Valorization of agricultural wastes for biofuel applications

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ABSTRACT

Continuous environmental degradation, volatility in the oil market, and unimpressive functioning of fossil-based (FB) fuels in compression ignition engines have expanded the tempo of the search for alternative fuels. Due to the astronomical rise in global population, improved agricultural, commercial, and manufacturing activities, enhanced farming and other food production and utilization ventures, agricultural waste generation, renewable fuel consumption, and emission of toxic gases. The need for cost-effective, readily available, and environmentally benign agricultural waste to biofuels has never been more crucial. Biofuels are renewable, biodegradable, low-cost, and eco-friendly fuels that are produced by microorganisms from waste lignocellulosic biomass. Conversion of agricultural wastes to biofuel does not exacerbate food security, contributes to waste management, prevents environmental degradation, and ensures energy security. This study reviews the conversion of agricultural wastes into biofuels with special emphasis on bioethanol, biohydrogen, biobutanol, biomethane, biomethanol, and biodiesel for various applications. It is safe to conclude that wastes generated from agricultural activities and processes are useful and can be harnessed to meet the affordable and accessible global renewable energy target. The result of this investigation will improve the body of knowledge and provide novel strategies and pathways for the utilization of agricultural wastes. Going forward, more collaborative and interdisciplinary studies are required to evolve state-of-the-art, ecofriendly, and cost-effective conversion pathways for agricultural wastes to promote the utilization of the generated renewable fuels. More human, financial, and infrastructural investments are desirable to motivate the conversion of agricultural waste into biofuels to ensure environmental sanitation and sustainability, promote renewable fuel utilization, and avert the raging implosion of our planet.

1. Introduction

Rapid population growth, improved economic activities, sociocultural tendencies, and industrialization have elicited a dramatic surge in energy consumption in recent decades. For example, the world population was about 7.3 billion in 2018 rose to 7.592 billion in 2018 and has been anticipated to reach 8.184 billion, 8.548 billion, and 9.735 billion in 2025, 2030, and 2050 respectively (Worldometers, 2022). During the same period, available statistics show that the total energy consumption rose from 543 EJ (EJ) in 2015 to 575 EJ in 2018 and has been projected to further rise to 617 EJ, 648 EJ in 2025, 2030, and 2050 respectively (Figure 1) (Statista, 2022e). The use of renewable energy for various applications is one of the feasible options in curtailing the unpalatable environmental impact of the extraction, refining, and utilization of fossil-based (FB) fuels. This has motivated international organizations, environmentalists, and governments to continue to encourage researchers and fuel refiners with improved funding, investments, policies, and human capacity toward developing affordable and environmentally friendly energy sources, most especially biofuel. Consequently, the global biofuel production rose from an abysmal 187 thousand barrels of oil equivalent (mboe) per day to 1677 mboe per day (Statista, 2022a). To further sustain and improve on this trend, there has been an increased investment into biofuel production which has led to a rise in the market value. Informed sources projected that the market size of biofuel production which was 120.6 billion US Dollar in 2020 will increase to 141 billion US Dollar, 172.76 billion US Dollar, 201.21 billion US Dollar in 2025, 2028, and 2030, respectively (Statista, 2022b).

Generally, global waste generation has continued to increase with the rise in population, urbanization, and effects of the improved economic
and industrial activities. Managing the huge waste generated has been one of the protracted challenges confronting humanity over the past few decades despite the various efforts to stem the tide. For example, the total global waste generated in 2016 was 2.02 billion tons. This figure is expected to rise to 2.59 billion tons in 2030 and 3.4 billion tons in 2050 (Statista, 2018). The market value of the world waste management that was USD 1.61 trillion in 2020 has been predicted to become USD 2.5 trillion in 2030 with East Asia and the Pacific generating the highest quantity of waste (Figure 2) (Statista, 2022). Agricultural waste forms an integral part of these wastes. Available statistics showed that about 998 million tons of agricultural waste are created yearly with the majority of these wastes deposited at dumpsites or incinerated with adverse environmental consequences (Obi et al., 2016). The quantum of waste generated from the agricultural sector has increased dramatically due to increased food production and consumption to feed an ever-growing population and provide raw materials for the industrial sector.

Figure 1. Global energy consumption and population growth 2015–2050.

Figure 2. Global waste generation by region (millions of tons).
Agricultural wastes are the materials generated from agricultural activities and processes along the value chain. They are generated in the form of raw materials, byproducts, or final products of diverse activities and processes. Since the materials can no longer be used, they are termed as waste and discarded and thrown away (Awogbemi et al., 2021b; Yía-Mella et al., 2022). Agricultural wastes are categorized as offcuts, crop residues, industrial wastes, animal wastes, and food-retaied wastes (Guo et al., 2021; Pattanaik et al., 2019). Figure 3 shows the major classification of agricultural wastes and their examples.

The waste generated from the agricultural sector, if not appropriated handled and managed, can constitute environmental hazards, contaminate aquatic and terrestrial habitats and impact human health. Waste management strategies such as waste reduction, waste reuse, and waste recycling needs to be accorded the desired consideration. Since strategies for achieving zero waste from agricultural activities are not easy to be achieved, efforts should be intensified for waste minimization. Adoption of some of the ecofriendly strategies aim at using the waste generated for other purposes, without treatment or processing, are also needed. Conversion of agricultural waste to useful forms appears to be the most ecofriendly, economical, and sustainable pathway for managing waste. Valorization of agricultural waste, as a form of waste conversion and recycling strategy, not only contribute to clean environment, socioecconomic development, resource conservation and recovery, but also assist in achieving energy security and circular economy (Chilakamarry et al., 2022).

