

Agricultural Waste as a Sustainable Feedstock for Biofuel Production: A Comprehensive Review

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Abstract

Countries all over the world are running out of fossil resources due to the world's population growth and the necessity to exploit natural resources to get fossil fuels. Although fossil fuels have long been a significant source of energy, they are unsustainable and harmful to the environment. A cheap, accessible source of environmentally safe agricultural waste has never been more important for biofuel production. Biofuels are cheap, environmentally benign, renewable, and biodegradable. They are created by microbes from discarded lignocellulosic biomass. Agricultural waste conversion into biofuel does not improve food security, but it does aid in waste management, stop environmental deterioration, and ensure energy security. The goal of the current project is to investigate the production of biofuels from agricultural waste, with a focus on bioethanol, biohydrogen, biomethane, biochar, and biodiesel for diverse uses. The classifications of these fuels based on the raw material and the liquid, solid, and gas states, as well as based on the physical state, are first, second, and third generation biofuels, which are explained in this study. As a result, wastes generated by agricultural processes and activities have value and can help achieve the goal of affordable and accessible worldwide renewable energy.

Keywords: Agricultural Residues, Lignocellulosic Biomass, Biofuel Technologies, Bioethanol Production, Biodiesel Synthesis, Biohydrogen Generation, Biomethane Production, Biochar Applications, Renewable Energy Systems, Waste-to-Energy Conversion, Sustainable Development, Advanced Biofuels

1. Introduction

Majority of the world's energy needs are met by oil, coal, and natural gas. At the current rate of consumption, these limited resources will be depleted in a short time (Basic et al., 2018). As a result of depleting fossil fuel reserves, widespread industrialization, countries' growing reliance on imported energy, and a rise in fuel prices around the world, an energy crisis is just now emerging. Another issue is the environmental catastrophe produced by the growth in fuel use and inaccuracy in its use (Pagano et al., 2023). To exclude those two crises, researchers are continuously seeking new sources of energy. Alternative energy sources that are affordable, accessible, and ecologically beneficial might be projected as sources.

A diverse range of fuels known as "biofuel" are made mostly from plant-based energy sources (Ajanovic, 2011). The use of biofuels has been shown to reduce carbon emissions and mitigate climate change. The world waste management market was valued at 1.61 trillion dollars during recent forecasts and will reach 2.5 trillion dollars per year in 2030. Agricultural wastes are a fundamental part of these wastes. Accessible statistics revealed that about 998 million tons of agricultural waste are generated annually, the majority of which are deposited in landfills or burned with adverse environmental consequences (Marti & Puertas, 2021). Because more food is being grown and eaten to feed a growing population and provide raw materials for the industrial sector, the agricultural sector is making a lot more trash than it used to. Agricultural wastes are categorized as crop residues, industrial wastes, animal wastes, and food wastes. The waste produced from the agricultural sector, if not handled and managed properly, creates environmental threats, pollutes water and land habitats, and affects human health. Thus, waste management strategies such as waste reduction, waste reuse, and waste recycling, should be considered (Obi et al., 2016).

It is possible to slow down environmental deterioration and protect the environment for future generations by using biofuel made from agricultural waste. Carbon dioxide emissions can be decreased by using biofuels for various purposes. Biofuels can encourage and contribute to the eradication of poverty, constructive social change, the creation of jobs, and economic growth. Hence, one of the sustainable waste management techniques to ensure health, recover resources, and preserve the environment's carbon balance is the conversion of agricultural waste into biofuel. (Cheng et al., 2012).

Biomass undergoes a variety of transformations, including chemical and biochemical heating, to become its constituent parts and the desired end product.

