4 Biochemical Approach for Transformation of Agricultural Waste to Bioenergy and Other Value-Added Products Through the Bioelectrochemical System

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Abstract

Agricultural industries are the largest waste producer that comprises a major problem worldwide due to the adverse effect of agro-waste on the environment, economy, and social life. Annually 1300 million tons of trash are produced from the agricultural fields, out of which up to 50% are raw materials dumped without treatment. Therefore, minimising agricultural solid waste is imperative to combat its detrimental effects on the health of humans and other animals. Furthermore, agro-waste contains different bioactive compounds such as lignin, cellulose, chitin, and polyphenolic compounds; therefore, it can be envisaged as a potential source for producing biofertiliser, biofuel, biogas, enzymes, vitamins, antioxidants, and other value-added products. Additionally, utilising agro-waste as a raw material diminishes production costs and provides the scope of additional revenue for the reliant industries. Also, the synchronised recovery of renewable energy and wastewater treatment through bioelectrochemical systems (BES) utilising agro-waste products as feedstock demonstrates a waste biorefinery approach leading towards a sustainable circular bioeconomy. Therefore, this chapter elucidates the application of different agro-waste products in the field

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of BES and their effects on bioenergy production and other value-added product recoveries. Moreover, this chapter aims to enlighten the readers on the advancements in biochemical processes for agro-waste remediation and biochemical conversion technologies to recover valuable biochemicals. In addition, different roadblocks associated with biochemical conversion technologies, considering recommendations and future perspectives, are also highlighted. Additionally, recent developments in potential imminent research areas of agro-waste-assisted BES have also been covered to make this nascent technology ready for large-scale implementation.

Keywords

Agro-waste · Bioactive compounds · Biochemical conversion · Value-added products · Bioelectrochemical system

4.1 Introduction

The scarcity of energy is a continually growing global worry that has been spurred on by an increase in population, rapid industrialisation, and engineering advancements (Ghasemi et al. 2013). Moreover, the excessive consumption of nonrenewable energy sources, such as coal, petroleum, other crude oil, and natural gas, to meet the rising global energy demand of the population worldwide is another major concern that could trigger an energy crisis in the near future (Ahmad and Zhang 2020). In addition to the exhaustion of fossil fuels and associated detrimental impacts on ecological systems, the open disposal of agro-waste in developed and underdeveloped nations significantly contributes to environmental spoilage, which is another significant worldwide issue. In order to conquer the dilemma of the global energy crisis and lessen associated environmental risks, scientists are striving towards using eco-friendly and renewable energy sources (Kabeyi et al. 2022). Therefore, recuperating bioelectricity and other gaseous and liquid biofuels from a variety of agro-waste may suggest a renewable economic explanation that opens the possibility of fulfilling the global energy demand.

Increased global population, urbanisation, economic expansion, and shifting production and consumption patterns contribute to the abundance of bio-waste generation. Specifically, agricultural bio-waste, a typical renewable energy source with plenty of nutrients and easily biodegradable organic materials, are obtained from various biological sources and industrial processes. These waste products can be decomposed easily under both aerobic and anaerobic conditions. One of the most prevalent techniques for recovering resources from trash is anaerobic digestion, which converts organic waste into biogas, while leaving behind additional resources like value-added nutrients (Kamperidou and Terzopoulou 2021). Moreover, starch, cellulose, protein, hemicellulose, and lipids are the key components of these bio-wastes, and they can be used as inexpensive raw materials to generate value-added products. However, further treatment should be required to treat xenobiotic compounds, heavy metals, and other contaminants prior to disposal in the ecosystem. Therefore, a distinct approach is obligatory to recover the bioenergy while remediating the primary pollutants in wastewater. Thus, recovery of power along with other biofuels through a single bioelectrochemical system (BES) using agro-waste as the substrate may propose a renewable, economical elucidation for the circular bio-economy.

In this veneration, BES provides an enormous opportunity for synthesising renewable bioenergy and other valuables while simultaneously purifying wastewater (Ghangrekar et al. 2022). The organic material in wastewater can be metabolised by exoelectrogens and generate protons, electrons, and CO_2. While electrons are transferred through the external circuit connected between the anode and the cathode of a BES, where they are typically combined with oxygen to produce H_2O with the reaction of protons released in bulk anolyte that migrate towards the cathode through the proton exchange membrane (PEM). In the case of a microbial fuel cell (MFC), biochemical energy is converted to electrical energy during the flow of electrons from the anode to cathode via an external circuit. On the other side, external power is provided to endorse the H_2 generation through microbial electrolysis cell (MEC) (Koul et al. 2022).

The cutting-edge BES technology has the capacity to produce valuable chemicals while simultaneously producing sustainable and renewable energy using wastewater as substrate. In 1911, Potter initially developed a galvanic cell utilising platinum as the cathode for power generation via cultivating two exoelectrogens such as *Saccharomyces cerevisiae* and *Escherichia coli* (Potter 1911). This widened the door for further research that centred not only on bioenergy production and wastewater treatment rather also on resource recovery from different wastewater. For improved power generation and pollution removal, hybrid systems such as membrane bioreactors have also been combined with MFC (Bhowmick et al. 2019). One such effort combines an MFC with an agro-waste-derived membrane bioreactor to handle medium-strength effluent (Bhowmick et al. 2019). Nevertheless, the difficulties and expenses related to the fabrication of reactors and cultivation of exoelectrogens might hinder its widespread application on a real-scale.

For the utilisation of inexpensive components in MFC systems to weaken the overall cost, waste-derived biomass may offer an intriguing alternative to expensive electrocatalysts. Therefore, this chapter focuses on agricultural waste and the techniques used to turn it into valuables including bioenergy in terms of liquid and gaseous biofuel, enzymes, antibiotics, ethanol, and single-cell proteins. In light of this, employing agro-biomass waste, such as food, sludge, and forestry wastes, is a tempting initiative of commercialising BES. Furthermore, the environmental and health risks associated with BES during wastewater treatment and bioenergy recovery can be significantly decreased by using waste biomass resources as energy sources.

The potential use of biomass waste as a substrate for different BES has been confirmed by a number of preceding research, including those on algal biomass, and lignocellulosic biomass and agro-based wastewater or effluents (Sani et al. 2021; Ali et al. 2020; Wang et al. 2021). Further, Chakraborty et al. (2020) developed a low-cost biochar-derived PEM by pyrolysing food waste at 600 °C and achieved 81% of chemical oxygen demand (COD) removal efficiency from the MFC fabricated with this membrane (Chakraborty et al. 2020). The same research group also elucidated the economic sustainability of this biochar, which had a maximum power yield per unit cost of PEM that was 26-folds greater (0.278 W/$) than Nafion 117 (0.011 W/$) (Chakraborty et al. 2020).