Outcome of precious investigations on the diverse pathways for waste conversion and recycling have been reported. For example, Taghizadeh-Halsisraei et al. (2017) engaged in a comprehensive study of the production of biofuel from citrus fruit while Sadeek et al. (2020) generated biofuel from waste cooking oil. Similarly, a recent study that investigated the socioeconomic, cultural, and ecological evaluation of biofuel production from waste from agricultural sector publicized the viability and feasibility of the various conversion processes. The use of thermal, chemical, and biological conversion processes was adjudged effective in converting agricultural waste to high quality biofuel without compromising ecological diversity and environmental standards. The conversion efficiency of between 70-95 % was recorded in most of the studies (Koutinas et al., 2016; Prysteryiak and Tokarchuk, 2020). Also, Sharma and Dubey (2020) applied hydrothermal and carbonization methods to convert food waste to biofuel while the duo of Uzojiina et al. (2018) employed pyrolysis and other techniques to convert waste plastic to come to form biofuels. Microorganisms such as Ruminococcus, Clostridium acetobutylicum Clostridium difficile, Pseudomonas sp. CL3 and Clostridium sp. TCW1 have been active in the valorization of wastes into biofuels and other useful products (Shanumgum et al., 2019). These microorganisms biologically degrade the waste in an ecofriendly but slow process. More specifically, agricultural waste including rice straw, maize cobs, sugarcane bagasse, oil cakes (Dhanya, 2022), banana peel (Gupta et al., 2022), rice husk, sawdust, wheat straw (Zhou et al., 2022), and other agricultural residues (Rose, 2022) were converted to biooil, biogas, biodiesel, bioethanol, biobutanol, enzymes, organic acids, and other valuable products. The outcome of these studies confirmed the economic, ecological, and other gains of the transformation of agricultural wastes into biofuel for diverse usage.

Notwithstanding the milestones already achieved in this research area, the relevant question desiring practical answer is whether the issue of waste management in general and agricultural waste conversion in particular has been sufficiently investigated. The inspiration motive for the present study, therefore, is to advance the trajectory of the methods and body of knowledge for the conversion of agricultural wastes into biofuels. The aim of this study is to engage in an up-to-date review of technologies for the transformation of agricultural wastes into advanced biofuels. The scope of the current study is limited to the application of agricultural waste as feedstock for the generation of biodiesel, bioethanol, biomethane, biobutanol, biomethanol. The outcome of this investigation will further expose the contemporary developments in the techniques for the conversion of waste generated from diverse agricultural endeavors into biofuels with a view to stimulating broaden research space in this area. The research will update the existing information and offer requisite knowledge to farmers, biofuel refiners, researchers, environmental enthusiasts, law makers, policy formulators, investors, government at various levels, and other stakeholders on the application of agricultural wastes to meet the global renewable fuel demand and spare our planet from further environmental devastation.

2. Global biofuel production

The diminishing global oil resources, volatile crude oil prices, and the ecological impact of fossil-based fuel usage have resulted in increased attention on biofuel production and utilization. Biofuels are regarded as a practical replacement for FB fuels to minimize climate change, promote energy security, and mitigate hazardous emissions from transport engines. Globally, biofuel production has continued to increase. Informed sources reported that biofuel production was 59 Million Tons of Oil Equivalent (Mtoe) in 2010 became 96 Mtoe in 2019 and is predicted to rise to 98 Mtoe in 2022 (iesa, 2019). Similarly, the global emission of CO2 rose from 33.13 Billion Metric Tons (BMT) in 2010 to 36.44 BMT in 2019 and are expected to become 38 BMT in 2022 (Statista, 2020) (Figure 4). The decrease in world biofuel generation and CO2 emission iesa, 2020 is due to the COVID 19-imposed restrictions. The lockdown impeded vehicular movements, social, economic, industrial activities, and other activities where fuels are being consumed.

Notwithstanding the myriad gains of the utilization of renewable fuels for diverse applications, the fuel/food debates, emission of toxic

![Figure 3. Classifications and major examples of Agricultural droppings.](image-url)
Wastes generated from agricultural activities are classified as lignono-cellulosic biomass and are composed of complex molecular structures such as cellulose, hemicellulose, lignin, ash, and some extractives, mainly, protein. During degradation, the structures of the wastes are first decomposed into simple monomers preparatory to their conversion into different configurations (Ge et al., 2021; Stefanidis et al., 2014). Most agricultural wastes are populated with more proportion of cellulose than both hemicellulose and lignin. Cellulose is an important structural component of lignocellulosic biomass. It is a hard, fibrous, impenetrable polysaccharide, arranged in chain form arranged in packs of microfibrils to maintain the stability of a plant structure. The mechanical stability, strength, and chemical fingerprint of biomass are determined by its cellulose characteristics (Dhyani and Bhaskar, 2018).

Hemicellulose is the random heterogeneous structure of branched polysaccharides situated in the cellulose and the main connection between cellulose and lignin. It is derived from a heterogeneous assembly of sugars such as d-xylose, d-mannose, and d-galactose and is composed of arabans, xylans, galactans, etc (Peng et al., 2012; Muthalib et al., 2021). Hemicelluloses are not soluble in water solution but readily dissolve in alkaline, weak acid, and enzymatic media. They possess less mechanical strength than cellulose and are easily susceptible to chemical attacks and modifications. The potential of biomass to be converted to biofuel is largely determined by its hemicellulose content (Kumari and Singh, 2018).

Lignin is an integral part of a plant and is second only to cellulose. The formation of cell walls, stiffness, resistance to water, and the physical, chemical, and microbial attack are governed by the lignin content of the woody biomass water. It helps the plant in conducting water from the soil and provides structural backing for the growing plant (Dhyani and Bhaskar, 2018; Kumari and Singh, 2018; Zhang et al., 2021). Most agricultural wastes and crop residues are composed of, on dry basis, between 35-50 % cellulose, 20–35 % hemicellulose, 15–20 % lignin, and 15–20 % extractives (ash, protein, etc.). Figure 5 shows the major components of agricultural waste while Table 1 compiles compositional contents of some of the common agricultural wastes.
4. Biofuels from agricultural wastes

Given the enormous wastes generated from the agricultural sector, and their impact on humans, animals, and the environment, it’s best they are converted into biofuel. The translation of agricultural wastes to biofuel, therefore, is one of the sustainable waste management strategies to ensure sanitation, resource recovery, and maintaining the carbon balance in the environment. Biochemical or thermochemical processes remain the two sustainable ways to convert agricultural wastes into biofuels. The biochemical conversion pathway, which is a combination of biological and chemical processes, is commonly used to convert agricultural wastes with high moisture, cellulose, and hemicellulose contents, and a C/N ratio greater than 30 % to biodiesel, biomethane, bioethanol, and biobutanol. Conversely, the thermochemical conversion pathway is best suited for the conversion of agricultural wastes with high lignin percentage, low moisture content, and a C/N ratio of less than 30 %. The thermochemical route combines the thermal and chemical methods for the synthesis of bio syngas, biooil, biochar, and biocoal. From the standpoint of energy utilization and greenhouse gas (GHG) emission, biochemical conversion is preferred to thermochemical conversion (Ibarra-Gonzalez and Rong, 2019; Pattanaik et al., 2019).

