustainable supply of bioresources. The combination of bioeconomy with circular economy is beneficial for the optimized utilization and reusage of resources for fuel and chemicals.

The bio-based materials synthesized have ecological kind characteristics like zero-toxicity, being easily degradable, and being biocompatible that support an environment-friendly movement, and hence encourage a greener ecology globally. Various ecological problems like global warming, pollution, and waste disposal as well as depletion of natural resources can then be controlled. For instance, the synthesis of fuels and chemicals which considerably replace conventional fossil fuels can aid to reduce pollution that validates harmful impacts in soil and the atmosphere. Together, a waste biorefinery–circular bioeconomy technology can
guarantee environmental security. The presence of ecological security stimulates a food safety for the world.

**Biorefinery framework—approaches**

The replacement of petroleum refineries to decrease the dependence on fossil resources is an important measure to be taken nowadays. As an alternative, in a biorefinery framework, various approaches have been carried out. René and Bert have classified the biorefinery approach based on the raw materials, type of technology, and released products [100]. The advantage of biorefinery includes the less reliability on fossil fuels and thus better environmental impacts. It also assures the maximal conversion of bioresources into products and thus the improved sustainability of the entire process system. In green biorefinery, the biomass gets separated to cake and juice which are rich in fiber and protein which contain starch, cellulose, enzymes, minerals, and other components. The major advantages include that it can utilize a wide range of green biomass for the synthesis of industrially important chemicals such as lactic acid and proteins. Depending on the type of raw material used and its source, other than green biorefinery, lignocellulosic, whole-crop, and marine biorefinery has been established.

By categorizing the biorefinery based on the technology used, it is majorly divided into biochemical and thermo-chemical platforms. During the process, the raw materials were converted to value-added products by releasing the contents in the biomass in readily usable sugars and fermentation feedstock. Biochemical platforms were used to extract sugars mainly from lignocellulosic biomass. About thermo-chemical platforms, it utilizes a variety of raw materials of low cost for the treatment and mainly used for industrial applications. The combination of different biorefinery along with the suitable platform will nurture the valorization of bio-waste. Various technological models were also put forward and they are namely acidogenic model, carbon dioxide model, photosynthetic model, bioelectrogenic model, and nutrient recovery model based on the intermediates and end product formation as well as the technology used. The major advantages of biorefinery approach includes the maximum utilization and synthesis of various byproducts from a single biomass. As an example, in biohydrogen production, other byproducts such as 1,3-propanediol, butyrate, and ethanol are the major byproducts which utilize more than half of the raw feedstock. For each mole of glucose, 1.58 mol H₂ and 0.90 mol ethanol can be recovered after the process. Other than the advantage of being high-cost chemicals, these end by products can also be served as the starting material for other chemical synthesis [77, 85].

**Conclusions**

MSW and industrial waste streams have been burdening commercial, environment, and political bodies. These waste-by-products are carbohydrate-rich sinks, characterized to be the polymeric units of reducing and non-reducing sugars that can be valorized into value-added products like alcohols, acids, gases, lipids, and other secondary metabolites. The fuels like bio-ethanol, biodiesel, butanol, and hexanol have a significant impact in the transportation and industrial sector, where the petroleum-derived fuels can be either replaced or blended with these biobased gaseous or liquid fuels. Short-chain fatty acids and carboxylic acids have interest in various industrial sectors like plastics, nutraceuticals, other speciality, and bulk chemicals. The demonstration of these bioprocesses creating waste to wealth can address various global, environmental, health, and societal concerns. To commercialize these processes, further research resembling the economic feasibility of petroleum-derived processes should be performed and validated.

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