Additionally, different agro-waste effluents served as the substrate for exoelectrogens in MFC to enhance the system's performance. For instance, palm oil mill effluent inoculated with anaerobic sludge has been treated in a single chamber MFC and achieved a maximum of 304 mW m^{-2} of power density along with 45% of COD removal efficiency (Baranitharan et al. 2015). Furthermore, hydrolysate formed after converting the solid residue present in agro-waste like rice husk, wheat straw, and corn stover into carbohydrate-rich fermented products during solid or semisolid-state fermentation can also be utilised as a substrate in MFC (Schievano et al. 2016). Therefore, this chapter devoted an effort to thoroughly evaluate the sources and varieties of agro-waste, management issues, and a wide variety of agro-waste treatment technologies to turn bio-waste into bioenergy. Also, the prospective advantages of transforming agro-waste into value-added products through BES and future recommendations for the commercialisation of this technology are overviewed. Thus, the utilisation of green and inexpensive agro-waste in BES enables an inventive strategy of concurrent wastewater treatment along with resource recovery, thus demonstrating the concept of the circular bio-economy.

4.2 Agro-Waste Sources as Raw Material

Agricultural wastes or agro-wastes are crop residues and/or first processed raw agricultural products such as fruits, vegetables, dairy products, poultry, meat, and other products (Obi et al. 2016). Generally, agro-waste is generated during agricultural activities such as farming, horticulture, nursery plots, seed production, market gardens, dairy livestock breeding, grazing, and forestry or woodland production (Lim and Matu 2015). Moreover, agro-wastes can be classified as solid, liquid, or slurry depending on their physical state and be generically categorised into crop residues, agro-industry wastes, livestock wastes, and fruit and vegetable wastes (Fig. 4.1).

According to grain-to-residue conversion factors and grain production data, crop residue production has more than tripled from 1589 million tons (Mt) in 1960–1961 to 5280 Mt in 2020–2021 (Shinde et al. 2022). Hence, it is necessary to utilise these massive pools of unused resources that can be transformed into valuable assets with multiple beneficial industrial applications. Crop residual wastes left on crop-cultivated land, including leaves, stoners, straws, seed pods, etc., are the most abundant organic wastes that can be easily transformed into value-added products. The agro-waste such as rice straw, wheat straw, corn stover, etc. are extensively utilised to produce ethanol and other value-added liquid fuel. However, many other crop residues including rotten fruits and vegetable at the cultivation farm can be used

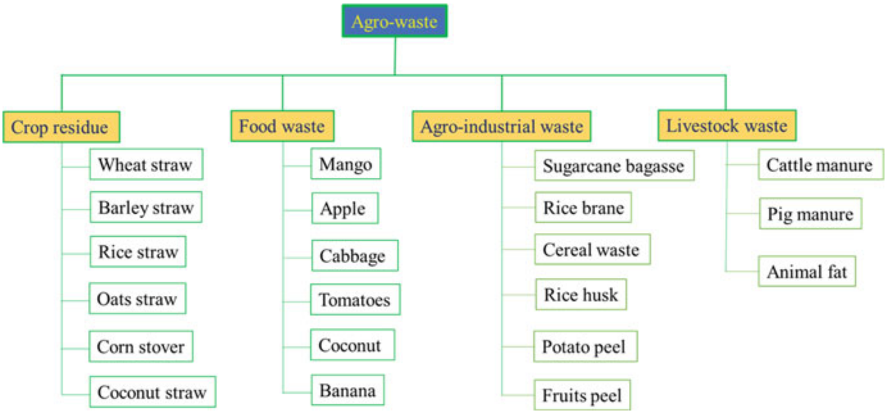

Fig. 4.1 Classification of agro-waste derived from natural and environmental sources

to recover other valuable products such as biochar, biogas, fertiliser, secondary metabolites, antioxidants, and so on.

Agro-industrial waste management provides multidimensional output in the form of valuable product recovery and also retardates its harmful impact on the environment and human and animal health. Moreover, due to some of the constituents in agro-industrial waste, it has gained much attention as a raw material for different sustainable products and bioenergy production (Beltrán-Ramírez et al. 2019). With an estimated annual bagasse production of 180.73 Mt worldwide, sugarcane bagasse, a lignocellulosic waste, is the major contributor to agro-industrial waste (Pattanaik et al. 2019). Different agro-industrial residues, such as waste products from the food, alcoholic, and vegetable and fruit peels, and fruit pomace after extraction of juice are extensively utilised for the production of enzymes and other valuables. In addition to starch residue derived from starch-manufacturing industries, various other by-products such as sugarcane bagasse, molasses from sugar manufacturing industries, de-oiled seed cake from edible oil manufacturing industries, chicken skin, egg, meat, and animal fat from slaughterhouses and meat processing industries have been found to have a noteworthy impact on the production of diverse value-added products (Lopes and Ligabue-Braun 2021). Other major contributors of agro-industrial waste are waste from the palm oil industry, apple pomace, orange peel, and some nonfood-based waste such as de-oiled seed cake of nonedible oil from *Jatropha curcas* and *Pongamia pinnata*.

Livestock is another foremost agro-waste source, which are classified as liquid manure (urinary waste), solid manure (farmyard manure), and other industrial or municipal wastewater generated. Livestock-based waste includes manure and organic materials in the slaughterhouse, wastewater from the bathing of animals, and maintaining sanitation in slaughterhouses. The annual livestock waste generation in India is about 3 Mt (Kumari and Dhawal 2020). As most livestock farms are built near or in the residential area, air pollutants such as H_2S and CH_4 and odours from livestock waste are serious concerns; therefore, proper waste management is required to alleviate this issue. A prevalent greenhouse gas, CH_4, accounts for roughly 30% of global anthropogenic greenhouse gas emissions; however, animal wastes alone account for 32% of global CH_4 emissions, which are also responsible for significant energy loss (Kimothi et al. 2020). According to the Indian Council of Agricultural Research's, New Delhi, report, the annual energy loss of 38×10^8 Giga calories was estimated from livestock waste CH_4 emissions (Kimothi et al. 2020). Using cutting-edge scientific technology, livestock waste can be recycled to combat rising energy prices, promote sustainable agriculture, and mitigate environmental threats. Moreover, livestock is an essential component of the agricultural circular bioeconomy, converting non-edible biomass into high-quality food and recycling large amounts of nutrients to the agroecological system via farmyard manure.

4.3 Applications of Different Agro-Waste Materials

Utilising agro-wastes as raw materials can be an optimistic approach to subordinate production costs as well as environmental pollution (Sadh et al. 2018). The lignocellulosic agro-industrial residues usually have high concentrations of glucose, xylose, mannose, arabinose, and other organic compounds that can be anaerobically oxidised to produce bioethanol and valuable biogas. On the other hand, lipid-containing agro-waste is considered as a potential feedstock for biodiesel and biogas production. Moreover, agro-waste is a rich source of bioactive compounds that further add to its applications for real life in recovering fertiliser, plant secondary metabolites, antibiotics, and other valuable products.