4.1. Bioethanol

Bioethanol is a renewable liquid biofuel produced from the fermentation of sugar and starch component of natural materials, usually plants derivatives or agricultural wastes. Bioethanol, or simply ethanol, is the most common liquid biofuel consumed globally. The demand for bioethanol has continued to motivate increased production. The global demand for bioethanol which was put at 100.2 billion litres in 2016 has been projected to become 134.5 billion litres by 2024 (Bu/C20c/C19c et al., 2018).

It must be noted that not all the produced bioethanol is used as fuel. Bioethanol is also used to produce disinfectants, beverages, personal care products, and feedstock for the chemical and pharmaceutical industries. However, over 40 % of global ethanol production is used as fuel or fuel additives. The production of fuel ethanol increased from over 26 million gallons in 2016 to more than 29 million gallons (IEA, 2019). Though global production dropped to 26 million gallons (IEA, 2020) due to the impact of covid 19 pandemic. Production has since climbed to over 27 billion gallons in 2021 (Statista, 2022d). The global ethanol market size was recorded that was about USD 89.1 billion (IEA, 2019) has been estimated to exceed USD 155.6 billion by 2030 (Precedence Research, 2022). The growth is expected to be propelled by increased utilization of ethanol as biofuel, renewed interests in bioethanol as a fuel, and increased demand for bioethanol as a feedstock for the chemical and pharmaceutical industries.
sustainable replacement to fossil-based fuels, and government policy on environmental degradation remedies, among others.

Bioethanol is mainly used as an internal combustion engine fuel to blend with gasoline. This approach offers performance and economic benefits to the consumers. The use of bioethanol/gasoline blend in transport engines leads to 90% CO2, 60–80% SO2, and about 40% particulate matter emissions (Halder et al., 2019; Hoang and Nghiem, 2021). The drastic reduction in these toxic emissions helps to minimize air pollution, ensures environmental security, and reduces the emission of GHGs and other cancer-causing compounds such as ethylbenzene, xylene, toluene, and benzene. Also, because bioethanol is produced mainly from waste biomass as feedstocks, it is generally cost-effective and contributes to waste management and sanitation.

Most of the social, economic, environmental, operational, and technical issues relating to bioethanol generation and consumption have been a subject of debate in the past few decades. The application of starch crops such as corn, sugarcane, or sweet sorghum as feedstocks has sparked food vs fuel debates and ethical concerns in various fora (Xu et al., 2015). These have directed research efforts to be increasingly concentrated on the applicability of non-food feedstock alternatives for bioethanol production. The use of lignocellulosic biomass such as municipal and industrial waste, wood, and the agricultural residue is seen as a better alternative based on economic, availability, sanitary, and environmental considerations. Though there is no systematic analytical framework for feedstocks ranking, the use of agricultural wastes such as crop residues, waste wood, and other categories of waste biomass as feedstocks has gained traction and enjoys wide acceptability.

The share of bioethanol in biofuel production has reached about 65% due to improved production methods, the use of locally and readily available feedstocks easy, and the continuous demand for bioethanol for various applications (Awogbemi et al., 2021a). Currently, Bioethanol is produced from various agricultural wastes and crop residues such as sugarcane bagasse, sweet sorghum bagasse, rice straw, barley straw, wheat straw, sorghum straw, corn stover, cassava peels, sugar beet, wood, etc. These materials are nonedible, cheap, and readily available at a reasonably low cost. Their use as feedstock for fuel production does not...
Biohydrogen production and utilization technologies have gained significant patronage during the past few decades due to unravelling demand for clean and nonpolluting renewable energy. The total global biohydrogen production which was 1.8 million metric tons in 2015 has been predicted to become 19 million metric tons by 2030, and further to 65 million metric tons by 2050, going by the current government policies and targets on migration to clean energy (Statista, 2021). Similarly, Arismendy Pabón et al. (2020) and Anu et al. experimented with rice husk and rice straw, they reported 44 % and 18.07 g/L bioethanol production, respectively. The outcome of other investigations into the conversion of banana peels (John et al., 2020), potato peel waste (Hossain et al., 2018), wheat straw (Adeyemi et al., 2019), rice straw (Adeyemi et al., 2019), apple wood (Zhang et al., 2019), palm wood (Raja Sathendra et al., 2019), and corn cobs (Sewunke-Sukai and Gueguim Kana, 2018) into bioethanol are presented in Table 2. The aggregate of opinions from these investigations confirms the applicability of agricultural wastes as cheap substrates for bioethanol generation.

### 4.2. Biohydrogen

Biohydrogen is clean, non-toxic, carbon-free, and advanced biofuel produced from biomass through biological and thermochemical processes. It is a colourless, tasteless, odourless, highly combustible renewable fuel, and a sustainable substitute for FB fuels. Its high energy content (120–142.9 MJ/kg) and calorific value (143 GJ/ton) make it valuable and the most preferable of all the biofuels. Biohydrogen offers diverse applications in the transportation, electricity generation, food and beverage, pharmaceutical, and industrial sectors, provides economic and social benefits, a major contributor to the circular economy (Kumari and Singh, 2018; Zhang et al., 2022). However, the application of biohydrogen as an internal combustion engine fuel does not liberate CO2, gaseous pollutants, and other precursors of the greenhouse effect. Rather, the combustion of biohydrogen yields water thereby guaranteeing ecological quality and mitigating climate change. Though the technology for the production of biohydrogen is still relatively expensive and competitive, the use of easily available, sustainable, environmentally friendly, and renewable biomass gives it an edge over other renewable fuels (Awogbemi et al., 2022; Kumar Gupta et al., 2013).