2- Biofuels

Biofuel is a type of fuel derived from organic matter. This means that biofuel originates from plants and is therefore renewable (Popp et al., 2014). The primary source of energy in biomass is solar energy, which is stored in the plant through photosynthesis. Hence, their intake does

not contribute to an increase in atmospheric carbon dioxide. Although there are numerous sources for biofuel production, the primary sources include sugar-rich plants (such as sugarcane, sugar beets, sweet sorghum, and sweet potato), starch-rich plants (such as corn), and oil-rich plants (such as soybean, jatropha oil palm). Many thermal processes, chemical conversions, and biological conversions can turn the energy held in plants and biomass into useable energy for humans (Wetterlund et al., 2012). There are many sorts of biofuels. These materials include a considerable degree of variation. Thus, they are categorised in distinct respects. Biofuel can be classified depending on its source material and physical state, among other factors. Based on the raw materials used in their production, biofuels, particularly liquid biofuels, have been categorized into the first, second, third, and fourth generations. The production of these fuels has improved and increased with the development and introduction of each new generation (Havlk et al., 2011).

- First-generation fuels, also known as conventional biofuels, are derived from food and agricultural products. The production of this type of biofuel increases food insecurity and the ensuing crises. The first generation of biofuels is derived from sugar, starch, oil, as well as animal and vegetable fat, using currently known processes or technologies. These fuels consist of biodiesel, bioalcohol, ethanol, and biogases including methane. In this generation, valuable and occasionally strategic food must be cultivated solely for the production of biofuel, which jeopardizes food cycle security, and the cultivation of crops for biofuel production is not fundamentally economical (Souza et al., 2017).
- Second-generation biofuels are derived from non-food products or agricultural waste, in particular lignocellulosic biomass. These fuels' raw materials are not considered food. The raw materials used in this generation may consist of agricultural and food wastes and residues, as well as products that have no nutritional value for humans and are grown on poor-quality land at very low costs. Similarly, forest and green space wastes are lignocellulosic materials that contribute to the production of second-generation biofuels. Despite the many benefits of this generation of fuels, it may be challenging to extract fuels from their raw materials (Ozturk et al., 2017).
- Biofuel made from algae is called "algae fuel" or "third-generation biofuel." During photosynthesis, algae takes in carbon dioxide and turns it into oxygen and plant matter (biomass). Algae production for fuel has not yet found a place on a large scale in the business world. Still, there have been feasibility studies done to get high performance. Making third-generation fuels doesn't cut down on food production and doesn't need farmland or fresh water (Popp et al., 2014).
- Engineered plants or biomass that have better energy yields make up the fourth generation of biofuels. This kind of material can grow on non-agricultural terrain without water and requires less cellulose degradation. The fourth generation of biofuels not only produces energy sustainably, but also helps to remove carbon dioxide from the

atmosphere. Growing biomass materials absorb carbon dioxide and turn second-generation biofuels into fuel using the same process (Arismendy Pabon et al., 2020).

Biofuel extracted from biomass can be used in dissimilar ways regarding the type of process and the envisioned aim. In terms of physical properties, biofuels are classified into three groups: solid, liquid, and gas, which, according to the characteristics of each of them, have different efficiency (Adnan et al., 2019).

The best ways to get energy from biomass are to burn it or use its energy directly while it is still solid. One of the oldest fuels used by humans, which is known today as solid biofuel, was agricultural waste and plants, which were used to provide thermal energy or lighting. Actually, any renewable and biological material that can be burned is considered biofuel. Among the prime sources of biofuels, we can mention wood waste, residues of agricultural products, sugarcane, grains, household waste, charcoal, and plant and vegetable oils, all of which are solid sources and can be burned (Ajanovic, 2011).

In recent decades, liquid biofuels have attracted the most attention from academics and governments all around the world due to their widespread use. Many chemical and biological processes produce these fuels. Several studies have been conducted on the manufacturing of liquid biofuels in light of the societies' expanding use of these fuels. Several established and emerging nations have liquid biofuels in their national energy goals, and nations including the United States, Brazil, and EU members are attempting to cut greenhouse gas emissions and get ready for energy storage shortages. Bioethanol dominates the production and consumption of liquid biofuels globally, accounting for over 80% of both. Biodiesel comes in second, accounting for less than 20% of global production and consumption (Marti & Puertas, 2021). Among the renewable sources, one of the oldest used fuels is biogas, which is being used in numerous parts of the world. This fuel which comes from the digestion process is a clean fuel that does not cause environmental pollution (Kapoor et al., 2020).