4.3.1 Production of Bioenergy from Different Agro-Waste

The agro-waste rich in fermentable cellulose, such as sugarcane molasses, sugarcane bagasse, and corn stalk, produces ethanol and biogas. In contrast, lipid-rich agro-waste, such as nonproductive oil seeds, is a feedstock for biodiesel production (Donzella et al. 2022). Moreover, bioenergy production depends on the types of agro-waste; in this regard, anaerobic digestion of 74 manures and 78 crop straw resulted in the bio-methane production of 335.5–620.4 STP mL g^{-1} VS for manures and 434.0–540.3 STP mL g^{-1} VS for crop straws (Wang et al. 2019). Similarly, a comparative ethanol recovery from yeast culture on lignocellulosic agro-waste such as sugarcane bagasse, rice straw, corncob, and sweet sorghum bagasse was investigated by Nunta et al. (2023). The investigation revealed that fungal strain *Candida tropicalis* cultivated with rice straw generated maximum 15.3 g L^{-1} of ethanol after 24 h of cultivation (Nunta et al. 2023). Operating parameters also affect biofuel yield; for instance, at optimal 92.59 °C hydrolysis temperature, 30 min operation time, and 1% acid concentration, Berhe and Sahu achieved a maximal yield of 10.86 mL ethanol per 50 g of sugarcane bagasse biomass (Berhe and Sahu 2017). Moreover, Donzella et al. (2022) recovered 55% of lipids from pumpkin peel through yeast fermentation by cultivating oleaginous yeasts *Rhodosporidiobolus azoricus* and *Cutaneotrichosporon oleaginosum* (Donzella et al. 2022).

Hydrogen is considered the most suitable alternative future fuel for transport and other sectors (National green hydrogen mission GOI). Zhang et al. (2020) investigated the biohydrogen production from cornstalk; a maximum of 424.3 mL H_2 g^{-1} of cornstalk was reported at two-stage fermentation (dark fermentation followed by photo-fermentation) in this investigation (Zhang et al. 2020). In another investigation of biohydrogen production from thermochemically pretreated corncob using a mixed culture bio-enhanced with *Clostridium acetobutylicum*, a maximal biohydrogen yield of 132 L kg^{-1} of corncob biomass was reported (Medina-Morales et al. 2021). Therefore, the application of different agro-wastes for both liquid and gaseous fuel productions can be a promising carbon neutral revelation, which would alleviate the nuisance of global warming and energy crisis.

4.3.2 Other Biochemicals' Recovery

Agro-waste is one of the most cost-effective substrates for extracting biochemicals of commercial value, such as microbial pigments, fragrance compounds, antioxidants, antibiotics, and plant growth hormones. Utilising agro-waste as feed-stock for biochemical synthesis reduces environmental and health risks, while simultaneously enhancing the economic value of the bioprocess. For instance, orange peel is an agro-waste that generates enormous quantities and it is a source of natural pigments such as carotenoids; for example, the carotenoids yield of 97.4 ± 17.1 μg g^{-1} of dry biomass (orange peel) was reported in an investigation (Murador et al. 2019). Similarly, anthocyanins have multiple health benefits, and their extraction from food waste has recently become a topic of interest (Diaconeasa et al. 2022).

Cutin and suberin are biopolymers made from fatty acids and aromatic compounds. Cutin is the primary component of the cuticle, which is the waxy, water-repellent outermost layer of exposed cell walls. Few approaches have been recently discovered to extract cutin monomers from various agro-wastes on an industrial scale (Heredia-Guerrero et al. 2017). Agro-waste also contains many bioactive compounds such as polyphenols, tannins, flavonoids, vitamins, essential minerals, fatty acids, volatiles, anthocyanins, pigments, bioactive peptides, whey, and colostrum (Ben-Othman et al. 2020). Asagbra et al. (2005) investigated the presence of antibiotics in agro-waste in which peanut shells were identified as the most productive substrate for tetracycline (4.36 mg g^{-1}), followed by corncobs (Asagbra et al. 2005). Therefore, agro-waste is a plausible source for pharmaceuticals and other nutrients and minerals, rendering it a feasible option that will aid in fulfilling the increasing demand for nutrients in the health sector.

Biochar is a carbon-rich material produced by incomplete combustion of biological material such as agro-waste in the absence or with a limited amount of oxygen (Susilawati et al. 2020). Conversion of agro-waste to biochar is one of the most sustainable approaches for carbon sequestration and soil amendment agent.

Soil fertility degradation and nutrient depletion are common threats to agroecosystems, posing a challenge for modern agricultural practices aimed at balancing soil fertility factors (Pradhan et al. 2020). In this regard, agro-biochar has recently gained adequate interest due to its agronomic applications. Biochar derived from agricultural sources is utilised as a soil amendment to enhance the physical and chemical properties of soil, thereby augmenting the soil's nutrient accessibility and water retention potential. Furthermore, the burial of biochar in soil results in a gradual decomposition process, thereby functioning as a durable carbon reservoir. Additionally, biochar also influences soil microbiology and enzyme activity, which helps to enhance plant growth and crop yield (Enaime and Lübken 2021).

A recent investigation demonstrated that applying agro-biochar as fertiliser enhances crop growth; however, its combination with mineral fertiliser could improve its physiological attributes regarding chlorophyll fluorescence indicators (Mustafa et al. 2022). Moreover, due to their structure, agro-biochar can have diverse applications, such as electrode material for fuel cells, supercapacitors, and batteries, and feedstock of activated carbon and carbon nano-filaments (Wahi et al. 2015; Khedulkar et al. 2023). Agro-biochar is also considered a clean and alternative energy source of fossil fuels. The biochar yield depends on the parameters such as pyrolysis temperature, biomass, and pyrolysis time; the biochar from vegetable waste (cauliflower, cabbage, banana peels, and corn cob residues) showed a yield of 20–30% at the pyrolysis temperature range of 300–500 °C (Pradhan et al. 2020).

Applying agro-waste as fertiliser is an economic practice in terms of saving the cost required for chemical fertiliser. A biochar's carbon content H/C ratio is a significant property for its utilisation; stable carbon content, low H/C ratio, and high surface area and pore volume are desired for its high quality as fertiliser. In this regard, when cassava rhizomes, cassava stems, and corncobs were used for biochar production, the chemical analysis showed that corncobs yielded the highest C (81.35%) and H (2.42%) content with high surface area (Wijitkosum and Jiwnok 2019). In addition, organic fertiliser obtained from agro-waste improves soil fertility by enhancing soil aggregation, hydraulic conductivity, water-holding capacity, degree of compaction, bulk density, and resistance to wind and water erosion. Thus, it concluded that agro-waste could be the economical and sustainable feedstock for bioenergy production, fertiliser production, biochemical production, and other valuables and so on.