Biohydrogen production and utilization technologies have gained significant patronage during the past few decades due to unravelling demand for clean and nonpolluting renewable energy. The total global biohydrogen production which was 1.8 million metric tons in 2015 has been predicted to become 19 million metric tons by 2030 and further to 65 million metric tons by 2050, going by the current government policies and targets on migration to clean energy (Statista, 2021b). Similarly, the global biohydrogen production market share which accounted for about USD 103 billion in 2017 has been estimated to become USD 183 billion in 2023 and USD 207 billion in 2026 (PRNewswire, 2018; Statista, 2021a). The consumption of biohydrogen for various applications is expected to increase by 8–10 % by 2025 (Kumar Gupta et al., 2013).

Fermentation and biophotolysis are the two popular methods for biohydrogen production. However, recent advances have shown that biohydrogen is also produced by microbial electrolysis, thermochemical gasification, pyrolysis, solar gasification, and supercritical conversion techniques have been employed. These production pathways don’t require intense energy consumption, are more eco-friendly, economically, generated better yield, and are more sustainable than the conventional methods (Singh et al., 2015). Table 3 compiles the summary of the description, reaction equation, advantages, and disadvantages of major methods of biohydrogen production. In choosing feasible feedstocks for biohydrogen production, economic, availability, biodegradability, and productivity factors play important roles. Other factors to be considered include the C/N ratio, chemical oxygen demand (COD), volatile solids (VS) content, and the existence of inhibitory compounds that determine product yield (Keskin et al., 2019).

After a series of investigations on the availability, viability, and biodegradability of various wastes (municipal solid waste, livestock waste, industrial residue, etc.) and renewable feedstocks for biohydrogen production, the use of agricultural wastes has demonstrated great potential, ease of conversion, and product yield.

Researchers including Dong et al. (2018) produced biohydrogen from rice straw after pretreating the feedstock with cold alkali/urea (−8 °C to −20 °C), and subjected the pretreated feedstock to Thermoanaerobacterium thermosaccharolyticum M18 strain, and reported a maximum biohydrogen production of 22.08 mmol/L. In another study, Zhang et al. (2020) pretreated corn stalk with an alkaline-enzymolysis method and subsequently converted the pretreated corn stalk to biohydrogen through dark-fermentation, photo-fermentation, and two-stage fermentation methods with the appropriate strain of inoculum. The fermentation of the feedstock yields 168.9 mL/g, 357.6 mL/g, and 424.3 mL/g for dark-fermentation, photo-fermentation, and two-stage fermentation, respectively. Similarly, Shanmuqam et al. (2018) attained a biohydrogen yield of 402.01 mL/g when sweet sorghum stover was converted through anaerobic fermentation. They have earlier removed 76.93 % lignin by enzymatic pretreatment. Other scholars including Mirza et al. (2019), Bhurat et al. (2021), Tosuner et al. (2019), Medina-Morales et al. (2021), and Zainal et al. (2018) converted sugarcane bagasse, potato peel, rice husk, corn cob, and palm oil mill effluent (POME) to biohydrogen, respectively, as shown in Table 4. The outcome of the works of these researchers confirms the previous assertion of Awogbemi et al. (2022) on the feasibility of agricultural residues as feedstock for biohydrogen generation.

### 4.3. Biomethane

Biomethane is a renewable gaseous biofuel generated from the upgrading of a methane-rich gas called biogas through the removal of CO2 and other contaminants in biogas. Biomethane is also produced from the gasification of woody biomass, municipal solid waste, and agricultural wastes, through a process called methanation. Characteristically, crude biogas produced by anaerobic digestion of organic material contains 50–70 % CH4, 30–40 % CO2 and some traces of H2O, H2S, NH3, N2, siloxane, and solid matter while the upgraded version of biogas called biomethane contains 95–97 % CH4 and about 1–3 % CO2 by volume (Baccioni et al., 2018; Seong et al., 2020). Areas of application of biomethane include electricity generation, heating, and operation of power plants. In recent years, biomethane is used as sustainable fuel to replace biogas and natural gas to power automobiles and other internal combustion engines to reduce the emission of CO2 (Aggarangsi et al., 2022; Orecchini et al., 2021). Advantages of the application of biomethane include reduction or elimination of carbon emissions, low production cost, ensures sustainable environment, and energy independence. However, biomethane emits an offensive odour and portends a high risk of explosion. Also, CH4 which is the main component of biomethane is a strong GHG and a major contributor to global warming. Despite these shortcomings, the production and utilization of biomethane have continued to increase.

The annual global production of biomethane is 2020 was put at 32 TW-hour (TWh), despite the impact of the covid 19 pandemic. However, this figure has been projected to climb to about 9.5 TWh in 2023 (European biogas, 2021). Currently, Europe is the region with the highest actual production output of biomethane, producing about 1.8 million metric tons per annum (MTPA) followed by the United States and Canada.
Table 3. Summary of methods of bioethanol production from agricultural waste.