The production of biofuel from agricultural waste can still be accomplished using biochemical or thermochemical techniques. The biochemical conversion pathway combines chemical and biological processes to produce biodiesel, biomethane, and bioethanol from agricultural waste with a high moisture, cellulose, and hemicellulose content and a carbon-to-nitrogen ratio of above 30%. Agricultural waste with a high lignin percentage, low moisture content, and a carbon to nitrogen ratio of less than 30% is better suited for thermochemical conversion. The thermochemical route combines heat and chemical processes (Ma et al., 2021).

2-1- Bioethanol

As technology has advanced, there has been a potential for utilising lignocellulosic materials and fermenting them to produce alcohol on a global scale. Throughout, it is normal practice to

produce cellulosic materials in large quantities from various types of carbohydrates, and much research is being done on industrializing lignocellulosic materials and turning them into ethanol. Ethanol is the most prevalent bioalcohol produced by biomass-based microbial fermentation of agricultural sugars (Zheng et al., 2023). Since petroleum stocks are quickly depleting, ethanol has become a viable alternative liquid fuel, largely because it resembles petroleum in terms of its fuel properties. It is common knowledge that ethanol has a high octane rating. The viability of ethanol production is significantly impacted by the technological and financial challenges associated in hydrolyzing its constituent monosaccharides. Special factors including the thorough development of the process, the separation of products, and the recovery of by-products should be taken into account for it to be economical and successful on an industrial scale. Research and development for the cost-effective generation of ethanol from cellulosic materials is now concentrated on the crystalline and sticky character of cellulose, its resistance to different hydrolysis techniques, and the synthesis of fermentable sugars (Trubetskaya et al., 2023).

Bioethanol is a liquid biofuel that can be made over and over again. It is made by fermenting sugar and starch from natural materials, usually plant products or agricultural waste. Bioethanol, or simply ethanol, is the most common liquid biofuel consumed worldwide. The demand for bioethanol has continued to drive production growth. It is projected that the global demand for bioethanol, which reached 100.2 billion liters in 2016, will reach 134.5 billion liters by 2024 (Busic et al., 2018). Though over 40% of global ethanol production is used as fuel or fuel additives, bioethanol is mostly used as an internal combustion engine fuel for blending with gasoline. This approach offers performance and economic benefits to consumers. A severe reduction in toxic emissions helps to minimize air pollution, ensure environmental safety, and reduce emissions of greenhouse gases and other carcinogenic compounds such as ethylbenzene, xylene, toluene, and benzene. Likewise, since bioethanol is primarily produced from waste biomass as feedstock, it is generally cost-effective and contributes to waste management and sanitation. These issues have progressively focused research efforts on the application of non-food feed substitutes for bioethanol production. The use of lignocellulosic biomass such as urban and industrial waste, wood, and agricultural residues is a better alternative based on economic, availability, health, and environmental considerations. Testing of rice husk and rice straw revealed bioethanol production rates of 44% and 18.07 grams per liter, respectively (Arismendy Pabon et al., 2020).

Fermentation is one process used to make ethanol. This process involves a strain of sugar yeast that uses oxygen-free metabolism to create ethanol and carbon dioxide. With regard to the scarce supply of sugar and starch, on the one hand, their high cost and, on the other, the clearing of forests to make way for the planting of starch seeds on agricultural land, have rendered these two key sources of bioethanol production unsuitable from an economic and environmental standpoint. Lignocellulosic-based materials have drawn a lot of interest (Limarta et al., 2020).

The world's most plentiful renewable biomass is produced from these resources, which are produced at a rate of 10 million tons annually. Three components make up the structure of lignocellulosic materials: cellulose, hemicellulose, and lignin. Before the fermentation process, lignocellulosic materials are first turned into glucose through the hydrolysis process, and then glucose is transformed into bioethanol through the fermentation process. In general, there are three ways to turn lignocellulosic materials into bioethanol: one-stage hydrolysis with concentrated acid, two-stage hydrolysis with dilute acid, and enzyme hydrolysis (Giwa et al., 2023).