4.4 Traditional Agro-Waste Conversion Technologies

4.4.1 Biochemical Conversion

4.4.1.1 Anaerobic Digestion

The primary feature of agro-waste is its high organic content, which makes it useful for energy recovery and other value-added biochemicals' generation through anaerobic digestion. Anaerobic digestion is a complicated biological process in which

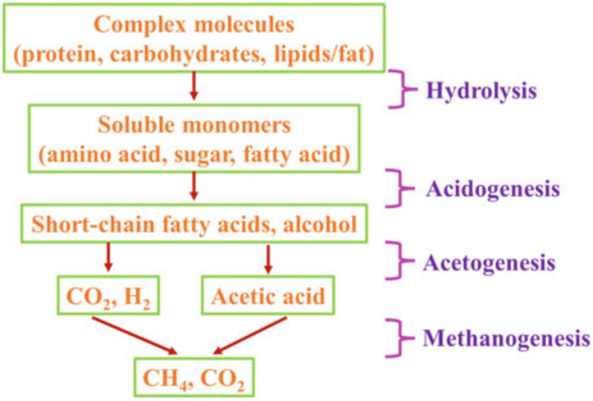

Fig. 4.2 Metabolic pathways of anaerobic digestion of biomass

anaerobic bacteria decompose organic material in the absence of oxygen. The anaerobic digestion of organic waste follows broadly four-step fermentation pathways, hydrolysis, acidogenesis, acetogenesis, and methanogenesis, as shown in Fig. 4.2.

The main valuable products derived from the anaerobic digestion of agro-waste are biogas (CH_4 and CO_2) and digestate. During anaerobic digestion, the nitrogen in the protein is mineralised into ammonium, and the total P and K are also retained in the digestate (Schievano et al. 2011). Due to the presence of these nutrients in the digestate, it is applied to agricultural land as fertiliser. On the other hand, biogas is used primarily as fuel for heating and lighting purposes; however, it can be further transformed into alcohol or syngas (Riya et al. 2021). Biogas generated in anaerobic digesters is composed of methane (50–80%), carbon dioxide (20–50%), and between 0.2% and 0.4% hydrogen sulphide (highly toxic gas). However, the proportion of these gases in biogas is dependent on feedstock and process management (Demirbas and Ozturk 2005). Generally, the heating value of the biogas produced is in the range of 18–25 MJ m^{-3} depending on methane content (Demirbas and Ozturk 2005). The storage of biogas is impracticable due to its poor calorific value and corrosive nature. However, the benefits significantly exceed the aforementioned drawbacks. Anaerobic digestion makes it possible to handle and dispose of vast amounts of poultry, swine, and dairy waste, minimising the odour issue. This process also stabilises the waste, and the digested sludge is relatively odourless while retaining its original fertiliser value.

4.4.1.2 Fermentation

Fermentation is a biological process frequently promoted by the microorganism-derived release of enzymes that convert simple sugars into low molecular weight compounds such as alcohols and acids. The fermentation of two of the most prevalent sugars follows the two processes as shown below in Eqs. (4.1) and (4.2) (Garba 2021):

$$\text{Glucose fermentation}: C_6H_{12}O_6 \rightarrow 2C_2H_6O + 2CO_2 \tag{4.1}$$

$$\text{Fructose fermentation}: 3C_5H_{10}O_5 \rightarrow 5C_2H_6O + 5CO_2 \tag{4.2}$$

During fermentation, fermentable cellulosic biomass, such as sugarcane molasses, sugarcane bagasse, and corn stalk, could be converted into alcohol through biochemical pathways (Garba 2021). These pathways involve many patterns in which hydrolysis and fermentation processes are conducted in the same or different reactors, such as separate hydrolysis and fermentation, simultaneous saccharification and fermentation, and consolidated bioprocessing.

The fermentation of banana waste under the optimum condition of 60 °C temperature, pH of 7.5, 5% of inoculums size, and 5 days of incubation time, a maximum ethanol yield of 0.41 g g^{-1} of substrate was obtained on co-culturing ethanologenic *Clostridium thermocellum* CT2 with *Clostridium thermosaccharolyticum* HG8 on alkali-treated banana waste (Harish et al. 2010). In an investigation, a maximum of 249 mg gds^{-1}L-lactic acid was obtained after 5 days of solid-state fermentation (SSF) of cassava bagasse and sugarcane bagasse under the optimised conditions with a conversion efficiency of about 99% of the initial reducing sugars (John et al. 2006).

In addition to alcohol and acid production, SSF by utilising agro-waste produces enzymes, vitamins, antioxidants, animal feed, antibiotics, and other compounds (Sadh et al. 2018), for instance, the extraction of pullulanase enzyme from agro-waste using SSF (Kumar et al. 2022). Another example is laccase production with the utilisation of agro-waste substrates in SSF processes (Ghosh and Ghosh 2018). The most difficult aspect of converting agro-waste into fermentable sugars, such as hexose and pentose, is balancing the synthesis of inhibitors and desirable products. To avoid inhibitors' production and optimise hexoses' and pentoses' synthesis, microbial metabolism in the breakdown and saccharification of the biomass could be taken into account.

4.4.2 Thermochemical Conversion

The major thermochemical conversion of agro-waste to heat, biochar, biogas, and liquid fuels (bio-crude) are combustion, pyrolysis, gasification, and liquefaction. Among these thermochemical conversions, combustion is the most frequently practised for heat and electricity generation methods.

4.4.2.1 Direct Combustion

One of the oldest methods of biomass conversion is the burning of agricultural waste for the generation of fuel. Even today, it is a relatively popular practice to burn agricultural trash through stoves and pot fires for cooking and heating purpose. Lignin-rich biomass is preferred for combustion (Yan et al. 2019); however, compared to other biomass conversion processes, the process is somewhat less selective for biomass feedstock. The combustion of agro-waste-based feedstock is converted mainly to heat, CO_2, water, and a smaller quantity of other compounds depending on the composition of biomass and process parameters. The agro-waste contains more ash-forming minerals along with C, H, and O (Saxena et al. 2009; McKendry 2002). Agro-waste has more oxygenated compounds compared to traditional fossil fuels, owing to the carbohydrate content of biomass, in which dry biomass typically includes 30–40% of O_2 (McKendry 2002). During the combustion of agro-waste-based biomass, a portion of the needed O_2 is supplied by the bound O_2 in the biomass, while the remaining oxygen is provided via air injection. Combustion remains the leading method for converting agricultural waste to energy or fuels, accounting for about 95% of all biomass energy used today (Obi et al. 2016).