| Methods              | Description                                                                 | Reaction equation                                                                 | Advantages                                                                                                               | Disadvantages                                                                                           | Remark                                                                                                 | References                                                                 |
|----------------------|-----------------------------------------------------------------------------|-----------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------|
| Direct biophotolysis | Involves breaking down of water molecules into hydrogen and oxygen in presence of light by photoautotrophic microalgae | $2H_2O + \text{Light} \rightarrow 2H_2 + O_2$                                    | • Low-cost process  
  • Water and light only as feedstock  
  • Improved energy conversion   | • Requires high light intensity  
  • Low photochemical efficiency  
  • Concurrent production of H2 and O2   | • Process is economically beneficial   | (Bear et al., 2022; Show and Lee, 2013) |
| Indirect biophotolysis | Generation of biohydrogen from water through algal photosynthetic conversion of solar energy to hydrogen. | $12H_2O + \text{Light} \rightarrow 12H_2 + 6O_2$                                  | • Hydrogen production from algae and water  
  • Easy tapping of atmospheric nitrogen   | • Continuous decomposition of H2 and O2   | • Easy hydrogen production process   | (Miandad et al., 2017) |
| Photo-fermentation   | The process of converting organic substrates to biohydrogen using photosynthetic microorganisms through biochemical reactions comparable to anaerobic conversion. | $CH_3COOH + 2H_2O + \text{Light} \rightarrow 4H_2 + 2CO_2$                    | • Utilization of light energy by bacteria  
  • Varieties of wastes can be converted  
  • High conversion efficiency  
  • Simple and easy process  
  • Almost 100 % feedstock conversion   | • High cost of implementation  
  • Slow conversion rate  
  • Compulsory pretreatment  
  • Low product generation   | • More research needed  
  • Cost reduction measures are needed   | (Bear et al., 2022; Miandad et al., 2017) |
| Dark fermentation    | Process of fermentative conversion of organic substrates to biohydrogen by microorganisms in the absence of light. | $C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 4H_2 + 2CO_2$                  | • Cheap and easy process  
  • High product yield  
  • H2 production without light  
  • Use of diverse feedstock  
  • Simple reactor  
  • Valuable byproducts   | • Separation of H2 from producer gas and CO2  
  • Unfavourable thermodynamic process due to high H2 pressure  
  • Low COD removal  
  • Unpredictable H2 yield   | • Affordable process  
  • More research required  
  • Use of novel technologies recommended   | (Bear et al., 2022; Khourzaitabar, 2020) |
| Microbial electrolysis | Microbial conversion of organic materials to H2 and CH4 by electrolysis method. | $C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 4H_2 + 2CO_2$  
  Anode: $CH_3COOH + 2H_2O \rightarrow CO_2 + 8e^- + 8H^+$  
  Cathode: $8H^+ + 8e^- \rightarrow 4H_2$ | • Conversion of wastes to biohydrogen  
  • Innovative hydrogen production from agricultural wastes   | • Inadequate knowledge of metabolic pathways  
  • Low H2 generation at low electrode power  
  • High voltage requirement is a challenge   | • Ecofriendly process  
  • Measures needed to improve the process   | (Azwar et al., 2014) |
| Thermochemical gasification | Partial oxidation of biomass to generate syngas under a reducing atmosphere. | $C_6H_{12}O_6 + O_2 + H_2O \rightarrow CO + CO_2 + H_2 + \text{Other gases}$ | • Maximum conversion rate  
  • High H2 yield   | • High cost of syngas storage  
  • Tar removal   | • Cost reduction measures needed   | (Sadhwani et al., 2013) |
| Pyrolysis            | Thermal decomposition of substrates to synthesize H2 without the use of any oxidizing agents. | NA                                                                              | • High product yield  
  • Generation of chemicals and minerals as by products   | Catalysts deactivation   | Appropriate catalyst to be developed   | (Arregi et al., 2016) |
| Solar gasification   | A thermochemical conversion of biomass into syngas by using solar energy as heat source to stimulate the reactions. | NA                                                                              | • Good H2 yield  
  • Improved conversion efficiency at low temperature  
  • Pulverization of feedstock not necessary  
  • Minimum CO2 generation   | Expensive solar collector   | Cost reduction measures needed   | (Boujijat et al., 2020) |
| Supercritical conversion | Thermochemical production of hydrogen from supercritical water as gasifying agent. | $2C_6H_{12}O_6 + 7H_2O \rightarrow 9CO_2 + 2CH_4 + CO + 15H_2$               | • High H2 content  
  • No need to dry feedstock  
  • High conversion efficiency  
  • Production of other clean gaseous fuels   | Difficulty in selecting supercritical medium   | • Simple and easy process  
  • Multiple products   | (Tushar et al., 2020) |

NA = Not Applicable; COD = Chemical Oxygen Demand; H2 = Hydrogen; CH4 = Methane; CO2 = Carbon dioxide.
with 0.6 MTPA. However, the Asia and Oceania region has the highest potential for future biomethane production (165 MTPA) followed by the United States and Canada (125 MTPA) and Latin America (105 MTPA) (Figure 7) (Statista, 2022c). Similarly, the global biomethane market valued at USD 1.9 billion in 2020 has been projected to rise to USD 4 billion by 2031 (Transparency market research, 2022). This trend is due to increased concerns for the environment, increased application of biomethane in the road and maritime sectors, and the effect of favourable policies for biomethane production and utilization. Besides, biomethane, as a net-zero fuel, will find more usage in the renewable energy mix towards mitigating environmental degradation. To meet the projected demand for biomethane, there is a massive investment for the expected deployment of biomethane to replace natural gas in the chemical, steel, food, and beverages industries.

Because of the high energy content of biomethane (36 MJ/m³) and net-zero emission characteristics, a lot of efforts and resources have been invested to ensure low-cost and environmentally sustainable production of biomethane. One of those interventions is the use of agricultural wastes for production. The C/N ratio of a typical feedstock is the most important factor that determines its anaerobic digestibility. Other factors

| Feedstock | Pretreatment | Methods | Microorganism name | Yield | Remark | References |
|-----------|--------------|---------|--------------------|-------|--------|------------|
| Rice straw | Alkalis      | Fermentation | Thermoanaerobacterium thermosaccharolyticum M18 | 22.08 mmol/L | Efforts needed to improve product yield | (Dong et al., 2018) |
| Corn stalk | Ca(OH)₂-enzymolysis | Dark-fermentation | Cow dung | 168.9 mL/g | Moderate product yield | (Zhang et al., 2020) |
| Corn stalk | Ca(OH)₂-enzymolysis | Photo-fermentation | Rhodobacter capsulatus MC122 | 357.6 mL/g | Improved product yield | (Zhang et al., 2020) |
| Corn stalk | Ca(OH)₂-enzymolysis | Two-stage fermentation | Step 1: Cow dung | 424.3 mL/g | High product yield | (Zhang et al., 2020) |
| Sorghum stover | Enzymatic delignification | Anaerobic fermentation | Trichoderma asperellum | 402.01 mL/g | Easy and low cost process | (Shanmugam et al., 2018) |
| Sugarcane bagasse | Thermal | Photo-fermentation | Rhodobacter capsulatus-PK | 513 mL/g | High energy consumption | (Mirza et al., 2019) |
| Potato peel | Mechanical and thermochemical | Dark fermentation | Sewage sludge inoculum | 2.63 mL/g | Low output | (Bhurat et al., 2021) |
| Rice husk | Mechanical | Solid-state fermentation | Clostridium termitidis and Clostridium intestinale | 5.9 mL/g | Pretreatment to be intensified | (Tosuner et al., 2019) |
| Corn cob | Thermochemical | Photo-fermentation | Clostridium acetobutylicum | 132 L/kg | More research needed | (Medina-Morales et al., 2021) |
| Raw POME | NS | Dark fermentation | POME sludge | 28.47 mL/g | Feedstock needs pretreatment | (Zainal et al., 2018) |

Table 4. Production of biohydrogen from some agricultural wastes.