2-2- Biodiesel

Biodiesel is the second liquid biofuel that can be used as a renewable substitute for fossil fuels. Similar to ethanol, biodiesel can be mixed with regular diesel fuel and used as car fuel. Biodiesel is typically created by accelerating the transformation of vegetable oils into monoalkyl esters of fatty acids. Due to its inherent resemblance to petroleum fuels, biodiesel has gained attention due to its ability to possess all of these fuels' essential features while also being biodegradable, non-toxic, and, most importantly, carbon neutral (Kumar et al., 2020). In reality, the majority of internal combustion engines are built on two core ideas that change little or nothing when using biofuel in place of petroleum fuel. Biodiesel is produced from triglyceride-containing fats from plants and animals. The most often used type of feedstock for the production of biodiesel is refined edible vegetable oils, which are obtained from seeds including soybean, rapeseed, sunflower, date, coconut, and flaxseed. The reaction that takes place when triglycerides and alcohols with a short carbon chain, like methanol and ethanol, come into contact is referred to as transesterification. The transesterification reaction uses a basic, acidic, or enzymatic catalyst (Figure 1). Because they are convenient and affordable, homogeneous base catalysts for ester exchange are commonly used in industry. Examples of these catalysts are potassium and sodium hydroxide (Awogbemi et al., 2021). Biodiesel shouldn't be used in low-temperature places since it can gel, clog engines, and harm fuel filters and hoses. Depending on the raw materials utilized and different manufacturing methods, the quality of biodiesel differs substantially between different fields. Moreover, while burning biodiesel in compression-ignition engines, as opposed to fossil-based diesel fuels, more NOx emissions are produced (Kanakdande et al., 2020).

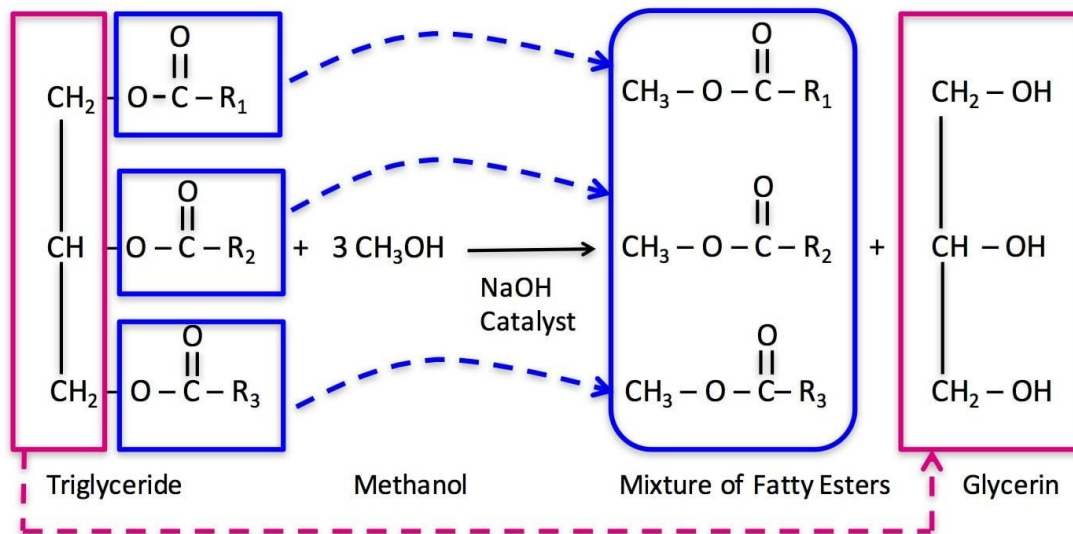


Figure 1. Biodiesel production process and breakdown of molecules

3-2- Biohydrogen

Biohydrogen is made by combining water, organic waste, and biomass. Hydrogen will be the fuel of the future because of its high conversion efficiency, rotational capabilities, and clean-burning characteristics. Thermal processes including gasification, gas or steam production, production from biological oils at high vapor pressure, and the enzymatic breakdown of sugars can all be used to make hydrogen from biomass (Ma et al., 2021). Biohydrogen generation from biomass is one of the cleanest ways to manufacture hydrogen in terms of the absence of greenhouse gases. Agricultural wastes are a great source of substrate for the synthesis of biohydrogen due to their wide availability and high carbohydrate content. They are also not only reasonably priced but also a great supply of these nutrients. Biohydrogen is a sophisticated biofuel made from biomass using biological and thermochemical processes. It is safe, non-toxic, and carbon-free. This fuel is renewable, highly flammable, tasteless, odorless, and colorless. The waste's carbohydrate component is broken down by primary enzymatic hydrolysis to produce reducing sugars as part of the anaerobic dark fermentation process used to produce hydrogen (Alexandropoulou et al., 2018).