The practice of crop cultivation necessitates the use of chemical fertilisers and other chemical compounds that are subsequently incorporated into the biomass. Additionally, the direct combustion of residual agro-waste from crop cultivation has been found to have significant negative health consequences, including but not limited to blurred vision, bronchial infection, dizziness, asthma, and fatigue. Moreover, the process of directly combusting agro-waste lacks control in terms of energy extraction, resulting in a significant amount of energy being lost to the atmosphere. This uncontrolled process also contributes to negative environmental effects, including local heat waves and greenhouse gas emissions; hence, direct combustion method of agro-waste conversion should be avoided.

4.4.2.2 Pyrolysis

Pyrolysis, an endothermic process, is the thermal depolymerisation of organic biomass in the absence of O_2 or the presence of inert gas such as N_2 in a closed chamber at a temperature range of 300–900 °C to produce biochar, liquid biofuel, and bio-gases (Fig. 4.3) (Prasad et al. 2023). The pyrolysis yield depends on temperature, moisture content, biomass composition, particle size, and heating rate. Hence, optimising pyrolysis conditions is essential for individual and mixed biomass for the recovery of valuables.

Though pyrolysis is a well-accepted economical method for agro-waste valorisation, it has limitations in producing pyro-oil with low hydrocarbon content with lower aromatic compounds. Co-pyrolysis and catalytic pyrolysis are practised these days to overcome the limitation associated with the yield produced. Co-pyrolysis entails the incorporation of two or more distinct biomass or polymeric feedstocks. The co-pyrolysis of cow manure and stems of the weed *Amaranthus retroflexus* L. were investigated in the ratio of 1:1, 2:1, and 4:1 at a heating rate of 10 °C min^{-1} in the temperature range from 40 °C to 1000 °C. The maximum yield composition including 36.95% of pyrolysis liquid, 24.99% of syngas, and 38.06% of

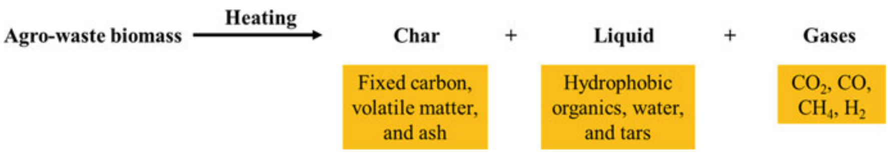

Fig. 4.3 Pyrolysis of agro-waste and the product formed

biochar was achieved through this co-pyrolysis method, whereas a maximum hydrogen concentration of 21.17% in the pyrolysis gas was reported with a 12.10% increased hydrogen output in 4:1 ratio as compared to 1:1 (Karaeva et al. 2022). The presence of a catalyst in pyrolysis influences the decomposition behaviour of agro-waste biomass as well as the composition and quality of pyrolysis yield. For instance, synthetic zeolite (ZSM-5) was shown to be useful for enhancing the deoxygenated aromatic content of pyrolysis products without decreasing liquid output (Kabakcı and Hacıbektaşoğlu 2017).

Thus, pyrolysis has been recognised as a viable option for the disposal of agro-waste as it can convert this biomass asset into granular charcoal, non-condensable gases, and pyrolysis oils, which, due to their high calorific value, can be used to produce valuable energy and chemical products (Trninić et al. 2016). However, a better comprehension of pyrolysis mechanisms is necessary for the development of thermochemical processes.

4.4.2.3 Gasification

Gasification is a commercial process that may turn any carbon-containing substance, such as coal, petroleum coke (petcoke), metallurgical coke (metcoke), or agro-waste biomass, into synthesis gas (syngas). The gasification process involves the thermochemical conversion of biomass at high temperatures (500–1400 °C), air pressures (up to 33 bar), and a low/absent oxygen concentration into a mixture of flammable gas (Biagini et al. 2014). Compared to combustion and pyrolysis, biomass gasification can recover more energy and a greater heat capacity (Lee et al. 2019). Conversion of carbon monoxide and hydrogen by pyrolysis and liquefaction is low, owing to the intricacy of these processes, which are highly dependent on operating conditions and the existence of secondary reactions caused by solid particles and volatiles. The easy catalytic methanation of carbon monoxide and carbon dioxide from syngas to synthetic natural gas is an additional advantage of the gasification process. Consequently, gasification is regarded as the optimal method of agro-waste valorisation and bioenergy production.

4.4.2.4 Liquefaction

Agro-waste-based biomass may be converted into bio-oil or bio-crude via liquefaction and pyrolysis. Thermochemical liquefaction entails the production of bio-oil at low temperatures and elevated pressure, irrespective of the use of a catalyst and in the presence of hydrogen. Hydrothermal liquefaction (HTL), also known as hydrous pyrolysis, is a well-established technique that converts biomass into bio-oil using subcritical water (SCW) at temperatures 250–374 °C and pressures range of 40 to 220 bar. In the HTL process, high pressure helps to keep water in a liquid condition; on the other hand, the combination of raised pressure and temperature decreases the dielectric constant and density, which makes hydrocarbons water-soluble. Characteristically, the HTL process employs biomass with a high moisture content to reduce the drying or dewatering step expense. In this regard, agro-waste as feedstock for liquefaction with adjustable moisture content could be a more sustainable approach for bio-oil production.

4.5 Agro-Waste Conversion Through Bioelectrochemical Systems

Bioelectrochemical systems are protuberant technology that serve the multi-faceted applications such as wastewater treatment, energy recovery, and synthesis of value-added products. Usually, BESs are categorised in accordance to biomass utilisation for value-added products' recovery (Fig. 4.4). For example, MFC utilises the biomass and generates electricity by exploitation of electroactive bacteria, whereas microbial desalination cell (MDC) can transform the chemical energy into electrical energy by cultivating electroactive microbes along with concomitant desalination of brine water. However, the energy generation during the anodic degradation cannot overcome the thermodynamic limitation of the synthesis reactions like hydrogen (H_2) and volatile fatty acid (VFA) production. To overcome this issue, H_2 gas can be synthesised in microbial electrolysis cell (MEC) through cathodic reduction of proton at abiotic cathodes by applying external voltage, while bio-cathodic reduction in the microbial electrosynthesis (MES) produces the short-chain volatile fatty acids, H_2, acidic acid, and other compounds by reduction of CO_2 and proton. For example, acetate (52.4 mM m^{-2} day^{-1}), isobutyrate (36.2 mM m^{-2} day^{-1}), propionate (41.6 mM m^{-2} day^{-1}), 2-piperidinone (26.7 mM m^{-2} day^{-1}), and traces of methyl derivatives of these compounds were recovered through MES (Das and Ghangrekar 2018).