Figure 7. Actual and potential global biomethane production in 2022, by region.
### Table 5: Production of biomethane from some agricultural wastes.

| Feedstock                  | Pretreatment                  | Microorganism name                          | Conversion pathway | Yield (mL/g VS) | Remark                                      | References                          |
|----------------------------|-------------------------------|---------------------------------------------|--------------------|-----------------|---------------------------------------------|--------------------------------------|
| Sugar Beet Leaves          | Enzymatic                     | Aspergillus niger, Aspergillus tubingensis, Neurospora intermedia | AD                 | 516             | Good yield (Undiandeye et al., 2022)        |                                      |
| Rice straw                 | Ozonolysis and thermal        | NS                                          | AD                 | 374             | Improved yield (Patil et al., 2021)         |                                      |
| Sugarcane trash            | Alkaline                      | NS                                          | AD                 | 187             | Low decomposition of the feedstock          |                                      |
| Wood waste                 | Microbial                     | Peronema Alg., Penicillium Opposporum       | AD                 | 224             | Low product yield                          |                                      |
| Corn stover and cattle dung| Enzymatic                     | NS                                          | AD                 | 49.1            | More research needed                       |                                      |
| Cassava peel and water hyacinth | Thermal                     | NS                                          | AD                 | 303             | Better pretreatment                         |                                      |
| Arachis hypogea seeds      | Anaerobic Digestion; NS       | Volatile solids; NS                         | AD                 | 31.07           | Feedback needs improvement                 |                                      |

**Notes:**
- AD = Anaerobic Digestion; VS = Volatile solids; NS = Not stated; mL = millilitre.
- Yield is calculated based on volatile solids (VS).

### 4.4. Biobutanol

Biobutanol is four-carbon butanol generated by microbial acetone-butanol-ethanol (ABE) fermentation from renewable feedstocks, usually sugar, starch, or cellulosic biomass. It is an advanced biofuel with higher heat of vaporization when compared with gasoline. The Alternative Fuels Data Center (2021) testifies that the high energy content elevated octane number, and lower volatility of biobutanol make it a realistic fuel for internal combustion engines. When used as a transport fuel, it generates fewer toxic emissions, less corrosive, and its immiscibility with water means it can be transported in the same pipeline infrastructure and reduce transport costs. Biobutanol has also found applications in diverse industrial and chemical sectors including paints/coatings, cosmetics, detergent formulations, chemical intermediates, and herbicides. It is also used as resins, plasticizers, and in the food and pharmaceutical industries (Azocleantech, 2020). It is easily fermentable and considered a more effective fuel than biomethanol and bioethanol. However, biobutanol suffers from low yield during fermentation, biofouling, is difficult to scale up, and the production process is not economically viable (Karthick and Nanthagopal, 2021).

The global market volume of biobutanol was 4.39 million metric tons (MMT) in 2015 became 5.23 MMT in 2021 and has been projected to rise to 6.72 MMT in 2029 (Figure 8) (Statista, 2022g). In terms of market value, the biobutanol market value that was valued at USD 90 million (iea, 2020) and is projected to climb to USD 114.7 million by 2026 (The expresswire, 2022). The projected growth is expected to be driven by increased population, the pursuit of carbon neutrality, and government policy on biofuel utilization. Also, increased demand for butyl acrylates, adhesives, textiles, and coatings in the Asia-Pacific, the Middle East, and include the VS, COD, nutrient content, biological oxygen demand (BOD), and the presence of inhibitory materials (Kamusoko et al., 2019). However, to boost the anaerobic digestibility and conversion efficiency, there is a need for pretreatment of feedstocks. Feedstocks can be pretreated by physical, biological, chemical, or thermochemical methods. A combination of these methods can also be adopted to enhance the cost-effective production of biomethane from agricultural waste (Dahunsi, 2020).

In recent research, Undiandeye et al. (2022) investigated the feasibility of sugar beet leaves as feedstock for biomethane production. The addition of Aspergillus- and Neurospora-based additives in an enzymatic pretreatment increased the anaerobic digestibility of the substrate and ensure a yield of 516 mL/g VS. In another study, Patil et al. (2021) employed ozonolysis and thermal pretreatments to synthesis biomethane from rice straw. The pretreatments advanced the biodegradability of the substrate. Biomethane was also generated from sugarcane trash by AD after initial treatment by KOH which led to a yield of 187 mL/g VS (Ketsub et al., 2021). The efforts of Navarro et al. (2020) and Baghbanzadeh et al. (2021) to generate biomethane from wood wastes were successful and a product yield of 224 mL/g VS and 49.1 mL/g VS were recorded, respectively.

Recently, co-digestion has been adopted to increase biomethane yield. In research, Joseph et al. (2019) experimented with the generation of biomethane from corn stover and cattle dung, using a two-stage thermophilic anaerobic co-digestion. After an initial thermal pretreatment, they reported a biomethane yield of 518.58 mL/g VS. Similarly, Housagul et al. (2014) anaerobically co-digested banana peel and waste glycerol for biomethane production and reported a yield of 652 mL/g VS. The high production yield recorded were traceable to the effects of the pretreatment and the co-digestion. The outcome of other investigations on the conversion of agricultural wastes into biomethane by Abou et al. (2021), Kumari and Das (2019), Bolado-Rodríguez et al. (2016), and Olatunji et al. (2022) are shown in Table 5. Conversion of agricultural wastes to biomethane contributes to waste management, reduces the impact of waste on the environment, promotes energy recovery, and ensures carbon. Also, the spent digestate is used as fertilizer to support horticultural practices and the growing of vegetables.
the African region, respectively, will contribute to the increased demand for biobutanol. The life cycle assessment of biobutanol is better than that of biomethanol and bioethanol, and therefore preferable (Butanol Mar-
ket). The adaptation of bio-based biomass feedstocks such as agricultural wastes and crop residues such as like corn, wheat, cassava peel, molasses, and sugar cane bagasse are aimed at ensuring the economic viability of biobutanol production.