Cellulase is a biocatalyst that aids in the fermentation of fermentable sugars from cellulosic biomass. After that, carbohydrates are fermented using a thermophilic heterotrophic process to create organic acids. The ensuing photoheterotrophic fermentation process converts organic acids to hydrogen. This method of producing hydrogen has the potential to replace fossil fuels as a viable alternative energy source because it is clean, doesn't emit greenhouse emissions, is renewable, and has a high energy content (142.35 kJ/g). Biohydrogen has a wide range of uses in the transportation, energy, food and beverage, medicinal, and industrial sectors. These uses are advantageous from an economic and social standpoint and play a significant role in the circular economy. By 2025, the consumption of biohydrogen is anticipated to rise 8–10%

across a range of applications (Kumari and Singh, 2018). There are two widely used processes for producing biohydrogen: fermentation and biophotolysis. However, recent discoveries have shown that biohydrogen can also be made through pyrolysis, solar gasification, thermochemical gasification, microbial electrolysis, and supercritical conversion methods. Compared to traditional processes, these production routes need less energy, are more ecologically friendly, perform better economically, and are more sustainable (Groom et al., 2008).

2-4- Biochar

It's an outdated technology to incinerate agricultural waste, which is done thermally to generate heat and energy. This process assists in reducing the volume of such garbage to 80–85% while also assisting in energy recovery from this waste. As a form of fertilizer, biochar, commonly referred to as bio-coal, is charcoal formed from plant biomass and agricultural waste. This substance can last for a very long time because it is stable and contains a lot of carbon. The updated "pyrolysis" procedure is used today to create biochar. The major steps in the incineration process are an early pretreatment step of drying and degassing, followed by pyrolysis and gasification, and lastly, oxidation, where the heat generated can be used to heat the process or generate electricity using steam turbines (Xiang et al., 2020). Volatile compounds and high moisture levels in food waste evolve during the drying and degassing step at temperatures between 100 and 300 °C without the use of any oxidizing agents. The primary product of bio-oil and synthesis gas, which consists of carbon monoxide and hydrogen, are produced as a result of the further degradation of organic matter at a temperature between 250 and 700 °C in the absence of oxygen during the pyrolysis process. Another by-product of biochar production is solid biochar. The carbonaceous product reacts with water vapor and carbon dioxide during the gasification process at a temperature between 500 and 1000 °C (Chi et al., 2021).

The effectiveness of fertilizers can be increased by biochar, which can also lower production costs and biological pollution. The soil is rejuvenated and becomes more fertile thanks to biochar. This kind of fertilizer boosts agricultural output while also defending plants against a few plant diseases. One of the key attributes of biochar that has a considerable impact on the stability of the structural quality of the soil throughout time is its lengthy useful life (Kamali et al., 2020). Food recycling, soil improvement, cost effectiveness, trash management, and long-term economic and reliable carbon sequestration are all possible with biochar. According to research, employing biochar in plants that require higher pH levels and more potassium fertilizers can enhance production. Increased organic matter, better water retention, increased cation exchange capacity, interaction with the soil nutrient cycle by adjusting soil pH and reducing nutrient leaching, as well as a reduction in the need for irrigation and fertilizer, are all positive outcomes of using biochar in agricultural soils. Biochar has a high specific surface area and a structure that allows it to absorb and deactivate heavy soil components (Lehmann &

Joseph, 2015). The management of agricultural waste is one benefit of biochar from an agricultural standpoint. The use of this combination has grown daily as a result of the expansion of organic agriculture on the one hand and atmospheric pollution on the other.