Agro-waste, such as wheat straw, rice straw, sugarcane bagasse, corn stover, and manure, is an economical and the most abundantly available carbon source and can be utilised for generating renewable electricity and other value-added products through the BES. Investigations related to treating lignocellulosic agro-waste by-products using MFC are extremely limited due to the recalcitrant nature of lignin and cellulosic matter. However, some investigations described the utilisation of hydrolysate obtained from the expulsion, pyrolysis, and acidic/enzymatic treatment of agro-waste for better power output in MFC (Fig. 4.4). For instance, a single-

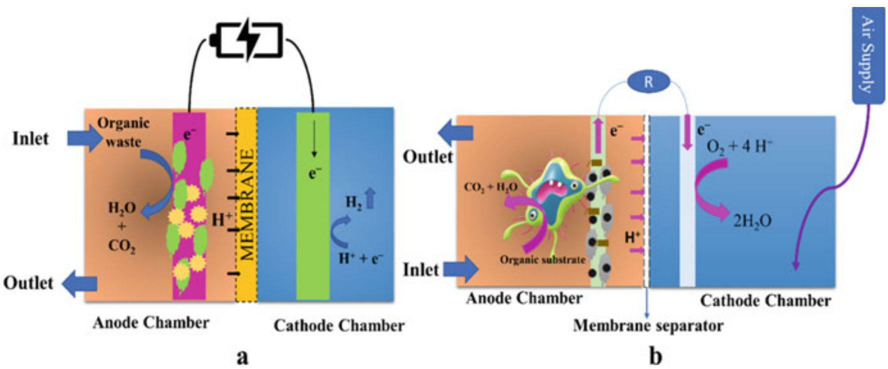

Fig. 4.4 Schematic representation of (**a**) microbial electrolysis cell and (**b**) microbial fuel cell for the production of bioelectricity and bio-hydrogen

chambered MFC supplied with the rice straw hydrolysate having initial COD of 400 mg L^{-1} produced the maximum power density, current density, and COD removal efficiency of 137.6 mW m^{-2}, 0.28 A m^{-2}, and 72.0 ± 1.7%, respectively (Wang et al. 2015).

In another investigation, a double-chambered MFC operated with the white rot hydrolysed wheat straw generated 20.13 ± 0.052 mW m^{-2} of power density and provided the favourable growth condition for exo-electrogenic biofilm formation on the anode of MFC (Pal et al. 2023). The hydrolysate is usually rich in carbohydrates, soluble sugars, amino acids, nutrients, proteins, and other compounds favourable for microbial growth and helps to achieve high COD degradation and electricity production. Apart from the lignin-rich waste, livestock waste has also been utilised as an effective source for the electricity generation. For example, Zhang and their co-researcher operated the duel chamber MFC using dairy manure as the substrate, effectively recovering the highest of 14 W m^{-3} power density in long-term (140 days) operation (Zhang et al. 2015). The investigation also demonstrates that the hydrophobic acid and hydrophilic segment of the manure were the part of the dissolved organic matter and have been removed (around 80%) by the exoelectrogens persist in the anodic chamber of this dual chamber MFC. Performance of MFC reported in few other investigations using different types of agro-waste is presented in Table 4.1 with their required pre-treatment methods and output achieved.

Production of H_2 and other biogas by utilising agro-waste through MEC is a recognised superior electrochemical technology for H_2, CH_4, and other valuables' production by utilising the organic waste as substrate (Fig. 4.4b). The H_2 was found to be generated at low thermodynamic cell voltage of 0.2–0.8 V through MEC compared to conventional threshold voltage (1.23 V) of electrolysis (Rozendal et al. 2006). Apart from thermodynamic point of view, the MEC also has advantage over electrolysis for H_2 production such as low cost of electrode, no oxygen production, and no acidic electrolyte requirement (Rousseau et al. 2020). Hence, applying the agro-waste for simultaneous generation of electricity and H_2 can propel the waste treatment and circular economy. For instance, the Kadier and co-researcher operated the MEC for treatment of the palm oil mill effluent, and 1.17 m^3-H_2 m^{-3} day-COD was produced at pH of 6.3 with the dilution (59%) as pre-treatment of palm oil mill effluent (Kadier et al. 2022). The investigation focusing on agro-waste treatment with MEC suggested that the high COD complex nature of the biomass needs pre-treatment as it could be toxic for the exo-electronics. For example, the pre-treated palm oil mill effluent by ozonation (mg COD: mg ozone = 102.78) and the H_2 production (77.1 mL g^{-1} of COD) efficiency enhances by the 20% compared to raw palm oil mill effluent (Tanikkul and Pisutpaisal 2014). Apart from the oil mill effluent, utilisation of other agro-waste-based MEC operations with suitable pre-treatment is presented in Table 4.2.

Coupling dark fermentation (DF) with MEC has been investigated to ameliorate the production of bio-H_2 from agro-waste (Fig. 4.5a). The combined DF-MEC has advantage over the traditional DF system, as it does not get affected by VFAs and alcohol accumulation, the thermodynamic limitations, and pH variation of process

Table 4.1 Recovery of electricity by utilising agro-waste through a bioelectrochemical system

Agricultural stream	BES configuration	Pre-treatment	COD removal efficiency	CE (%)	Power density (mW m^{-2})	References
Rice straw	Air cathode single chamber MFC	Hydrolysis	72	17.9	137.6	Wang et al. (2015)
Corn Stover	Air cathode single chamber MFC	Steam exploded	60	1.6	406.0	Wang et al. (2009)
Wheat straw	DC-MFC	Hydrolysis and dilution	NA	37.1	123.2	Zhang et al. (2009)
Wheat straw	DC-MFC	Hydrolysis and dilution	95	17.0	148	Thygesen et al. (2011b)
Cheese way	DC-MFC	Not required	60	3.9	1.3	Kelly and He (2014)
Palm oil mill effluent	Up flow single chamber MFC	Not required	90	NA	44.6	Cheng et al. (2010)
Cereal processing effluent	DC-MFC	Not required	95	40.0	81.0	Oh and Logan (2005)
Mustard plant effluent	DC-MFC	Not required	57	15.0	45.5	Guo et al. (2013)
Brewery wastewater	Air cathode single chamber MFC	Not required	93	28.0	96.0	Zhuang et al. (2010)

CE-Coulombic efficiency, *DC-MFC*- Double chamber microbial fuel cell, *NA*- Not available