The conversion of agricultural wastes into biobutanol has been exhibited by several researchers in recent years. Cheng et al. (2012) generated biobutanol from alkaline pretreated rice straw and sugarcane bagasse. Using bacterial microbiota obtained from sewage sludge, a biobutanol yield of 2.93 g/L and 1.95 g/L was recorded from rice straw and sugarcane bagasse, respectively. A biobutanol yield of 1.09 g/L was recorded after untreated corn cobs were fermented using Ruminococcus and Clostridium for xylan transformation (Shanmugam et al., 2019). In a related study, Cai et al. (2016) employed NaOH solution for the pretreatment of corn cob bagasse (CCB) to ensure delignification and cellulase accessibility before ABE fermentation. The outcome of the study revealed a biobutanol yield of 175.7 g/kg of CCB in an eco-friendly manner. Biological treatment was applied to wheat straw to reduce the concentration of lignin, hemicellulose, and amorphous cellulose and increase its biodegradability for fermentation to bio-
butanol. At the completion of the process, a biobutanol yield of 14.2 g/L was achieved and duly reported (Valdez-Vazquez et al., 2015).

### Table 6. Production of biobutanol from some agricultural waste.

| Feedstock         | Pretreatment | Conversion pathway | Microorganisms used                          | Yield     | Remark                  | References            |
|--------------------|--------------|--------------------|-----------------------------------------------|-----------|-------------------------|-----------------------|
| Rice straw         | Alkaline     | SSF                | *Pseudomonas sp. CL3* and *Clostridium sp. TCWI* | 2.93 g/L  | Process need improvement | (Cheng et al., 2012)  |
| Sugarcane bagasse  | Alkaline     | SSF                | *Pseudomonas sp. CL3* and *Clostridium sp. TCWI* | 1.95 g/L  | Better pretreatment required | (Cheng et al., 2012)  |
| Corn cob           | Non alkaline | Fermentation       | *Ruminococcus* and *Clostridium*              | 1.09 g/L  | Low yield               | (Shanmugam et al., 2019) |
| Corn cob bagasse   | Alkaline     | ABE fermentation   | *Clostridium acetobutylicum*                  | 175.7 g/kg CCB | Enhanced yield          | (Cai et al., 2016)     |
| Wheat straw        | Biological   | ABE fermentation   | *Clostridium beijerincki* 10132 and *Clostridium cellulovorans* 35296 | 14.2 g/L  | Low-cost process        | (Valdez-Vazquez et al., 2015) |
| SSB                | Enzymatic hydrolysis | Fermentation | *Clostridium acetobutylicum NRRL B-591* | 117 g/kg SSB | Productive feedstock   | (Khalili and Amiri, 2020) |
| Sugar cane molasses| NS           | Fermentation       | *Clostridium acetobutylicum*                  | 18.03 ± 0.17 mg/l | Feedstock needs to be treated | (Owuna et al., 2018) |
|                    | NS           | Fermentation       | *Clostridium difficile*                     | 10.01 ± 0.01 mg/l | Easy process            |                       |
|                    | NS           | Fermentation       | *Clostridium perfringens*                  | 14.19 ± 0.11 mg/l | Low-cost process        |                       |
| OPEFB              | Mechanical   | SSF                | *Clostridium acetobutylicum*                | 3.97 g/L  | Better pretreatment required | (Md Razali et al., 2018) |

CCB = corn cob bagasse; ABE = Acetone-Butanol-Ethanol; SSB = sweet sorghum bagasse; NS = Not stated; OPEFB = oil palm empty fruit bunch; SSF = simultaneous saccharification and fermentation.
4.5. Biomethanol

Biomethanol is an oxygenated renewable fuel produced from biomass and biodegradable wastes containing sugars and starch. The high-octane number and competitive price of biomethanol make it available to be blended with gasoline or ethanol as a cost-effective fuel for ICEs. The application of biomethanol for transport applications ensures complete combustion and ultimately reduced the emission of GHGs. The absence of a carbon-to-carbon bond with oxygen in the molecular structure of biomethanol ensures reduced formation and emission of soot. Other notable advantages of biomethanol as an ICE fuel include high performance, low flammability, low combustion temperature, and reduced NOx emission. However, biomethanol has low energy content, corrosivity, viscosity, and poor ignition quality. Also, incomplete combustion of biomethanol results in the emission of formaldehyde and formic acid, and other contaminants (Sima, 2020).

Apart from its application as a transport fuel, methanol is the preferred alcohol for transesterification reaction due to its low price, ease of recovery, better reactivity, and its affinity for azeotrope formation. Other applications of methanol include the production of methyl tertiary-butyl ether, formaldehyde, acetic acid, chloromethane, and other organic chemicals. Methanol is often used as a solvent, automotive antifreeze, and industrial production of inks, synthetic resins, adhesives, coating compounds, and pharmaceuticals (Bhardwaj et al., 2021). Methanol is usually synthesized from synthetic gas or biogas. But advances in technology have shown that wood, agricultural wastes, crop residues, sewage, municipal solid waste, and other biodegradable biomass can be utilized as a low-cost feedstock for sustainable methanol production.

Owing to its diverse applications, the global methanol demand and supply rose from about 85.4 million metric tons (MMT) and 85 MMT in 2016 to over 110.2 MMT and 110 MMT in 2021, respectively (Methanol.org, 2020), as shown in Figure 9. The market price of methanol which was USD 29 billion in 2020 has been estimated to become over USD 55 billion in 2030 (Globe News wire, 2022). The projected increase in market value is due to increased investment in the infrastructure and technologies for methanol production and utilization. There is an expected rise in the application of methanol in automotive (as a transport fuel, antifreeze agent for automobile radiators), manufacturing (as feedstock for foam, plastics), chemical (for paints and explosives), electronics, marine, and pharmaceutical industries. Gasification has been recognized as the most feasible method of biomethanol production. However, other conversion pathways such as pyrolysis, liquefaction, AD, and other biological methods have also been used to convert biomass into biomethanol (Gautam et al., 2020).