2-5- Biomethane

One well-known and important component of our country's energy future is biomethane. And as a component of a wider array of renewable energy sources, such as biogas, which is gaining more attention as the globe moves toward a diversified and sustainable energy mix (Adnan et al., 2019). A methane-rich gas termed biogas is upgraded by removing CO₂ and other contaminants to produce biomethane, a renewable gaseous biofuel. By a procedure known as methanation, woody biomass, municipal solid waste, and agricultural waste can all be gasified to produce biomethane. Specifically, the raw biogas created by the anaerobic digestion of organic waste has a mixture of 50–70% CH₄, 30–40% CO₂, and trace amounts of H₂O, H₂S, NH₃, N₂, siloxane, and solid debris. Although biomethane, a more advanced form of biogas, comprises 95–97% CH₄ and 1-3% CO₂ (Prussi et al., 2019).

Biomethane can be used to create electricity, heat houses, and run power plants. In order to reduce CO₂ emissions, biomethane has been used as a sustainable fuel to power vehicles and other internal combustion engines in place of biogas and natural gas in recent years. The benefits of using biomethane include minimizing or eliminating carbon emissions, cheap production costs, preserving a sustainable environment, and energy independence. Although biomethane has an unpleasant smell and a potential for explosion, its principal component, CH₄, is a potent GHG and one of the primary contributors to global warming. The production and consumption of biomethane are still rising despite these shortcomings. Today, Europe has the biggest real production of biomethane, producing roughly 1.8 million tons per year, followed by the United States and Canada with 0.6 million tons per year. However, the Asia-Pacific area (165 million tons annually), the United States and Canada (125 million tons annually), and South America have the biggest potential for future biomethane production (105 million tons per year). Likewise, it is anticipated that the global market for biomethane would increase from \$1.9 billion in 2022 to \$4 billion in 2031. (Statista, 2022).

Due to the high energy content of biomethane (36 MJ/m³) and the fact that it produces no net emissions, a lot of effort and resources have been expended to ensure that it can be produced affordably and environmentally friendly. One of those actions is the creation of agricultural waste. The most important component affecting a typical feed's anaerobic digestibility is its C/N ratio. VS, COD, nutritional content, biological oxygen demand (BOD), and inhibitors are further considerations (Jingura & Kamusoko, 2017). Anaerobic digestion is the biological breakdown of organic materials without the presence of oxygen, producing biogas and stabilized compounds as a byproduct. The process in landfills is the easiest to comprehend illustration. The generated biogas can be used for both domestic and commercial uses and has

a moderate calorific value due to its high methane content. Nonetheless, preparation of raw materials is required to improve anaerobic digestibility and conversion efficiency. Pretreatment techniques for raw materials might be physical, biological, chemical, or thermochemical. These techniques can be used in conjunction to increase the production of biomethane from agricultural wastes (Salman et al., 2017).

Conclusion and the future of biofuels

The challenges posed by the huge volume of waste generated from agricultural activities and crop residues can be ameliorated by converting such waste materials into useful forms. The valorization of these wastes into biofuels is still an environmentally friendly and economically feasible option. Biofuel is a term for types of fuels that have plant or animal origin and from a chemical point of view, it is called monoalkyl esters containing long chains of fatty acids. Biodiesel, bioethanol, biochar, gaseous diesel fuels such as methane and hydrogen are types of biofuels. Bioethanol is the most common biofuel and is obtained from the fermentation of sugars, rich starches of grains such as corn, wheat, sugarcane, and agricultural and wood waste. Biodiesel is actually monoalkyl esters of long chain fatty acids that are formed from the reaction of vegetable or animal oils with sodium hydroxide in the presence of methanol or ethanol catalyst. Biochar is charcoal prepared from plant biomass and agricultural waste, which are burned in the presence of little or no oxygen. Biodiesel and bioethanol are the most important fuels used in the transportation industry. One of the benefits of biochar is the management of agricultural waste. It also causes soil purification, increase in water retention capacity, cation exchange capacity and soil carbon content. . In general, biofuel production can be profitable, create employment and reduce the use of land. In addition, it will improve the properties of cultivated soils and reduce greenhouse gas emissions. Of course, this requires correct and principled management.

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