(Ndayisenga et al. 2021). However, the complexity of lignocellulosic compounds of agro-waste also possesses the challenge to DF-MEC. Hence, the pre-treatment of substrate becomes necessary for better yield of H_2 production through DF-MEC, and pre-treatment methods have been reviewed extensively in the latest literature (Awogbemi and Von Kallon 2022). The integrated DF-MEC system is usually operated in a two-stage process for converting the pre-treated agro-waste into H_2. Initially, the pre-treated substrate is fed to the DF chamber and optimise the conversion of substrate into VFAs, H_2, alcohols, and CO_2. Later, the effluent with high concentration of VFAs and alcohols (0.6 g-VFAs per g-VS) transferred to MEC for suitable conversion into H_2 by applying an external potential (0.2–1.0 V), which overpass the thermodynamic limit of conversion of VFAs to H_2 by the electrogenic

Table 4.2 Generation of biogas (H_2 and CH_4) through the hybrid bioelectrical systems

Agricultural stream	BES configuration	Pre-treatment	COD removal efficiency	Applied voltage (V)	Hydrogen/biogas production	References
Cassava starch	DF with single chamber membrane free MEC	Not required	58%	0.6	245 mL H_2 $gCOD^{-1}$	Khongkliang et al. (2017)
Waste sugar beet juice	DF with DC-MEC	Not required	57%	0.6	3.2 mol H_2 mol^{-1} hexose	Dhar et al. (2015)
Cheese way	DF with DC-MEC	Dilution	NA	1	94.2 L H_2 $kgVS^{-1}$	Moreno et al. (2015)
Cellulose	DF with DC-MEC	Not required	NA	NA	0.24 m^3 H_2 $m^{-3}day^{-1}$	Wang et al. (2011)
Wheat straw	DC-MEC	Hydrolysis	95%	0.7	0.61 m^3 H_2 m^{-3} MEC day^{-1}	Thygesen et al. (2011a)
Lignocellulos	DC-MEC	Alkali treatment	NA	0.8	28.67 L H_2 kg^{-1}	Zhang et al. (2019)
Rice straw	DC-MEC	Alkali and heat treatment	NA	0.8	2.46 mmol H_2 L^{-1} day^{-1}	Wang et al. (2017)
Straw	Combined AD-MEC reactor	Not required	NA	1	116.18 mL·CH_4 $(g\ VS)^{-1}$	Yan et al. (2022)
Swine manure	Combined AD-MEC reactor	Not required	NA	0.7	2.96 m^3CH_4 m^{-3}	Yu et al. (2019)
Dairy manure	Combined AD-MEC reactor	Not required	NA	1	143 L CH_4 $(kgVS)^{-1}$	Ding et al. (2021)

DF: dark fermentation, *DC-MEC:* double chamber microbial electrolysis cell, *AD-MEC:* anaerobic digestion microbial electrolysis cell, *NA:* not available

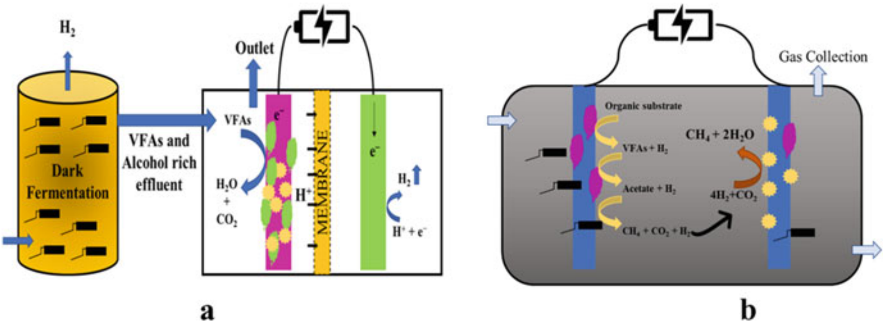

Fig. 4.5 The working diagram of hybrid Bioelectrochemical systems (**a**) DF-MEC (**b**) AD-MEC

bacteria. The investigations regarding the H_2 production by DF-MEC with the optimised parameters have been presented in Table 4.2.

Another significant gaseous product such as methane (CH_4) is also extensively recovered through MEC by the employment of different agro-wastes as substrate. The hybrid MEC, combining the anaerobic digestion and MEC, was examined for enhanced CH_4 production (Fig. 4.5b). Moreover, the widely spread anaerobic digester can be easily converted to the AD-MEC, and the methane production can be improved from 50% to 300% at an optimal 0.5–1.5 V power supply. The addition of the MEC enhances AD effectiveness by the prompt degradation of VFAs and other organic matter. Apart from it, AD-MEC transforms the microbial dynamics of the reactor by promoting the hydrogenotrophic methanogens compared to the acetoclastic methanogens (Wang et al. 2022). The hydrogenotrophic methanogens have a higher tolerance to pH, temperature, NH_4^+, and shorter generation time; these properties of the hydrogenotrophic methanogens enhance the methane production by tolerating the flux in these parameters. Few investigations focusing on the agro-waste have shown high methane production using AD-MEC (Table 4.2). The BES system either standalone or with combinations has shown good efficiency for the utilisation of the agro-waste; however, the investigation needs to overcome the limitations of electrode cost, extracellular electron transfer, and membrane cost involved in the BES. Thus, further investigation needs to focus on the synthesis of the different components of BES to overall reduce the cost of the fabrication and operations. The investigations regarding the utilisation of the agro-waste as the primary component for the membrane and cathode have been discussed below.

4.5.1 Other Applications of Agro-Waste-Derived Products in BES

The BES work on the principle of bioelectrochemistry needs highly efficient electrode and membrane for its operations. Usually, the carbon-based electrodes have been employed in BES fabrication due to its cost-effectiveness, high surface area, electricity conductivity, and good biocompatibility (Zhou et al. 2011). In addition to the electrode, the membrane and cathode catalyst also plays crucial role in the BES operation. For example, the investigation focusing on the distinctive commercial membrane found that the membranes such as Nafion 117 (514 mWm^{-2}), CMI 7000 (514 mWm^{-2}), and AMI 7001 (514 mWm^{-2}) achieved different current densities due to their difference in the internal resistance, ionic conductivity, and proton transfer ability (Kim et al. 2007).

Similarly, the different cathode catalysts such as Pd (63.942 mWm^{-2}, 25.82%) and Mn (63.942 mWm^{-2}, 17.47%) nanomaterial have shown diverse power density and coulombic efficiency in the MFC based on their ORR potential (Das et al. 2020). Hence, the utilisation of the agro-waste based electrode, cathode catalysts, and membrane can reduce the overall fabrication cost of the BES and can incentivise the plant-based BES operations. For example, the membrane costs up to 50% of the overall cost, hence, the application of agro-waste-based membrane such as coconut shell, can reduce the cost of the MFC fabrication. Neethu and co-researcher applied the coconut shell as the membrane, and more power density (3.2 W m^{-3}) was observed compared to the commercial Nafion membrane (1.8 W m^{-3}). Furthermore, the oxygen mass transfer coefficient and proton transmission efficiency of coconut shell membrane was also comparable to the Nafion membrane (Neethu et al. 2018).