The conversion of some forest biomass to biomethanol was demonstrated using the gasification method. Though there was no record of any pretreatment operation during the process, the reaction was adjudged energy-efficient and economically viable with a biomethanol yield of 0.59 kg/kg biomass reported (Arteaga-Pérez et al., 2016). In another study, Shamsul et al. (2017) deployed a novel 2L batch glass bioreactor for the fermentation of goat manure to biomethanol. The feedstock was pulverized to <5 mm particle size to reduce the crystallinity of cellulose and enhance the digestibility during the fermentation process. At the end of the experiment, a biomethanol yield of 6.8 g/L was achieved. Similarly, Anitha et al. (2015) subjected grass, leaves, corn stover, and banana peels to mechanical and thermal pretreatment procedures prior to the conversion to biomethanol. At the end of the 7 days digestion process, biomethanol yields of 1.11 g/mL, 0.92 g/mL, 1.08 g/mL, and 0.98 g/mL were recorded for grass, leaves, corn stover, and banana peels, respectively. Kasnuri et al. (2019) reported product yield of 3.09 wt% when sugarcane bagasse was pyrolyzed and converted to biomethanol. Not much work has been done on the conversion of agricultural wastes into biomethanol (Table 7), further investigations are therefore recommended for the utilization of agricultural wastes as feedstock for biomethanol production.

4.6. Biodiesel

Biodiesel is a renewable, biodegradable, and eco-friendly form of liquid biofuel. It consists of long-chain fatty acid esters and is usually produced from vegetable oils, animal fats, recovered restaurant grease, and used cooking oil (Awogbemi et al., 2021a; Onuh et al., 2021). Biodiesel is a sustainable replacement for fossil-based fuels, and it is found to prolong engine life and emits fewer GHGs and other poisonous pollutants. It is non-toxic, has a high flash point, and has better combustion efficiency when compared with fossil-based diesel fuel. The challenges of high production cost and conflict with the food chain have been addressed by the adaptation of non-edible feedstock for biodiesel production (Awogbemi et al., 2021b). However, biodiesel is unsuitable for use in low-temperature climates, prone to gelling, clogging the engine, and blocking fuel filters and hoses. Due to the use of diverse feedstocks and production methods, there are wide variations in the quality of biodiesel across jurisdictions. Also, the combustion of biodiesel in
Though there are no records of direct production of biodiesel from agricultural wastes, the application of microalgal technology in the last decade has popularized the synthesis of biodiesel from microalgae. Recently, new techniques for cultivating microalgae from agricultural wastes for strategic biodiesel production have been developed (Hoang et al., 2022). Kakkad et al. (2015) produced biodiesel from microalgae cultivated on an untreated banana peel and sugarcane bagasse. The authors recorded biodiesel yields of 420 mg/L and 400 mg/L for banana peel and sugarcane bagasse respectively and the product meets international standards. Similarly, Arora et al. (2016) synthesized biodiesel from oleaginous microalgae grown on an extract from sugarcane bagasse and reported a biodiesel yield of 112 ± 5.2 mg/L. Other reported production of biodiesel from corn stover (Le et al., 2017; Shafiei Alavijeh et al., 2020) cassava starch (Zhang et al., 2022a), pineapple waste (Kanakdande et al., 2020), and rice bran oil (Ibrahim et al., 2020) are shown in Table 8.

5. Conclusion and future perspectives

The increased global population, agricultural activities, and food processing have triggered increased agricultural waste generation, sanitation challenges, and emission of hazardous gases from decaying materials. This study has provided sustainable and environmentally friendly strategies for effective agricultural waste management and bioengineering approaches to waste minimization, conversion, and utilization. Also, it has been shown that agricultural wastes can be converted into bioethanol, biomethane, biohydrogen, biobutanol, biomethanol, and biodiesel for transport and power generation sectors. The conversion of agricultural wastes into biofuels offers ecological, sanitary, economic, industrial, and technical benefits while the use of the generated biofuels as transport engine reduces the emission of GHGs, ensures better engine performance, promote smoother engine running, and prolongs engine lifespan.

The challenges pose by the huge volume of waste generated from agricultural activities and crop residues can be ameliorated by the
O. Awogbemi, D.V.V. Kallon Heliyon 8 (2022) e11117

Author contribution statement

Conversion sector. An uninterrupted and sustainable supply of agricultural enterprises desirous of investing in the waste management and utilization of waste to useful products. Interdisciplinary research on cost analysis, sensitivity analysis, energy, and exergy analysis, techno-economic assessment, and life cycle assessments are needed to understand the complex processes and molecular kinetic of waste degradation and conversion. The deployment of appropriate innovative technologies such as computational fluid dynamics, machine learning, artificial intelligence, statistical modeling, and optimization tools are needed to improve process parameters, reactor design and optimization, design parameters, cost, time, and manpower requirements to improve conversion efficiency and product quality. Extensive studies are needed on how to deploy robotic technologies smart cameras, mobile devices, smart metering, and other innovative technologies to monitor and control the waste conversion techniques towards ensuring high product quality.

Going forward, governments across jurisdictions should encourage farm owners on the benefit of converting their wastes into useful products. Burning of agricultural wastes not only reduces soil fertility but generates smoke that further degrades the environment. Waste management practices that escalate environmental pollution, erosion, soil, and water contamination, and impair human health should be jettisoned. There is a need for more enlightenment to reduce the impact of cultural and religious beliefs that discourage waste conversion and utilization. Incentives and tax holidays should be provided for small and medium scale enterprises desirous of investing in the waste management and conversion sector. An uninterrupted and sustainable supply of agricultural waste will ensure the availability of low-cost feedstock for conversion to biofuel. More human and material investments are needed to support the conversion of agricultural waste into renewable biofuels to ensure environmental sustainability, promote renewable fuel utilization, and avert the impending environmental disaster.

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