Apart from the raw coconut shell, the coconut shell char-based membrane was also investigated by the same research group and reported that the coconut shell-based membrane (36 × 10^{-6} cm^2 s^{-1}) has more proton diffusion coefficient than Nafion (4.64 × 10^{-6} cm^2 s^{-1}), consequently leading in more electricity production (Neethu et al. 2019). Researchers also investigated that the higher silica present in the agro-waste (rice husk and straws) accelerates the hydration property of the membrane, thus improving the membrane property. For instance, ceramic membrane modified with rice husk ash was explored in the MFC, and higher power density (2.14 W m^{-3}) with lower ohmic (47.1 Ω) resistance was observed compared to the control membrane (2.14 W m^{-3}, 91.3 Ω) (Raychaudhuri and Behera 2020). More detailed applications of agro-waste biomass in BES are listed in Table 4.3. Hence, the application of the silica or other similar oxide-rich agro-wastes can be a way forward to reduce the membrane cost in the BES application, resulting field-scale applicability of the system.

Moreover, the agro-waste-based cathode catalysts have also been explored to boost the oxygen reduction reaction (ORR) and power density of the BES. The activated char derived from agro-waste facilitates the higher ORR activity due to natural nitrogen compounds present in waste, such as pyridinic and pyridine (Yuan et al. 2014). The naturally present nitrogen compounds also create defects on carbon during char synthesis and upsurge the edge plane exposure, which further enhances the catalytic activity (Maldonado and Stevenson 2005). Apart from the nitrogen compounds, the agro char catalysts also found effective compared to the metal-based catalysts as it has long-term operational stability and is low cost and has higher chemical stability and good mass transfer capacity and electrical conductivity.

The investigations of olive mill waste-based char synthesis through pyrolysis were implemented as cathode catalysts in MFC, where 15 times more power density (271 mW m^{-2}) was achieved as compared to the commercially available carbon black (17.3 mW m^{-2}) (Sciarria et al. 2020). The higher power density of the Oliver

Table 4.3 The applications of agro-waste biomass in BES systems

Applications	Type of BES	Agro-waste	Inoculum	Power density (mW m^{-2})	References
As substrate	DC-MFC	Rapeseed cake	*Shewanella oneidensis* strain 14,063	33	Fernando et al. (2012)
		Corn steep liquor		39	
		Molasses		26	
	DC-MFC	Palm oil mill effluent	*Klebsiella variicola*	5.83 W m^{-3}	Islam et al. (2018)
As anode	DC-MFC	Coffee wastes	From domestic waste	3927	Hung et al. (2019)
	DC-MFC	Onion peels	Mix sludge	742	Li et al. (2018)
	DC-MFC	Compressed milling	Anaerobic mix sludge	532	Huggins et al. (2014)
As cathode	Air cathode MFC	Watermelon rind	From a stable operating reactor	0.262 W m^{-3}	Zhong et al. (2019)
	Air cathode MFC	Alfalfa leaf	From a stable operating reactor	1328.9	Deng et al. (2017)
	DC-MFC	Compressed milling residue	Anaerobic sludge	532	Huggins et al. (2014)
As proton exchange membrane	Air cathode MFC	Banana peel	Septic tank sludge	41.08	Chakraborty et al. (2020)
	DC-MFC	Coconut shell	Septic tank anaerobic sludge	3.7 W m^{-3}	Neethu et al. (2019)

DC-MFC: double chamber microbial fuel cell

mill waste was attributed to the oxygen and nitrogen compound present on the surface of the char. Apart from the cathode catalysts, the agro-waste has also been applied as the electrode material in the BES operation. As an example, the compressed milling residue anode (532 mW m^{-2}) produced the comparable power density (532 mW m^{-2}) to the commercial granular activated carbon and graphite granules (566 mW m^{-2}) (Huggins et al. 2014). The similar investigations focusing on the use of different agro-waste-based electrodes for application in MFC have been reviewed extensively in recent literature (Park et al. 2020; Mano 2020). In overall evolution, the application of the agro-waste can make the BES operation economically viable and can reduce the cost up to 90% compared to commercially available electrodes and membrane (Huggins et al. 2014).

4.6 Recommendation and Future Scope

Agriculture, being one of the largest sectors in the world, generates a considerable quantity of agro-waste. In the present era, the global perspective of agro-waste is changing fast in response to the need for environmental sustainability and conservation. Consequently, agro-waste is no longer regarded as garbage, rather a raw material for producing a variety of value-added products. However, reducing agro-waste generation by properly managing agro-products is still the best way to save the economic value and pollutant generation. The conversion of agro-waste to bioenergy is a sustainable solution to the agricultural sector's escalating refuse disposal problem and rising energy demand. The transformation of agro-waste to bioenergy can provide pure and renewable energy sources while reducing greenhouse gas emissions and promoting environmental protection. Furthermore, to fully realise the potential of agro-waste to bioenergy, certain recommendations must be followed, and future scopes should be explored.

Developing novel techniques and technologies is essential for bioenergy production from agricultural waste. This includes research and development in biogas production, biofuel production, and heat transfer. This will facilitate the efficient and cost-effective conversion of agricultural refuse into bio-energy. In this regard, BES for agro-waste remediation can be regarded as more sustainable than conventional conversion methods for producing valuable goods. Nonetheless, the BES is still in the embryogenic stage, and much research into the systems is necessary for their upscaling. Furthermore, very few articles are addressing agro-waste-based BES; thus, there is much scope for research in this area. Hence, future investigation for agro-waste remediation employing a BES system shall focus on factors such as water-to-agro-waste ratio, pre-treatment of agro-waste before being used as substrate in BES, and selection of microbial inoculum with respect to available agro-waste and reactor modification for better operation and outcomes. Upscaling of BES for practical application is still missing; bench-to-field-scale BES in this regard should also be investigated. The application of agro-waste-derived PEM and electrodes should also be investigated for the economic feasibility of the BES system.

4.7 Conclusions

The cutting-edge BES has substantial potential for producing bioelectricity and biofuels as well as recovering other valuables. However, the operating expenses associated with this advanced technique need to be reduced severely by developing inexpensive bio-based electrocatalyst and membranes, which would be a major step towards its commercialisation. Moreover, the productivity obtained through BES also needs to be ameliorated considerably, by employing easily available nutrient efficient agro-waste. Enhancing the yield of valuables acquired through fermentation would increase the revenue generated by these procedures, ensuring the economic and renewable sustainability of BES. Therefore, for the efficacious commercialisation and field-scale demonstration of BES, bio-based approach is essential to resolve the numerous roadblocks in the way towards the scaling-up of these inventive technologies.

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